Inorganic Syntheses

Volume VIII

Inorganic Syntheses

Volume VIII

Advisory Board

McGraw-Hill Book Company

New York San Francisco Toronto London Sydney

PREFACE

This volume of INORGANIC SYNTHESES contains sixty-eight contributions. Two articles of a review nature are included, one on metal derivatives of β-keto imines (β-imino ketones) and the other on the chemistry of the noble gases.

As in the earlier volumes, each synthesis has been checked experimentally in a different laboratory than that from which it was submitted. Furthermore, each synthesis has been critically scrutinized by the members of the Editorial and Advisory Boards and, after editing, has been sent to author and checker for approval of the edited manuscript. As in previous volumes, addresses of those submitting and checking syntheses are the addresses in effect at the time the work was done. In addition, a change in address, when applicable, is indicated for the senior author for convenience in correspondence.

The Editorial and Advisory Boards of INORGANIC SYNTHESES encourage contributions both from this country and abroad and are pleased with the increasing number of scientists of other countries who are submitting or checking syntheses. Twenty-five of the sixty-eight contributions in this volume originated in or were checked in laboratories abroad.

In accord with previous practice, the syntheses in this volume are arranged on the basis of the Mendeleev periodic classification, with subdivision into A and B groups. Inasmuch as the placing of syntheses within a given chapter is arbitrary depending upon which element of the compound is chosen for the classification, the practice of listing appropriate syntheses from other chapters at the beginning of each chapter is continued in Volume VIII.

Nomenclature, particularly for compounds containing elements of periodic groups VA and VIA, often presents problems. In some cases, general agreement has not yet been reached among experts in the field. For example, names considered for $Cl_3P{=}N{-}P(O)Cl_2$ during the editing of synthesis 22 were trichlorophosphazophosphorus(V) oxychloride, (trichlorophosphoranylidene)amidophosphoryl dichloride, (trichlorophosphoranylidene)phosphoramidic dichloride, and (dichlorophosphinyl)phosphorimidic trichloride. The compound $(PNCl_2)_4$ used as a starting material in syntheses 20 and 21 and often referred to simply as "tetrameric phosphonitrile chloride" or "phosphonitrile chloride, cyclic tetramer," may alternatively be named octachlorocyclotetraphosphazatetraene or, more systematically, 1,3,5,7,2,4,6,8-tetrazatetraphosphocine 2,2,4,4,6,6,8,8-octachloride.

Emphasis has been placed on the use of systematic nomenclature consistent with recommendations of the International Union of Pure and Applied Chemistry and/or the Chemical Abstracts Service. However, in some instances, a factor such as a strong preference of the author or common usage has influenced the choice. In several such instances, an alternative name as a synonym has been included at least once within the article. For example, in synthesis 20, three names are given for the eight-membered ring compound $N_4P_4(OC_2H_5)_8$: octaethoxycyclotetraphosphazatetraene; tetrameric ethyl phosphonitrilate; and 2,2,4,4,6,6,8,8-octaethoxy-2,2,4,4,6,6,8,8-octahydro-1,3,5,7,-2,4,6,8,-tetrazatetraphosphocine (the last being the name preferred by the Chemical Abstracts Service). It is hoped that until agreement is reached on a logical unambiguous system of nomenclature the names used in this volume will be adequate for complete clarity.

It is a pleasure to acknowledge the election of Professor Stanley Kirschner, Department of Chemistry, Wayne State University, Detroit, Michigan, to the new position of Secretary of the Editorial Board. Contributions to future volumes are invited and should be submitted to Professor Kirschner. Manuscripts should be in accord with the *Notice to Contributors* section, which follows the *Preface* in this volume. Competent checkers are essential to the success of INORGANIC SYNTHESES. Persons who are interested in helping with this important function should communicate with Professor Kirschner.

The editor-in-chief for Volume IX is Professor S. Young Tyree, Jr., Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, and for Volume X is Dr. Earl L. Muetterties, Central Research Department, Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, Delaware.

Several new members of the Editorial Board have been elected to the Editorial Board since the publication of Volume VII:

Professor L. Malatesta, Universita Di Milano, Milano, Italy
Professor Howard C. Clark, University of Western Ontario, London, Ontario, Canada
Professor F. Albert Cotton, Massachusetts Institute of Technology, Cambridge, Massachusetts
Professor Richard H. Holm, University of Wisconsin, Madison, Wisconsin
Dr. John K. Ruff, Rohm and Haas Company, Huntsville, Alabama

Professor Malatesta begins his term of service with Volume IX; the other four new members, with Volume X.

This volume is dedicated to the late Professor Francis P. Dwyer, who at the time of his death was a member of the Editorial Board. The Boards acknowledge with respect and appreciation the fine contributions Professor Dwyer made to the work of INORGANIC SYNTHESES and in a broader sense to the field of inorganic chemistry.

The editor-in-chief takes pleasure in expressing his appreciation to his colleagues on the Editorial and Advisory

Boards for their fine help in the preparation of this volume. He is especially grateful to Miss Janet D. Scott for her work on nomenclature and indexing. Appreciation is expressed also to Professor Roy M. Adams, Chariman of the Committee on Inorganic Nomenclature for the Division of Inorganic Chemistry of the American Chemical Society, and to Dr. Kurt L. Loening, Director of Nomenclature for the Chemical Abstracts Service, for advice on several specific questions with respect to nomenclature. The editorial help of Mr. Theodore A. Michelfeld and Dr. John R. Demuth of the University of Nebraska is gratefully acknowledged. The editor wishes also to thank Miss Corrine Newton, Miss Camilla Connell, Miss Connie Svolopoulos, and Miss Georgianne Kozisek for their capable assistance in typing the manuscript.

The editors hope that users of INORGANIC SYNTHESES will call to their attention any errors or omissions. The suggestions and criticisms of readers are helpful and are much appreciated.

Henry F. Holtzclaw, Jr.

NOTICE TO CONTRIBUTORS

The INORGANIC SYNTHESES series is published to provide all users of inorganic substances with detailed and foolproof procedures for the preparation of important and timely compounds. Thus the series is the concern of the entire scientific community. The Editorial Board hopes that all chemists will share in the responsibility of producing INORGANIC SYNTHESES by offering their advice and assistance both in the formulation and laboratory evaluation of outstanding syntheses. Help of this type will be invaluable in achieving excellence and pertinence to current scientific interests.

There is no rigid definition of what constitutes a suitable synthesis. The major criterion by which syntheses are judged is the potential value to the scientific community. An ideal synthesis is one which presents a new or revised experimental procedure applicable to a variety of related compounds, at least one of which is critically important in current research. However, syntheses of individual compounds that are of interest or importance are also acceptable.

The Editorial Board lists the following criteria of content for submitted manuscripts: Style should conform with that of previous volumes of INORGANIC SYNTHESES. The *Introduction* should include a concise and critical summary of the available procedures for synthesis of the product in question. It should also include an estimate of the time required for the synthesis, an indication of the importance and utility of the product, and an admonition if any potential hazards are associated with the procedure. The *Procedure* should present detailed and unambiguous laboratory directions and be written so that it anticipates possible mistakes and misunderstandings on the part of the person who attempts to duplicate the procedure. Any unusual equipment or procedure should be clearly described. Line drawings should be included when they can be helpful. All safety measures should be clearly stated. Sources of unusual starting materials must be given, and, if possible, minimal standards of purity of reagents and solvents should be stated. The scale should be reasonable for normal laboratory operation, and any problems involved in scaling the procedure either up or down should be discussed. The criteria for judging the purity of the final product should be clearly delineated. The section on *Properties* should list and discuss those physical and chemical characteristics that are relevant to judging the purity of the product and to permitting its handling and use in an intelligent manner. Under *References*, all pertinent literature citations should be listed in order.

The Editorial Board determines whether submitted syntheses meet the general specifications outlined above. Every synthesis must be satisfactorily reproduced in a different laboratory than that from which it was submitted.

Each manuscript should be submitted in duplicate to the Secretary of the Editorial Board, Professor Stanley Kirschner, Department of Chemistry, Wayne State University, Detroit, Michigan, 48202, U.S.A. The manuscript should be typewritten in English. Nomenclature should be consistent and should follow the recommendations presented in "The Definitive Rules for Nomenclature of Inorganic Chemistry," *J. Am. Chem. Soc.*, **82,** 5523 (1960). Abbreviations should conform to those used in publications of the American Chemical Society, particularly INORGANIC CHEMISTRY.

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For other corrections, see synthesis 10 (page 37) and synthesis 40 (page 157).

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CHAPTER IA

ALKALI METAL COMPOUNDS

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CHAPTER IB

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1. BIS(4-IMINO-2-PENTANONATO)COPPER(II) AND BIS(3-PHENYLIMINO-1-PHENYL-1-BUTANONATO)-COPPER(II)

SUBMITTED BY ARTHUR W. STRUSS* AND DEAN F. MARTIN†
CHECKED BY NORMAN E. GRISWOLD‡

This synthesis is an example of chelate exchange, the advantages of which are noted later.[1] Attempts to prepare bis(3-phenylimino-1-phenyl-1-butanonato)copper-(II) by direct combination of the β-keto imine (β-imino ketone) and ammoniacal copper(II) nitrate have not been successful.[2] However, the compound can be obtained from reaction of the β-keto imine and bis(4-imino-2-pentanonato)-copper(II) [bis(4-amino-3-penten-2-onato)copper(II)] prepared by the method of Holtzclaw, Collman, and Alire.[3]

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‡ University of Nebraska, Lincoln, Neb.

Procedure

A. BIS(4-IMINO-2-PENTANONATO)COPPER(II)

$$\begin{aligned}&2CH_3COCH_2C(=NH)CH_3 + Cu(NO_3)_2 \cdot 3H_2O + 2NH_4OH \rightarrow \\ &\qquad [CH_3COCHC(=NH)CH_3]_2Cu + 2NH_4NO_3 + 5H_2O\end{aligned}$$

To a solution of 11.5 g. (0.116 mol) of acetylacetone imide (4-imino-2-pentanone)* in 100 ml. of 95% ethanol is added 14.5 g. (0.06 mol) of copper(II) nitrate 3-hydrate in 300 ml. of water containing 13.5 ml. of concentrated (15 *N*) aqueous ammonia. The reaction mixture is shaken vigorously until a gray precipitate forms, and the mixture is allowed to stand at room temperature overnight. After filtration, the crude material (yield, about 14.3 g.; m.p. 190 to 192°, decomp.) may be recrystallized if desired from about 200 ml. of 95% ethanol. In this way, about 12 g. of dark needles results, and additional material (1 g.) may be obtained by heating the filtrate to boiling and adding enough water (about 100 ml.) to initiate crystallization. The total yield of purified material is at least 13 g. (87%), m.p. 190 to 192°, decomp. *Anal.* Calcd. for $C_{10}H_{16}N_2O_2Cu$: C, 46.23; H, 6.21; N, 10.78. Found: C, 45.61; H, 6.03; N, 10.87. By checker: C, 46.10; H, 6.41; N, 10.75.

B. BIS(3-PHENYLIMINO-1-PHENYL-1-BUTANONATO)-COPPER(II)

$$\begin{aligned}&[CH_3CO{=}CHC(=NH)CH_3]_2Cu + \\ &\qquad 2C_6H_5COCH_2C(=NC_6H_5)CH_3 \rightarrow \\ &[C_6H_5CO{=}CHC(=NC_6H_5)CH_3]_2Cu + \\ &\qquad 2CH_3COCH_2C(=NH)CH_3\end{aligned}$$

A solution of 2.37 g. (0.01 mol) of 3-phenylimino-1-phenyl-1-butanone[4] and 1.3 g. (0.005 mol) of bis(4-imino-2-pentanonato)copper(II) in 75 ml. of 95% ethanol is heated at

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* Acetylacetone imide is available from the Aldrich Chemical Company, Milwaukee, Wis.

reflux for one hour. During this time, dark green platelets form. The reaction mixture is cooled in an ice-water bath and the green platelets collected by filtration (1.6 to 2.1 g.). Additional material (0.5 to 0.8 g.) is obtained by heating the filtrate to boiling, adding water (about 50 ml.) to initiate crystallization, and allowing the mixture to cool slowly. The crude material is recrystallized from 95% ethanol (in the proportion of 325 ml. of 95% ethanol for 2.4 g. of the crude material). The yield is about 1.7 g. (64%) of green platelets, m.p. 180 to 182°. *Anal.* Calcd. for $C_{32}H_{28}O_2N_2Cu$: C, 71.69; H, 5.26; N, 5.23. Found: C, 71.58; H, 5.17; N, 5.30. By checker: N, 5.40.

Properties

Bis(4-imino-2-pentanonato)copper(II) is obtained as short dark gray, almost black, needles from 95% ethanol. The compound melts with decomposition at 190 to 192°. Prominent bands in the infrared absorption spectrum of the compound have been listed and discussed.[3]

Bis(3-phenylimino-1-phenyl-1-butanonato)copper(II) crystallizes as green platelets (from 95% ethanol) which melt at 180 to 182°. The compound has been partially resolved into optical enantiomers by means of a chromatographic technique.[5]

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CHAPTER IIA

2. COMPLEX CARBONATES OF BERYLLIUM

SUBMITTED BY A. K. SENGUPTA*
CHECKED BY S. VON WINBUSH†

Beryllium hydroxide and the rather complex compounds obtained by the addition of ammonium carbonate, or the carbonates or hydrogen carbonates of the alkali metals, to solutions of beryllium salts are soluble in an excess of these reagents.[1] Debray[2] reported the isolation of compounds with formulas $3K_2Be(CO_3)_2 \cdot Be(OH)_2$ and $3(NH_4)_2Be(CO_3)_2 \cdot Be(OH)_2$ from solutions prepared by dissolving beryllium hydroxide in solutions of potassium carbonate and ammonium carbonate, respectively. Atterberg[3] considered these compounds to be mixtures, and Humpidge[4] later assigned the formula $2(NH_4)_2Be(CO_3)_2 \cdot Be(OH)_2$ to the ammonium compound. Recently, Pirtea[5] reported the isolation of the complex compound $[Co(NH_3)_6][(H_2O)_2Be_2(CO_3)_2(OH)_3] \cdot 3H_2O$.

The preparation of hydrated complex carbonatoberyllates of the form $M_6[Be_4O(CO_3)_6]$, where M is either $\frac{1}{3}[Co(NH_3)_6]^{3+}$ or K^+, is described in the following procedure. Inasmuch as the potassium compound can be completely dehydrated at ordinary temperatures, the formulation of the carbonatoberyllate anion with a single oxygen atom is preferred to writing the formula with two hydroxyl groups.

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Procedure

A. HEXAAMMINECOBALT(III) OXOHEXACARBONATOTETRABERYLLATE 10- AND 11-HYDRATES, $[Co(NH_3)_6]_2[Be_4O(CO_3)_6]\cdot xH_2O$

($x=$ 10 or 11)

By varying the concentration of the solution of alkali metal hydrogen carbonate or of ammonium carbonate, the salt can be obtained as either a 10- or 11-hydrate and in any of three crystalline modifications best described as being needle-like, tetrahedral, or polyhedral in character.

1. Needle-like modification: $[Co(NH_3)_6]_2[Be_4O(CO_3)_6]\cdot 11H_2O$. A solution composed of 3 g. (0.02 mol) of beryllium sulfate 4-hydrate dissolved in 10 ml. of water is added with constant stirring to a solution of 10 g. (0.1 mol) of ammonium carbonate in 35 ml. of water. When the precipitate that appears when the solutions are mixed has redissolved, the resulting solution is added with constant mechanical stirring to 170 ml. of an aqueous solution which contains 6 g. (0.02 mol) of hexaamminecobalt(III) chloride and 13 g. (0.14 mol) of ammonium carbonate. A voluminous mass of fine, slender, reddish-yellow crystals separates immediately. After a few minutes, the crystals are filtered by suction, are washed successively with water and ethanol, and are air-dried. The yield of $[Co(NH_3)_6]_2[Be_4O(CO_3)_6]\cdot 11H_2O$ is 3.9 g. (98%). *Anal.* Calcd. for $[Co(NH_3)_6]_2[Be_4O(CO_3)_6]\cdot 11H_2O$: N, 18.03; H, 6.27; C, 7.72; Be, 3.87. Found: N, 17.88; H, 6.18; C, 7.72; Be, 3.78. By checker: N, 18.70; H, 6.21; C, 7.82; Be, 3.83.

2. Polyhedral modification: $[Co(NH_3)_6]_2[Be_4O(CO_3)_6]\cdot 10H_2O$. A solution containing 1 g. (0.006 mol) of beryllium sulfate 4-hydrate dissolved in 65 ml. of water is saturated with potassium hydrogen carbonate and filtered. A solution of 1 g. (0.004 mol) of hexaamminecobalt(III) chloride in 15 ml. of water is added dropwise to the mechanically stirred solution. After approximately one-half of the reagent has been added, light orange-colored crystals of hexaamminecobalt(III) oxohexacarbonatotetraberyllate 10-hydrate, $[Co(NH_3)_6]_2[Be_4O(CO_3)_6]\cdot 10H_2O$, begin to separate from the solution. When the addition of the reagent is complete, the solution is allowed to stand for a few minutes; the crystals are then collected by suction filtration, are washed successively with water and ethanol, and are air-dried. The yield is 0.85 g. (65%). *Anal.* Calcd. for $[Co(NH_3)_6]_2[Be_4O(CO_3)_6]\cdot 10H_2O$: N, 18.3S; H, 6.17; C, 7.87; Be, 3.94. Found: N, 18.30; H, 6.18; C, 7.79; Be, 3.81. By checker: N, 18.89; H, 6.12; C, 8.58; Be, 3.93.

3. Tetrahedral modification: $[Co(NH_3)_6]_2[Be_4O(CO_3)_6]\cdot 10H_2O$. A solution of any soluble beryllium salt (sulfate, nitrate, or chloride) is prepared in such concentration that approximately 140 ml. of the solution will contain 0.1 g. (0.01 mol) of beryllium. This solution is saturated with potassium hydrogen carbonate (about 38 g. of potassium hydrogen carbonate will be required) and is separated by filtration from the undissolved solid. The solution is stirred mechanically and to it is added, in one installment, 125 ml. of a solution containing 6 g. (0.02 mol) of hexaamminecobalt(III) chloride and 8 g. (0.08 mol) of potassium hydrogen carbonate. Precipitation of tetrahedral crystals of hexaamminecobalt(III) oxohexacarbonatotetraberyllate 10-hydrate, $[Co(NH_3)_6]_2[Be_4O(CO_3)_6]\cdot 10H_2O$, reddish cream in color, is immediate. The solution is allowed to stand for a few minutes, is filtered, washed successively with water and ethanol, and air-dried. The yield is 2 g. (87%). *Anal.* Calcd. for $[Co(NH_3)_6]_2[Be_4O(CO_3)_6]\cdot 10H_2O$: N, 18.38; H, 6.17; C, 7.87; Be, 3.94. Found: N, 18.26; H, 6.15; C, 7.78; Be, 3.91. By checker: N, 18.50; H, 6.16; C, 7.80; Be, 3.94.

B. POTASSIUM OXOHEXACARBONATOTETRABERYLLATE, $K_6[Be_4O(CO_3)_6]$

Pure beryllium hydroxide, freshly prepared from 12 g. (0.06 mol) of beryllium nitrate 4-hydrate, is dissolved by heating it in 100 ml. of an aqueous solution containing 16 g. (0.16 mol) of potassium hydrogen carbonate. The solution is cooled to room temperature and is filtered.

The clear solution is placed in a glass-stoppered Erlenmeyer flask, and to it ethanol is added gradually and with frequent shaking until a heavy oily liquid separates. Portionwise addition of ethanol and agitation of the flask are continued until no further increase in the volume of the heavy layer is apparent or precipitation of potassium hydrogen carbonate begins.

The heavy oily liquid is separated from the rest of the solution and is placed in another glass-stoppered flask. Water is added dropwise to the oily emulsion until it becomes clear. To this solution is added a volume of ethanol equal to approximately one-third the volume of the solution itself. After the mixture has been shaken and allowed to stand for a few minutes, two immiscible phases again result. The heavy oily liquid is again drawn off, and further extractions with water and with ethanol, respectively, are made (about 10 times*) until the dropwise addition of water causes a white flocculent precipitate to form. After the solution has stood several minutes, it is filtered through *dry* fine-textured filter paper (S & S 589[3] or Whatman 42) and placed in a desiccator.

After several days the potassium salt crystallizes from the syrupy solution as large transparent rhombohedra. The crystals are filtered by suction and quickly dried between folds of filter paper. After the crystals have been powdered and dried to constant weight over P_4O_{10} the composition corresponds to that of the anhydrous salt, $K_6[Be_4O(CO_3)_6]$. *Anal.* Calcd. for $K_6[Be_4O(CO_3)_6]$: K, 36.28; Be, 5.57; CO_2, 40.82. Found: K, 36.46; Be, 5.51; CO_2, 41.06. By checker: K, 36.17; Be, 5.50.

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* The checker reports that a minimum of 10 extractions is essential if the compound is to crystallize in a reasonable length of time.

Properties

Hexaamminecobalt(III) carbonatoberyllates are generally insoluble in water, but complete precipitation of beryllium is obtained only in procedures A-1 and A-3. Although potassium oxohexacarbonatotetraberyllate dissolves in water to form a clear solution, a white flocculent precipitate separates after a few minutes, indicating that the complex carbonate anion must be unstable in aqueous solution.

The sodium and ammonium analogs of the potassium compound can be prepared by the same procedure as described for the synthesis of the potassium compound. Both of the alkali metal compounds are hygroscopic in nature. The ammonium derivative cannot be obtained in a pure condition, because of its continuous evolution of ammonia and carbon dioxide.

Anhydrous potassium oxohexacarbonatotetraberyllate is thermally stable up to a temperature of 100°; the hexaamminecobalt(III) salts decompose at temperatures above 50°.

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CHAPTER IIB

3. DICHLORO(2,2′-IMINODIPYRIDINE)ZINC, DIACETATO(2,2′-IMINODIPYRIDINE)ZINC, AND DICYANO(2,2′-IMINODIPYRIDINE)ZINC

$$ZnCl_2 + NH(C_5H_4N)_2 \rightarrow [Zn\{NH(C_5H_4N)_2\}Cl_2]$$

$$Zn(OOCCH_3)_2 + NH(C_5H_4N)_2 \rightarrow [Zn\{NH(C_5H_4N)_2\}(OOCCH_3)_2]$$

$$Zn(CN)_2 + NH(C_5H_4N)_2 \rightarrow [Zn\{NH(C_5H_4N)_2\}(CN)_2]$$

Submitted by Joseph Simkin* and B. P. Block*
Checked by John A. Broomhead†

In Volume V of this series, syntheses were presented for coordination compounds of 2,2′-iminodipyridine [di-2-pyridylamine, $NH(C_5H_4N)_2$] with copper(II)[1] and cobalt-(II).[2] Nickel(II) has also been shown to coordinate with this ligand.[3] A similar behavior is exhibited by zinc salts, which form 1:1 derivatives if a 1:1 mol ratio of reactants is used. The specific choice of a solvent medium for synthesis is dictated by the solubility of the zinc compound. Either acetone or methanol may be used with zinc chloride, methanol with zinc acetate, and pyridine with zinc cyanide.

Procedure

A. DICHLORO(2,2′-IMINODIPYRIDINE)ZINC

Commercial 2,2′-iminodipyridine‡ is purified by recrystallization from ethanol (20 g. of 2,2′-iminodipyridine in 30

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† University of Queensland, St. Lucia, Brisbane, Australia.

‡ Available from Reilly Tar and Chemical Corp., Indianapolis, Ind.

ml. of hot ethanol to yield 18.5 g. of purified compound). A solution of 17.12 g. (0.10 mol) of the purified 2,2′-iminodipyridine in 280 ml. of reagent-grade acetone is added dropwise with vigorous stirring to a filtered solution of 13.63 g. (0.10 mol) of reagent-grade anhydrous zinc chloride in 30 ml. of reagent-grade acetone. (Granular anhydrous zinc chloride is preferable because of its ease of solution; if it is not available, sticks of zinc chloride should be powdered and weighed rapidly. Anhydrous zinc chloride powder may be obtained commercially or may be prepared by the method of Pray.[4]) The white precipitate which forms almost immediately is removed by vacuum filtration, washed with three successive 30-ml. portions of acetone, and dried to constant weight at 90 to 95°. The yield is 29.5 to 30.5 g. (96 to 99%). *Anal.* Calcd. for $[Zn\{NH(C_5H_4N)_2\}Cl_2]$: C, 39.06; H, 2.95; N, 13.67; Cl, 23.06; Zn, 21.26. Found: C, 39.1; H, 3.0; N, 13.9; Cl, 23.4; Zn, 21.2. By checker: C, 39.11; H, 3.22; N, 13.72.

B. DIACETATO(2,2′-IMINODIPYRIDINE)ZINC

NOTE: Parts B and C include modifications suggested by the checker and checked independently by the submitters.

A solution of 17.56 g. (0.08 mol) of zinc acetate 2-hydrate in 100 ml. of absolute methanol is filtered into a 250-ml. flask. To this solution is added with stirring a solution of 13.70 g. (0.08 mol) of 2,2′-iminodipyridine in 20 ml. of hot methanol. The solution is heated to boiling and then allowed to cool. White crystals are deposited. The mixture is cooled in ice and the product filtered off, washed with acetone, and dried at 90 to 95°. The yield is 20.1 g. (71%). *Anal.* Calcd. for $[Zn\{NH(C_5H_4N)_2\}(CH_3CO_2)_2]$: C, 47.41; H, 4.26; N, 11.85; Zn, 18.43. Found: C, 47.7; H, 4.1; N, 11.8; Zn, 18.4. By checker: C, 47.51; H, 4.57; N, 11.91.

C. DICYANO(2,2′-IMINODIPYRIDINE)ZINC

A solution of 3.51 g. (0.030 mol) of zinc cyanide in 250 ml. of pyridine is heated to boiling on a hot plate and filtered while hot. The solution obtained by dissolving 7.7 g. (0.045 mol) of 2,2′-iminodipyridine in the filtrate is heated to boiling and evaporated to dryness on a steam bath. The white residue is then finely ground, washed four times with 100-ml. portions of boiling absolute ethanol, and dried at 90 to 95° at 20 mm. pressure. The yield is 6.4 g. (74%). *Anal.* Calcd. for $[Zn\{NH(C_5H_4N)_2\}(CN)_2]$: C, 49.94; H, 3.14; N, 24.27; Zn, 22.65. Found: C, 49.4; H, 3.0; N, 24.1; Zn, 22.9. By checker: C, 49.33; H, 3.31; N, 23.99.

Properties

All three compounds are white solids. The acetato derivative melts at 254 to 259°, but the other two decompose on heating. All three are insoluble in carbon tetrachloride, acetone, ether, and benzene and soluble in *N,N*-dimethylformamide, *N,N*-dimethylacetamide, and pyridine. The acetato derivative is soluble in water, methanol, and ethanol. The chloro derivative is sparingly soluble in boiling water and insoluble in methanol and ethanol, whereas the cyano derivative is somewhat soluble in boiling ethanol and methanol and insoluble in water.

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CHAPTER IVA

See also: Bis(4-imino-2-pentanonato)copper(II) and bis(3-phenylimino-1-phenyl-1-butanonato)copper(II), synthesis 1
Complex carbonates of beryllium, synthesis 2
Dichloro(2,2′-iminodipyridine)zinc, diacetato(2,2′-iminodipyridine)zinc, and dicyano(2,2′-iminodipyridine)zinc, synthesis 3
Dichlorobis(2,4-pentanedionato)titanium(IV): (correction), synthesis 10
Tris(2,4-pentanedionato)zirconium(IV) chloride, synthesis 11
Potassium tetraoxalatozirconate, -hafnate, and -thorate, synthesis 12
Metal derivatives of β-keto imines (β-imino ketones), synthesis 13
Phenyllead(IV) azides, synthesis 15
Tetraphosphorus hexamethylhexaimide, synthesis 16
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4. SODIUM BIS(TRIMETHYLSILYL)AMIDE AND TRIS(TRIMETHYLSILYL)AMINE

Submitted by Carl R. Krüger* and Hans Niederprüm†
Checked by Max Schmidt‡ and O. Scherer‡

Alkali metal derivatives of hexamethyldisilazane are obtained by the reaction of hexamethyldisilazane with the corresponding metal alkyls or aryls,[1] with the metal hydrides,[2] or with the metal amides.[1] The use of sodium amide is much simpler and easier than the use of hydrides, and it is less expensive. Metal alkyls are usually not readily available commercially, making necessary another step in the synthesis if alkyls are used as starting materials. The procedure below provides for the preparation of sodium bis(trimethylsilyl)amide and then describes its use in the preparation of tris(trimethylsilyl)amine.

Tris(trimethylsilyl)amine may also be prepared from lithium bis(trimethylsilyl)amide, as described in synthesis 5 of this volume.

Procedure

A. SODIUM BIS(TRIMETHYLSILYL)AMIDE

$$(CH_3)_3Si—NH—Si(CH_3)_3 + NaNH_2 \rightarrow NaN[Si(CH_3)_3]_2 + NH_3$$

Caution. Extreme care should be taken in handling sodium amide, especially during the grinding of the material. Rubber gloves and a face mask should be worn, and the amide should be ground in small portions. Sodium amide, especially corroded pieces, has been reported to detonate without apparent cause. Contact with water should be carefully avoided.

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The reaction is performed in a 2-l. three-necked ground-joint flask, equipped with reflux condenser, sealed stirrer, gas inlet tube, and drying tube.

After the flask is flushed with dry nitrogen,* 78 g. (2.0 mols) of ground sodium amide, or the equivalent quantity of a commercially available suspension of sodium amide in benzene or toluene, is added to 1000 ml. of benzene dried over sodium. Then 322.8 g. (2.00 mols) of hexamethyldisilazane† is added in one portion to the suspension. After the addition, the reaction mixture warms up slowly. The reaction is completed by refluxing the stirred suspension for 48 hours or more, until only traces of ammonia are evolved. At this point, the solution should appear nearly clear and only slightly yellow, depending on the quality of the starting materials used. Traces of unreacted sodium amide are now removed by filtration of the hot solution with slight suction through a medium glass frit. Employing other than a slight vacuum may lead to evaporation of the solvent and clogging of the frit. The clear solution thus obtained is evaporated under vacuum using a precision-ground sealed stirrer to prevent bumping of the suspension. Sodium bis(trimethylsilyl)amide remains as a yellow-white powder. The yield is 275 to 300 g. (75 to 82%). This material is pure enough for most preparative purposes. *Care should be taken in cleaning the glassware used in the procedure. The glassware should be rinsed with methanol to destroy any remaining sodium amide residue before washing with water.*

Properties

Sodium bis(trimethylsilyl)amide, when recrystallized from anhydrous benzene, forms white prisms. It is soluble

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* Prepurified nitrogen may be first dried with concentrated sulfuric acid and then passed over Drierite or silica gel.

† Hexamethyldisilazane is available commercially from Peninsular Chem. Research, Inc., Gainesville, Fla. It may be prepared according to the procedure of R. O. Sauer and R. H. Hasek, *J. Am. Chem. Soc.*, **68**, 241 (1946) or by the method described in synthesis 5 of this volume.

in relatively nonpolar solvents such as benzene, toluene, and xylene and appears to be dimeric in these solvents. It forms addition compounds with diethyl ether, dioxane, tetrahydrofuran, and pyridine, and in adduct form is easily soluble in these solvents. If moisture is excluded, sodium bis(trimethylsilyl)amide may be stored indefinitely. Water and alcohols decompose it with formation of silanol, sodium hydroxide, and ammonia. The salt may be used to prepare a variety of silicon-nitrogen compounds[3–6] and is useful as a strong base in a variety of organic reactions.[8,9]

B. TRIS(TRIMETHYLSILYL)AMINE

$$NaN[Si(CH_3)_3]_2 + ClSi(CH_3)_3 \rightarrow N[Si(CH_3)_3]_3 + NaCl$$

NOTE: To prepare tris(trimethylsilyl)amine, it is not necessary to isolate or purify the sodium compound described in Part A; the trimethylchlorosilane may simply be added to a quantity equal to about 6% of the unfiltered benzene solution of sodium bis(trimethylsilyl)amide obtained in Part A. Otherwise, the procedure as described below is followed exactly.

Eighteen and four-tenths grams (0.1 mol) of sodium bis(trimethylsilyl)amide is placed in a dry 500-ml. three-necked flask equipped with reflux condenser, sealed stirrer, dropping funnel, and drying tube. The salt is dissolved in 200 ml. of dry absolute benzene with gentle heating (or if the portion of the benzene solution from Part A is used, the volume is brought up to 200 ml. by addition of dry absolute benzene). The resulting solution is stirred while a solution of 10.8 g. (0.1 mol) of freshly distilled trimethylchlorosilane in 50 ml. of dry benzene is slowly added. After a short period of time, the separation of sodium chloride begins. The reaction is completed by refluxing the mixture for 10 hours. If time is a factor, a shorter reflux time (as little as 3 hours) can be used satisfactorily but with a reduction in yield.

After cooling to room temperature, the suspension is filtered with suction through a medium glass frit, and the residue is washed twice with 50 ml. of dry benzene, yielding a colorless solution of tris(trimethylsilyl)amine. The solvent is removed by distillation, and from the remaining residue tris(trimethylsilyl)amine is isolated by distillation under normal pressure, using a small column, an air condenser, and a fractionation "udder." The fraction distilling between 214 and 216° solidifies in the receiving flask. Clogging of the condenser may be avoided by gentle heating with a Bunsen burner. The yield of tris(trimethylsilyl)amine is about 18 g. (80%). *Anal.* Calcd. for $N[Si(CH_3)_3]_3$: C, 46.28; H, 11.65; Si, 36.07; N, 6.00. Found: C, 46.40, 46.60; H, 11.65, 11.56; Si, 35.70; N, 6.06, 6.30.

Properties

Tris(trimethylsilyl)amine is a waxlike material that melts at 67 to 69° and boils without decomposition at 215° (or 85° at 13 mm.). It is easily soluble in nonpolar organic solvents, and, with splitting of the Si—N bond, in alcohols or acids. It is not affected by water and alkalies. The infrared spectrum[7] is reported to have absorption maxima due to Si—N stretching frequencies with the symmetric stretch at 430 $cm.^{-1}$ and the asymmetric stretch at 916 $cm.^{-1}$, indicating a nearly planar structure for the compound. The proton magnetic resonance spectrum[8] shows one single signal at 9.825 τ for a 5% solution in carbon tetrachloride. The compound shows no basic properties; addition of boron fluoride occurs only below −20°, forming an unstable adduct.

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5. LITHIUM BIS(TRIMETHYLSILYL)AMIDE AND TRIS(TRIMETHYLSILYL)AMINE

Submitted by E. H. Amonoo-Neizer,* R. A. Shaw,* D. O. Skovlin,* and B. C. Smith*
Checked by Joel W. Rosenthal† and William L. Jolly†

Ammonia reacts with trimethylchlorosilane to give hexamethyldisilazane, but tris(trimethylsilyl)amine is not formed by this reaction.[1] Hexamethyldisilazane reacts with *n*-butyllithium to give lithium bis(trimethylsilyl)amide, which is a strong nucleophilic reagent. Reaction of this product with trimethylchlorosilane gives tris(trimethylsilyl)amine.[2] The method is similar to that described by Wannagat and Niederprüm,[3] but it avoids the use of a sealed tube. Hexamethyldisilazyl derivatives of sodium and potassium have been investigated.[3] Tris(trimethylsilyl)amine has been prepared by Goubeau and Jiménez-Barberá[4] from the reaction of hexamethyldisilazane with sodium and styrene.

The procedure below describes the preparation of lithium bis(trimethylsilyl)amide and its subsequent use in the preparation of tris(trimethylsilyl)amine. Tris(trimethylsilyl)amine may also be prepared from sodium bis(trimethylsilyl)amide. The method is described in synthesis 4.

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A. LITHIUM BIS(TRIMETHYLSILYL)AMIDE

$$3NH_3 + 2(CH_3)_3SiCl \rightarrow [(CH_3)_3Si]_2NH + 2NH_4Cl$$
$$2Li + n\text{-}BuCl \rightarrow n\text{-}BuLi + LiCl$$
$$[(CH_3)_3Si]_2NH + n\text{-}BuLi \rightarrow LiN[Si(CH_3)_3]_2 + n\text{-}BuH$$

Procedure

A 1-l. three-necked flask is fitted with a reflux condenser, a stirrer, and an inlet for ammonia. (*Caution. Proper care should be exercised to make the equipment suitable for use with ether.*) A solution of 50.0 ml. (0.39 mol) of trimethylchlorosilane in 500 ml. of dry ether is placed in the flask. The solution is stirred for a period of 3 hours, and during this entire time, ammonia is bubbled through the stirred solution. Additional ether should be added from time to time, if necessary, to maintain approximately the original volume. The apparatus becomes coated on the inside with ammonium chloride as the reaction proceeds. At the conclusion of the 3-hour period, the ammonium chloride is removed by suction filtration under anhydrous conditions and then washed with ether. Fractional distillation of the combined filtrate and washings produces hexamethyldisilazane (b.p. 124 to 126°). The yield is 23.0 g. (73%).

The apparatus for the preparation of *n*-butyllithium[5,*] consists of a three-necked flask fitted with a mercury-sealed stirrer, a dropping funnel, and a reflux condenser. The apparatus is assembled *hot*, and air is immediately displaced by a stream of dry nitrogen which enters through the condenser. A solution of 37 ml. (0.35 mol) of *n*-butyl chloride in 50 ml. of *n*-pentane is added slowly (about one drop per second) to small pieces of lithium wire (5.0 g.; 0.71 mol) suspended in 80 ml. of *n*-pentane. Reaction begins after a short induction period (about 10 minutes), producing a

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[*] *n*-Butyllithium is also available commercially.

purple precipitate. The mixture is boiled for 2 hours under reflux by means of an infrared lamp, cooled, and filtered in an atmosphere of nitrogen through a glass tube packed with glass wool. The solution which remains, *n*-butyllithium in *n*-pentane, is diluted to a known volume, and a 2-ml. sample is allowed to hydrolyze. The hydrolysis product is standardized by titration with dilute hydrochloric acid. Yields are about 70%. *Excess lithium in the reaction flask is destroyed with 1-propanol in an atmosphere of nitrogen.*

The preparation of lithium bis(trimethylsilyl)amide must also be performed in an atmosphere of dry nitrogen. A solution containing 19 g. (0.3 mol) of *n*-butyllithium in 150 ml. of pentane is added slowly to a stirred solution of 66.0 ml. (0.32 mol) of hexamethyldisilazane in 100 ml. of ether. The reaction mixture is boiled under reflux for 30 minutes, and then the solvents are evaporated. Distillation *in vacuo* produces lithium bis(trimethylsilyl)amide (b.p. 80 to 84° at 0.01 mm.) as a colorless liquid. On cooling, the liquid solidifies to colorless crystals melting at 71 to 72°. The yield is 44 g. (88%). *Anal.* Calcd. for $C_6H_{18}LiNSi_2$: C, 43.1; H, 10.8; Li, 4.2; N, 7.8. Found: C, 44.6; H, 10.6; Li, 3.9; N, 8.4.

The distillation residue is destroyed with 1-propanol in an atmosphere of nitrogen.

Properties

Lithium bis(trimethylsilyl)amide is a colorless solid which is soluble in a variety of organic solvents suitable for reactive compounds such as organometallic substances or substituted metal amides. The compound melts at 71 to 72°. It is unstable in air and catches fire when compressed, but it is stable in an atmosphere of nitrogen. Reactions with a variety of nonmetallic halides give lithium halides and hexamethyldisilazyl derivatives.

B. TRIS(TRIMETHYLSILYL)AMINE

$$LiN[Si(CH_3)_3]_2 + ClSi(CH_3)_3 \rightarrow N[Si(CH_3)_3]_3 + LiCl$$

A solution of 2.6 ml. (0.021 mol) of trimethylchlorosilane in 20 ml. of ether is added to a stirred solution of 3.5 g. (0.021 mol) of lithium bis(trimethylsilyl)amide in 50 ml. of ether. (*Caution. An exothermic reaction takes place.*) The mixture is then boiled under reflux for 8 hours. Lithium chloride is removed by filtration in an atmosphere of nitrogen. The filtrate is evaporated to dryness (foaming may occur) and redissolved in petroleum ether (b.p. 60 to 80°). Any last traces of lithium chloride are removed by filtration. Evaporation of the solvent, followed by distillation of the residue, as described in synthesis 4, is required to isolate the tris(trimethylsilyl)amine. The product is a waxlike solid which has a melting point of 67 to 68° and a boiling point of 79° at 10 mm. pressure. The yield is 2.5 to 3.0 g. (50 to 60%). *Anal.* Calcd. for $C_9H_{27}NSi_3$: C, 46.3; H, 11.65; N, 6.0; Si, 36.1. Found: C, 46.3; H, 11.9; N, 6.2; Si, 36.3.

Properties

The properties of tris(trimethylsilyl)amine have been described in synthesis 4.

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Edited by Henry F. Holtzclaw, Jr.

6. SILICON TETRAISOCYANATE AND METHYLSILICON ISOCYANATES

$$SiCl_4 + 4AgNCO \rightarrow Si(NCO)_4 + 4AgCl$$

$$(CH_3)_nSiCl_{4-n} + (4 - n)AgNCO \rightarrow (CH_3)_nSi(NCO)_{4-n} + (4 - n)AgCl$$

Submitted by Roy G. Neville*† and John J. McGee*
Checked by Constance Wright‡ and Earl L. Muetterties‡

Silicon tetraisocyanate and methylsilicon isocyanates, of the type $(CH_3)_nSi(NCO)_{4-n}$ ($n = 1$, 2, or 3), were first prepared in 75 to 90% yields by treating silicon(IV) chloride or the appropriate methylchlorosilane with silver isocyanate in anhydrous benzene.[1] Forbes and Anderson[1] report that much smaller yields are obtained when lead cyanate is used instead of silver isocyanate. The following procedure, however, when performed with lead cyanate, produces 52 to 71% yields of the silicon isocyanates. Comments on the use of less expensive lead cyanate are therefore included along with the silver isocyanate method of preparation.

Procedures for the corresponding thiocyanate compounds are described in synthesis 7.

Procedure

A. SILVER ISOCYANATE AND LEAD CYANATE

Silver isocyanate is prepared by adding a solution of 487 g. (6.0 mols) of potassium cyanate in 1 l. of distilled water to a well-stirred solution of 1019 g. (6.0 mols) of silver nitrate in 1 l. of distilled water. The temperature of the mixture is kept below 25° by cooling in an ice bath as nec-

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essary. The precipitated silver isocyanate is filtered, washed with five 100-ml. portions of distilled water followed by two 100-ml. portions of acetone, pressed thoroughly, and drained. The white solid, spread on a large polyethylene tray and covered loosely by aluminum foil to prevent photodecomposition, is dried overnight by exposure to a stream of air *in a good hood.* Final traces of moisture are removed by placing the solid in a crystallizing dish in a vacuum desiccator (covered by aluminum foil) and evacuating for 3 hours.

Lead cyanate is similarly prepared from 1987 g. (6.0 mols) of lead nitrate and 973 g. (12.0 mols) of potassium cyanate.

High yields of the silicon isocyanates are obtained when freshly prepared silver isocyanate or lead cyanate is employed. When the silver or lead salt is several weeks old, or is dried in an oven, the yields of silicon isocyanates are about 20% lower.

B. SILICON TETRAISOCYANATE

Finely powdered silver isocyanate (660 g.; 4.4 mols; 10% theoretical excess)* is mixed with 800 ml. of anhydrous sodium-dried benzene contained in a 3-l. three-necked standard-taper flask fitted with a motor-driven stirrer, a thermometer, a 125-ml. dropping funnel, and a 300-mm. Allihn condenser topped by a Drierite-filled tube. Silicon(IV) chloride (170 g.; 1.0 mol) is added dropwise to the suspension over a 30- to 45-minute period with rapid stirring. The reaction is strongly exothermic, and the temperature of the mixture must be maintained below 45° by cooling the bottom of the flask, as necessary, in an ice-water bath. After the silicon(IV) chloride has been added, the mixture is heated at gentle reflux for 3 hours, with con-

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* A 10% excess of silver isocyanate or lead cyanate has repeatedly been found to give the highest yields of product. A 25% excess produces no greater yield. Stoichiometric amounts produce slightly lower yields. On the other hand, a 10% excess of silicon(IV) chloride results in only a 40% yield of silicon tetraisocyanate.[1]

tinuous vigorous stirring, and then cooled to room temperature. The blue-gray silver salts are filtered on a Büchner funnel fitted with Whatman no. 1 paper and washed with five 70-ml. portions of anhydrous sodium-dried benzene, or until no isocyanate odor can be detected in the solids. The pale yellow filtrate is distilled using a 50-cm. Vigreux column, which may be wrapped with aluminum foil to increase the speed of the distillation. After removing the benzene, the crude residual liquid is transferred to a 250-ml. flask and distilled, using the Vigreux column and collecting the fraction boiling at 185 to 189°. The yield of colorless liquid is 167 g. [85.3% based on silicon(IV) chloride].* *Anal.* Calcd. for $Si(NCO)_4$: C, 24.5; N, 28.6; Si, 14.2. Found (by checkers): C, 24.4; N, 28.7; Si, 14.1. On standing in the refrigerator, the liquid freezes to colorless crystals which melt at 26°.

When freshly prepared lead cyanate (642 g.; 2.2 mols; 10% theoretical excess) is employed in the above procedure instead of silver isocyanate, the reaction is only slightly exothermic. The silicon(IV) chloride can therefore be added at a fairly rapid rate after the reaction has been initiated by heating to 35 to 40°. The mixture is then refluxed with vigorous stirring for 3 hours. After the benzene is distilled, the yield of silicon tetraisocyanate is 121 g. [61.8% based on silicon(IV) chloride].

The preparation of silicon tetraisocyanate from finely powdered potassium cyanate gives only a 2% yield, in agreement with the observation of Forbes and Anderson.[1]

C. METHYLSILICON ISOCYANATES

Methylsilicon triisocyanate and dimethysilicon diisocyanate can be prepared from the appropriate methylchlorosilane and a 10% theoretical excess of the inorganic cyanate with the same equipment and procedure as employed in the synthesis of silicon tetraisocyanate. With

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* The checkers report a 63.4% yield with the scale reduced to 0.25 mol of silicon(IV) chloride as starting material.

silver isocyanate the yields of methylsilicon triisocyanate and dimethylsilicon diisocyanate are 88 and 84%, respectively. With lead cyanate the yields are 60 and 52%, respectively.

Because trimethylsilicon isocyanate boils at 91°, making its separation from benzene somewhat difficult, this isocyanate is more readily prepared by using the same volume of xylene instead of benzene. With this modification, the yield of trimethylsilicon isocyanate is 91% from silver isocyanate,* or 71% from lead cyanate. *Anal.* Calcd. for $(CH_3)_3SiNCO$: N, 12.2; Si, 24.4. Found (by checkers): N, 11.8; Si, 23.6.

Properties

Silicon tetraisocyanate is a stable white crystalline solid which melts at 26.0 ± 0.5° and boils at 185.6 ± 0.3°. It is soluble in benzene, chloroform, carbon tetrachloride, acetone, and petroleum naphtha. On exposure to moist air or water, it is rapidly hydrolyzed to gelatinous silica and cyanic acid. It reacts vigorously with most primary and secondary aliphatic and aromatic amines to produce, respectively, *N*-mono- or *N,N*-disubstituted ureas[2,3] and thus is useful in the synthesis of these classes of compounds.

The methylsilicon isocyanates are very similar in chemical and physical properties to silicon tetraisocyanate. They are colorless liquids at room temperature, possess pungent odors, and are strong lacrimators. The melting and boiling points, respectively, are as follows: trimethylsilicon isocyanate, −49.0 ± 3°, 91.0 ± 0.3°; dimethylsilicon diisocyanate, −31.2 ± 3°, 139.2 ± 0.3°; methylsilicon triisocyanate, −2.7 ± 0.5°, 170.8 ± 0.3°.

The compounds are readily hydrolyzed by water or moist air and react vigorously with most primary or secondary aliphatic or aromatic amines to produce *N*-mono- or *N,N*-disubstituted ureas.

* The checkers report a 71.1% yield with the scale reduced one-half.

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7. SILICON TETRAISOTHIOCYANATE AND METHYLSILICON ISOTHIOCYANATES

$$SiCl_4 + 4NH_4SCN \rightarrow Si(NCS)_4 + 4NH_4Cl$$

$$(CH_3)_nSiCl_{4-n} + (4 - n)NH_4SCN \rightarrow (CH_3)_nSi(NCS)_{4-n} + (4 - n)NH_4Cl$$

$$(n = 1, 2, \text{ or } 3)$$

Submitted by Roy G. Neville*† and John J. McGee*
Checked by Constance Wright‡ and Earl L. Muetterties‡

Silicon tetraisothiocyanate was first prepared by Miquel[1,2] and Reynolds[3] by treating silicon(IV) chloride with lead thiocyanate. Later, Forbes and Anderson[4–9] prepared many substituted silicon isothiocyanates by metathetical reaction of the corresponding chlorosilanes with silver thiocyanate. On the bases of molecular refraction studies, the latter workers concluded that the silane derivatives are isothiocyanates rather than the isomeric thiocyanates. Conclusive proof that these compounds are isothiocyanates is their formation in good yield from isocyanosilanes and sulfur:[10]

$$R_3SiNC + S \rightarrow R_3SiNCS$$

Although the silicon isothiocyanates have been prepared by treating chlorosilanes with the thiocyanates of sodium,

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potassium, ammonium, silver, lead, and copper, the best yields are obtained with silver thiocyanate or ammonium thiocyanate.[11] Procedures describing the use of these two salts are given below. Ammonium thiocyanate gives approximately 5% lower yields of the silicon isothiocyanates, whereas the silver salt gives less pure products.

Procedures for the corresponding cyanate compounds are described in synthesis 6.

Procedure

A. SILVER THIOCYANATE

A solution of 457 g. (6.0 mols) of ammonium thiocyanate in 1 l. of distilled water is added over a 15-minute period, with good stirring, to a solution of 1019 g. (6.0 mols) of silver nitrate in 1 l. of distilled water. The temperature is maintained below 25° by cooling the mixture in an ice bath. The precipitate is filtered through a sintered-glass funnel, washed with five 70-ml. portions of distilled water followed by two 50-ml. portions of acetone, pressed thoroughly, and drained. The white solid is then spread on a large polyethylene tray, covered loosely by aluminum foil to prevent decomposition by light, and dried overnight by exposure to a rapid stream of air *in a good hood.* Residual moisture is removed by placing the product in a crystallizing dish in a vacuum desiccator covered by aluminum foil and evacuating for 3 hours.

B. SILICON TETRAISOTHIOCYANATE

Finely powdered ammonium thiocyanate (190 g.; 2.5 mols; 25% theoretical excess) is mixed with 800 ml. of anhydrous sodium-dried benzene* contained in a 2-l. three-necked standard-taper flask fitted with a motor-driven stirrer, a thermometer, a 125-ml. dropping funnel, and a

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* If less benzene is employed, the resulting silicon isothiocyanate crystallizes, thus making separation of ammonium salts difficult.

300-mm. Allihn condenser equipped with a Drierite-filled tube. Silicon(IV) chloride (85 g.; 0.5 mol) is added to the suspension over a 5-minute period with rapid stirring. The reaction is only slightly exothermic. After gentle refluxing for 3 hours, during which vigorous stirring is maintained, the pale yellow mixture is cooled to about 70° and filtered (*hood!*) through a coarse-grade sintered-glass funnel. The solids are washed with five 60-ml. portions of hot benzene, or until the characteristic odor of the isothiocyanate can no longer be detected. The pale yellow filtrate is distilled through a 50-cm. Vigreux column to a residual volume of approximately 200 ml. The hot contents are immediately transferred to a 400-ml. beaker (*hood!*) and the flask rinsed with about 20 to 30 ml. of fresh benzene, which is then added to the main solution. On cooling (in a partially evacuated desiccator to prevent partial hydrolysis of the isothiocyanate by atmospheric moisture), silicon tetraisothiocyanate crystallizes from the concentrated benzene solution. The colorless crystals are filtered rapidly through a coarse-grade sintered-glass funnel, washed with 50 ml. of cold anhydrous sodium-dried benzene, pressed, and drained. Residual benzene is removed by placing the crystals in a vacuum desiccator and evacuating for one hour. The yield of silicon tetraisothiocyanate is 104 to 112 g. [80 to 86% based on silicon(IV) chloride]. An additional 10% of less pure isothiocyanate may be obtained by evaporating the mother liquor to dryness in a rotary evaporator.

When silver thiocyanate is employed in the above preparation, the resulting silicon tetraisothiocyanate is yellow. Silicon tetraisothiocyanate freshly prepared from ammonium thiocyanate is colorless, although on standing for several days the product assumes a pale yellow color.

C. METHYLSILICON ISOTHIOCYANATES

The three possible methylsilicon isothiocyanates are prepared by allowing the appropriate methylchlorosilanes to react with a 25% excess of ammonium thiocyanate in the same equipment and by the same procedure as employed in the synthesis of silicon tetraisothiocyanate. Crystalline methylsilicon triisothiocyanate can be isolated by filtration. Dimethylsilicon diisothiocyanate is isolated by distilling the benzene solution through a 50-cm. Vigreux column and collecting the fraction boiling at 60 to 66° at 1.0-mm. pressure (most of the product distills at 64° at 1.0 mm. pressure). Trimethylsilicon isothiocyanate is obtained by collecting the fraction boiling at 138 to 145° at 760 mm. pressure. The yields of methylsilicon isothiocyanates are: methylsilicon triisothiocyanate, 83%; dimethylsilicon diisothiocyanate, 86%; and trimethylsilicon isothiocyanate, 80%.

Properties

When freshly prepared from ammonium thiocyanate, silicon tetraisothiocyanate is a stable colorless crystalline solid which melts at 143.8° and boils at 313°. It is soluble in chloroform, carbon tetrachloride, acetone, benzene, and petroleum naphtha.

Silicon tetraisothiocyanate is rapidly hydrolyzed to gelatinous silica and thiocyanic acid on exposure to moist air or water. With primary or secondary aliphatic or aromatic amines, silicon tetraisothiocyanate reacts to produce *N*-mono- or *N*,*N*-disubstituted thioureas, respectively, in essentially 100% yields.[12]

In chemical reactions and physical properties the methylsilicon isothiocyanates are very similar to silicon tetraisothiocyanate. Methylsilicon triisothiocyanate* and dimethylsilicon diisothiocyanate are colorless solids at room temperature, whereas trimethylsilicon isothiocyanate is a colorless liquid. All possess pungent odors and are lacrimators. The melting and boiling points are respectively: methylsilicon triisothiocyanate, 72.4°, 266.8°; dimethylsilicon diisothiocyanate, 18.0°, 217.3°; trimethylsilicon isothiocyanate, −32.8°, 143.1°.

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* Like silicon tetraisothiocyanate, methylsilicon triisothiocyanate turns pale yellow on standing.

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8. TETRAPHENYLGERMANE AND HEXAPHENYLDIGERMANE

Submitted by Frank Glockling* and K. A. Hooton*
Checked by John C. Kotz† and A. W. Laubengayer†

A. TETRAPHENYLGERMANE

$$GeCl_4 + 4C_6H_5MgBr \xrightarrow{\text{tetrahydrofuran}} (C_6H_5)_4Ge + 2MgCl_2 + 2MgBr_2$$

The following procedure,[1] using tetrahydrofuran as solvent, is simpler and gives a higher yield of product (85%) than earlier methods.[2] Complete removal of excess magnesium is essential to avoid the formation of hexaphenyldigermane as a by-product.

Procedure

Phenylmagnesium bromide solution [resulting from the reaction of 88 g. (0.56 mol) of bromobenzene with 15.6 g.

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(0.64 mol) of magnesium turnings in 180 ml. of tetrahydrofuran] is filtered through a sintered disk into a three-necked flask. The sintered disk may be of coarse grade; nitrogen pressure may then suffice for the filtration. If a fine sintered disk is used, provision should be made for a vacuum on the system. The solution should be filtered while it is as warm as possible (35 to 45°). If some Grignard reagent precipitates on the filter, it may be washed through with a *small* amount of tetrahydrofuran.

A solution containing 10 g. (0.070 mol) of germanium(IV) chloride in 60 ml. of tetrahydrofuran is added to the solution of the Grignard reagent over a 10-minute period. The resulting mixture is heated under reflux in a nitrogen atmosphere with mechanical stirring for 18 hours. After cooling to room temperature, crude tetraphenylgermane is filtered rapidly to minimize hydrolysis of the excess Grignard reagent, which would impede filtration, washed on the filter first with dilute (20% by volume) acetic acid and then water, and dried in an oven at 120°. Concentration of the filtrate, followed by cautious hydrolysis with wet ethanol and then acid and water washings, may lead to the isolation of additional crude product. After crystallization from toluene, the product melts at 232 to 234°. The yield is 15.3 g. (85%). *Anal.* Calcd. for $(C_6H_5)_4Ge$: C, 75.7; H, 5.3; Ge, 19.07. Found: C, 75.5; H, 5.3; Ge, 19.06.

B. HEXAPHENYLDIGERMANE

$$GeCl_4 + 3C_6H_5MgBr \rightarrow (C_6H_5)_3GeBr + 2MgCl_2 + MgBr_2$$

$$(C_6H_5)_3GeBr + Mg \rightarrow (C_6H_5)_3GeMgBr$$

$$(C_6H_5)_3GeMgBr + (C_6H_5)_3GeBr \rightarrow (C_6H_5)_3GeGe(C_6H_5)_3 + MgBr_2$$

Germanium(IV) chloride reacts with aryl Grignard reagents *containing excess magnesium metal* largely according to the three equations given above.[1] Tetraphenylgermane is simultaneously formed by direct reaction of triphenylbromogermane with phenylmagnesium bromide. An earlier method[3] is successful only if the Grignard reagent contains excess magnesium.

Procedure

To a solution of phenylmagnesium bromide containing excess magnesium [prepared from 159 g. (1.01 mols) of bromobenzene and 28 g. (1.2 mols) of magnesium turnings in 500 ml. of ether] is added a solution containing 18 g. (0.13 mol) of germanium(IV) chloride in 200 ml. of toluene. The toluene–germanium(IV) chloride solution is added at such a rate as to maintain gentle reflux of the solution.

The mixture is heated under reflux in a nitrogen atmosphere with mechanical stirring for 4 hours. It is then filtered in air, rapidly to avoid hydrolysis, by using a coarse sintered-disk funnel having a large plate diameter (50 to 100 mm.) and a capacity of at least 200 ml. The crude crystals may be washed on the filter with ether in order to dissolve any precipitated Grignard reagent.

The resulting white solid is washed first with sufficient dilute (10% by volume) acetic acid to dissolve the excess magnesium and then with water. The insoluble white powder, consisting of crude hexaphenyldigermane, is then dried (either in the air or by heating at 100 to 150° in an oven) and extracted with chloroform in a Soxhlet extractor. Filtration of the chloroform extract and concentration of the filtrate to 20 to 30 ml. gives a yield of pure hexaphenyldigermane of 18.3 g. (69%). The crystals melt at 346 to 347°. *Anal.* Calcd. for $(C_6H_5)_6Ge_2$: C, 71.1; H, 5.0; Ge, 23.9. Found: C, 71.4; H, 5.0; Ge, 23.8.

Careful hydrolysis of the original filtrate from the Grignard reaction leads to the isolation of tetraphenylgermane in 5 to 6% yield.

Properties

Tetraphenylgermane and hexaphenyldigermane are white crystalline compounds, stable to air and water, and sub-

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limable in a vacuum.[2] Both are degraded smoothly to germanium(IV) oxide by a mixture of hot concentrated nitric and sulfuric acids. Bromination using bromine in 1,2-dibromoethane gives mainly triphenylbromogermane, although some further cleavage to the dibromide usually occurs. Both substances react with alkali metals in tetrahydrofuran or ethylene glycol dimethyl ether to give orange-brown solutions of $(C_6H_5)_3GeM$ (M = Li,K), from which a wide range of substituted germanes have been prepared.[4] Their infrared spectra show the following differences: $(C_6H_5)_4Ge$: 329 (s), 232 (m); 213 (m) $cm.^{-1}$. $(C_6H_5)_6Ge_2$: 322 (s), 267 (s) $cm.^{-1}$.

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9. POTASSIUM TRIOXALATOGERMANATE(IV)

$$GeO_2 + K_2C_2O_4{\cdot}H_2O + 2(H_2C_2O_4{\cdot}2H_2O) \rightarrow K_2Ge(C_2O_4)_3{\cdot}H_2O + 6H_2O$$

Submitted by Peter Arvedson* and E. M. Larsen*
Checked by George B. Kauffman† and Leslie W. Michael†

The trioxalatogermanate anion has been studied at least twice—by Tchakirian[1] and by Moeller and Nielsen.[2] Tchakirian lists some of the chemical and physical properties of the corresponding acid in solution, and Moeller and Nielsen report the separation of the optical isomers formed by the anion. These workers do not indicate

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any success in isolating the potassium salt of this anion. Willard and Zuehlke[3] state that Tchakirian attempted to isolate the potassium salt but found it too unstable. The preparation below was adapted from the preparations of corresponding tetraoxalatometallates (synthesis 12).

Procedure

A mixture of 75 ml. of water, 1.67 g. (0.016 mol) of germanium(IV) oxide, 2.94 g. (0.016 mol) of potassium oxalate 1-hydrate, and 4.04 g. (0.032 mol) of oxalic acid 2-hydrate is refluxed until the solids dissolve (about 2 hours). After the solution has cooled to 40°, it is transferred to a beaker, 80 ml. of 95% ethanol is added slowly with stirring, and the potassium trioxalatogermanate precipitates upon further cooling. The finely crystalline product is filtered on a Büchner funnel and washed with 25 ml. of an ice-cold 50:50 mixture of water and ethanol. The yield of the crude product is 4.7 g. (68%). The washed product is dissolved in 30 ml. of water at 70°. Thirty milliliters of 95% ethanol at room temperature is added to the warm solution and the mixture is allowed to cool to room temperature, whereupon large crystals of the desired product separate. These are washed on a Büchner funnel with 25 ml. of ice-cold absolute ethanol and then 25 ml. of ice-cold diethyl ether and finally dried to constant weight (about 2 hours) in an oven at 70°. The yield is 3.6 g. (52%). The yield can be increased by adding more ethanol to the refluxed solution, but with the likelihood of precipitating also some potassium oxalate or oxalic acid. *Anal.* Calcd. for $K_2Ge(C_2O_4)_3 \cdot H_2O$: K, 18.06; Ge, 16.79; C_2O_4, 61.00. Found: K, 18.03 ± 0.02; Ge, 16.70 ± 0.05; C_2O_4, 61.09 ± 0.09. By checkers: K, 18.04; C_2O_4, 61.06.

Analysis

The analyses for potassium and oxalate are relatively simple, but the analysis for germanium involves a number of operations.[3] To determine potassium, a known weight of the salt is heated in a covered crucible at 260° for 3 hours. This effectively removes the oxalate as carbon dioxide. The remaining solid is treated with concentrated (12 *N*) hydrochloric acid, allowed to evaporate to dryness, and again heated to 260°. With this treatment, the germanium in the sample is volatilized as germanium(IV) chloride. The residue is weighed as potassium chloride. The oxalate is determined by disolving a known weight of the sample in water, adding an excess of sulfuric acid, and titrating at 70° with standard permanganate. The germanium is determined by first heating the sample at 260° to remove the oxalate and then dissolving the remaining solid in a solution of 7 g. of potassium sulfide and 15 ml. of 40% acetic acid diluted with 25 ml. of water. The resulting solution is allowed to stand for about 5 minutes, and then carbon dioxide is bubbled through it. A mechanical stirrer is used to break up the bubbles. Any germanium present in the original sample should now be present as the $Ge_2S_5^{2-}$ ion, and any excess sulfide ion is removed by the carbon dioxide. To this solution is added a measured excess of triiodide, and the unreacted triiodide ion is then titrated with standard thiosulfate.

Properties

Potassium trioxalatogermanate is a white crystalline solid which decomposes at 180°, liberating carbon dioxide. It is very soluble in water but insoluble in ethanol, methanol, chloroform, and diethyl ether. The crystals are monoclinic with $a = 9.89$ A, $b = 17.56$ A, $c = 14.95$ A (all to ± 0.03 A), and $\beta = 68°$. The density is 2.02 g./cc. at 20°. There are six molecular units per unit cell.

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CHAPTER IVB

10. DICHLOROBIS(2,4-PENTANEDIONATO)-TITANIUM(IV): (CORRECTION)[1,2]

[Dichlorobis(acetylacetonato)titanium(IV)]

$$TiCl_4 + 2C_5H_8O_2 \rightarrow [Ti(C_5H_7O_2)_2Cl_2] + 2HCl$$

Dr. John P. Fackler, Jr.* has called attention to the fact that the work of K. C. Pande and R. C. Mehrotra[3] and more recent work by D. M. Puri, K. C. Pande, and R. C. Mehrotra[4] and by Woodruff, Marini, and Fackler[5] indicate that the product obtained by reaction of titanium(IV) chloride with 2,4-pentanedione is monomeric and nonconducting in benzene, carbon disulfide, and chloroform. Furthermore, several derivatives of the type $[Ti(C_5H_7O_2)_2(OR)_2]$ have been prepared by reaction with alcohols. On the basis of this information, the formula seems to be $[Ti(C_5H_7O_2)_2Cl_2]$, as shown in the equation above, instead of $[Ti(C_5H_7O_2)_3]_2[TiCl_6]$, as given in the previous articles on the preparation of bis[tris(2,4-pentanedionato)titanium(IV)] hexachlorotitanate(IV) (synthesis 34 of Volume II[1] and synthesis 12 of Volume VII).[2]

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11. TRIS(2,4-PENTANEDIONATO)ZIRCONIUM(IV) CHLORIDE

[Tris(acetylacetonato)zirconium(IV) Chloride]

$$ZrCl_4 + 3C_5H_8O_2 \rightarrow [Zr(C_5H_7O_2)_3]Cl + 3HCl$$

SUBMITTED BY VERA DORON,*† R. K. BELITZ,* AND STANLEY KIRSCHNER‡
CHECKED BY J. H. CRADDOCK§ and M. M. JONES§

Tris(2,4-pentanedionato)zirconium(IV) chloride has been prepared by the reaction of zirconium(IV) chloride and 2,4-pentanedione (acetylacetone) in chloroform.[1] The present synthesis is a modification of this earlier method. Zirconium(IV) also forms a tetrakis(2,4-pentanedionato) derivative, $[Zr(C_5H_7O_2)_4]\cdot 10H_2O$;[2] this is prepared in aqueous solution. The existence of the tetrakis compound shows an analogy of zirconium(IV) with cerium(IV) and thorium(IV), which give similar compounds with 2,4-pentanedione. In nonaqueous media, however, only three of the chlorides can be replaced by a β-diketone, yielding a compound in which the metal atom has a coordination number of six. In this respect zirconium seems to lie between cerium and thorium on the one hand and silicon, germanium, and titanium on the other, the last three forming complexes containing no more than three β-diketone groups per metal ion.

Procedure

NOTE: Care should be exercised to keep the exposure of the reactants and products to atmospheric and other moisture to a minimum.

A suspension of 10 g. (0.042 mol) of anhydrous zircon-

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ium(IV) chloride in approximately 100 ml. of anhydrous chloroform is allowed to react with 18 g. (0.180 mol) of 2,4-pentanedione in a 250-ml. round-bottomed flask. The suspension is refluxed (using a reflux condenser equipped with a 6-in. calcium chloride drying tube) until the evolution of hydrogen chloride ceases (*hood!*). The solution is then filtered rapidly through a Büchner funnel, equipped with a rubber stopper and a calcium chloride drying tube, into another 250-ml. round-bottomed flask. A pump protected by a suitable cold trap should be used to supply the vacuum—not an aspirator. The solution is boiled under continuous vacuum (pump) until crystallization begins. It is then allowed to stand under a vacuum maintained at approximately 2 mm. Hg for 2 days. If the filtrate is not sufficiently concentrated, a powdery material of variable composition tends to precipitate first. In this event, boiling should be continued until crystals first appear, and the powdery material should be filtered and discarded. The pure compound crystallizes in large, colorless prismatic crystals, which are filtered through a Büchner funnel in the manner described above, vacuum-dried at room temperature, and stored in a desiccator over anhydrous calcium chloride. Two or three crops can be recovered from the mother liquor. The total yield is 11 to 12 g. (60 to 66%). *Anal.* Calcd. for $[Zr(C_5H_7O_2)_3]Cl$: C, 42.49; H, 4.99; Cl, 8.36; Zr, 21.5. Found: C, 42.00; H, 5.30; Cl, 8.70; Zr (by checkers) 21.32.

The compound may also be prepared by using benzene as a solvent, from which it can be precipitated by the addition of petroleum ether, but with a somewhat lower yield (approximately 55%).

Properties

Tris(2,4-pentanedionato)zirconium(IV) chloride forms colorless prismatic crystals, which are decomposed by atmospheric moisture. The crystals are soluble in most

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organic solvents, including benzene, chloroform, acetone, and alcohol, but not in ether. The compound is soluble in water, with which it reacts to form 2,4-pentanedione, hydrochloric acid, and hydrated zirconium oxide. The crystals do not have a sharp melting point, but melt in the range 143 to 148°. The previously reported melting point,[1] 102 to 103°, suggests the possible existence of more than one crystalline form.

Separate molecular weight determinations by the ebullioscopic method using benzene and butanone as solvents provide values of 211 and 192, respectively. Inasmuch as the formula weight of $[Zr(C_5H_7O_2)_3]Cl$ is 424, these values indicate that the complex is practically completely ionized. This is confirmed also by conductometric measurements in benzene and butanone and by the ready precipitation of silver chloride by silver perchlorate in acetone solution.

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12. POTASSIUM TETRAOXALATOZIRCONATE(IV), -HAFNATE(IV), AND -THORATE(IV)

Submitted by Frederic A. Johnson* and Edwin M. Larsen†
Checked by Carl L. Rollinson‡ and James Lindsay‡

A. POTASSIUM TETRAOXALATOZIRCONATE(IV) 5-HYDRATE

$$ZrOCl_2 \cdot 8H_2O + H_2C_2O_4 \cdot 2H_2O + 3(K_2C_2O_4 \cdot H_2O) \rightarrow K_4Zr(C_2O_4)_4 \cdot 5H_2O + 2KCl + 9H_2O$$

The potassium and ammonium tetraoxalatozirconates have been studied by Paijkull,[1] Venable and Baskerville,[2]

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Mandl,[3] Rosenheim and Franck,[4] Pfeiffer,[5] and Boulanger.[6] Generally, the preparative procedures have been rather vague and the products not well characterized. The preparation below has been taken from no single source. The initial material obtained by this procedure is slightly contaminated with oxalate. A single reprecipitation from water with ethanol is usually sufficient to give a pure product. Precipitation of these compounds with alcohol, followed by drying with ether, may give products of varying water of crystallization depending upon the time taken to carry out the procedures. It is recommended that reagents be added from a dropping funnel and that the resulting solution be stirred with a magnetic stirrer.

Procedure

Five grams (0.016 mol) of recrystallized zirconium oxychloride (zirconyl chloride) 8-hydrate is dissolved in 200 ml. of water. Twelve grams (0.065 mol) of potassium oxalate 1-hydrate and 4 g. (0.032 mol) of oxalic acid 2-hydrate are dissolved in a second 200-ml. portion of water. The zirconyl solution is added to the oxalate solution slowly and with stirring (preferably from a dropping funnel and stirring the resulting solution with a magnetic stirrer). If at any point a gelatinous precipitate forms which remains after stirring, enough concentrated (12 *N*) hydrochloric acid is added to clear the solution (no more than 2 or 3 ml. of hydrochloric acid should be added). The solution is heated to boiling. If the solution is not clear at this time, it should be filtered or centrifuged to remove the solids.

After the boiled solution is cooled to room temperature, it is diluted to its original volume with water. The potassium tetraoxalatozirconate is precipitated by the slow addition of 300 ml. of absolute ethanol. The white, finely crystalline product is filtered on a Büchner funnel and washed with 25 ml. of ethanol. The precipitate is dissolved in

120 ml. of water at 70°. The solution is cooled to 30° and then treated with 75 ml. of absolute ethanol. The precipitate is filtered, washed with three 25-ml. portions of ethanol and two 10-ml. portions of diethyl ether, and finally dried in an oven at 50 to 60°. The yield is about 90%, calculated on the basis of the zirconium used. *Anal.* Calcd. for $K_4Zr(C_2O_4)_4 \cdot 5H_2O$: Zr, 13.22; C_2O_4, 51.08; H_2O, 13.06. Found: Zr, 13.18, 13.37; C_2O_4, 51.38, 51.34; H_2O, 12.82, 12.82.

B. POTASSIUM TETRAOXALATOHAFNATE(IV) 5-HYDRATE

$$HfOCl_2 \cdot 8H_2O + H_2C_2O_4 \cdot 2H_2O + 3(K_2C_2O_4 \cdot H_2O) \rightarrow K_4Hf(C_2O_4)_4 \cdot 5H_2O + 2KCl + 9H_2O$$

The hafnium compound has not been previously reported. The procedure for preparing it is analogous to that for the zirconium compound. A solution of 5 g. (0.012 mol) of recrystallized hafnium oxychloride 8-hydrate* in 75 ml. of water is added slowly with stirring (preferably adding the water from a dropping funnel and stirring the resulting solution with a magnetic stirrer) to a solution of 8.0 g. (0.043 mol) of potassium oxalate 1-hydrate and 2.0 g. (0.016 mol) of oxalic acid 2-hydrate in 125 ml. of water. The solution is heated to boiling, then cooled to 70°. The product is precipitated by the addition of 150 ml. of absolute ethanol. Better results are obtained if this addition is made to the hot solution. The precipitate is filtered, washed with 15 ml. of ethanol, redissolved in 100 ml. of hot (70°) water, and reprecipitated with 150 ml. of ethanol. The yield is essentially quantitative. *Anal.* Calcd. for $K_4Hf(C_2O_4)_4 \cdot 5H_2O$: Hf, 22.98; C_2O_4, 45.30; H_2O, 11.60. Found: Hf, 23.31, 23.35; C_2O_4, 45.33, 45.42; H_2O, 11.65, 11.68.

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* The $HfOCl_2 \cdot 8H_2O$ must be recrystallized to obtain a product which dissolves to give a clear solution. If a gelatinous precipitate appears when the hafnium oxychloride is dissolved, it may be removed by centrifuging before proceeding with the next step. This results in a corresponding lower yield of final product.

C. POTASSIUM TETRAOXALATOTHORATE(IV) 4-HYDRATE

$$Th(NO_3)_4 \cdot 4H_2O + 2(H_2C_2O_4 \cdot 2H_2O) \rightarrow Th(C_2O_4)_2 \cdot nH_2O + 4HNO_3 + (8 - n)H_2O$$

$$Th(C_2O_4)_2 \cdot nH_2O + 2K_2C_2O_4 \cdot H_2O \rightarrow K_4Th(C_2O_4)_4 \cdot 4H_2O + (n - 2)H_2O$$

The preparation of potassium tetraoxalatothorate 4-hydrate is based on the observation of Cleve[7] that insoluble thorium oxalate dissolves in boiling potassium oxalate solution under unspecified concentration conditions.

A solution of 20 g. (0.036 mol) of thorium nitrate 4-hydrate in 100 ml. of water is added (preferably from a dropping funnel with stirring of the resulting solution with a magnetic stirrer) to a solution of 10 g. (0.079 mol) of oxalic acid 2-hydrate dissolved in a second 100-ml. portion of water. The white precipitate thus formed is filtered on a sintered-glass funnel of medium porosity. Twenty-four grams (0.13 mol) of potassium oxalate 1-hydrate is dissolved in 200 ml. of water and added to a slurry of the initial precipitate. The resulting mixture is heated to boiling, filtered, and cooled. Seventy-five milliliters of absolute ethanol is added slowly to the cool solution, whereupon a copious white precipitate is formed. The precipitate is filtered on a Büchner funnel, washed with 25 ml. of ethanol and then 25 ml. of ether, and air-dried. The yield is about 26.5 to 28 g. (85 to 90% based on the thorium used). *Anal.* Calcd. for $K_4Th(C_2O_4)_4 \cdot 4H_2O$; Th, 28.57; C_2O_4, 43.32; H_2O, 8.88. Found: Th, 28.54, 28.63, 28.71; C_2O_4, 43.31, 43.35, 43.37; H_2O, 9.03.

Properties

The densities of these compounds, as determined pycnometrically in benzene at 25.0 ± 0.1°, are 2.17 g./cc. for the zirconium compound, 2.44 g./cc. for the hafnium compound, and 2.48 g./cc. for the thorium compound. The

$Zr(C_2O_4)_4^{4-}$ anion in the compound $Na_4Zr(C_2O_4)_4 \cdot 3H_2O$ is known to be a dodecahedron.[8]

The thorium compound (10 g.) reacts with water (100 ml.) to give an insoluble portion for which the oxalate/thorium mol ratio is 2.67 and a soluble portion which can be recovered by precipitation with alcohol and which has an oxalate/thorium mol ratio of 2.99. The remainder of the oxalate is lost by replacement by hydroxide ion and water and stays in solution. The zirconium and hafnium compounds, on the other hand, can be recrystallized from water with very little loss of oxalate.

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Edited by Henry F. Holtzclaw, Jr.

CHAPTER VA

See also: Bis(4-imino-2-pentanonato)copper(II) and bis(3-phenylimino-1-phenyl-1-butanonato)copper(II), synthesis 1
Complex carbonates of beryllium, synthesis 2
Dichloro(2,2′-iminodipyridine)zinc, diacetato(2,2′-iminodipyridine)zinc, and dicyano(2,2′-iminodipyridine)zinc, synthesis 3
Sodium bis(trimethylsilyl)amide and tris(trimethylsilyl)-amine, synthesis 4
Lithium bis(trimethylsilyl)amide and tris(trimethylsilyl)-amine, synthesis 5
Silicon tetraisocyanate and methylsilicon isocyanates, synthesis 6
Silicon tetraisothiocyanate and methylsilicon isothiocyanates, synthesis 7
Heptasulfur imide, synthesis 25
Imidosulfuric acid chloride, synthesis 26
Dialkylsulfamoyl chlorides, synthesis 27
N- and *N*,*N*′-Substituted sulfamides, synthesis 28
Dialkylamides of (trichlorophosphoranylidene)sulfamic acid, synthesis 29
Bis(trichlorophosphoranylidene)sulfamide, synthesis 30
Aminomethanesulfonic acid, synthesis 31
Diperoxotriamminechromium(IV), synthesis 33
Tris(4-*p*-toluidino-3-penten-2-onato)chromium(III), synthesis 38
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Iron carbonyl complexes of triphenylphosphine, triphenylarsine, and triphenylstibine, synthesis 48
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Tris(ethylenediamine)platinum(IV) chloride, synthesis 62
cis-Dichloro(ethylenediamine)platinum(II), synthesis 63

13. METAL DERIVATIVES OF β-KETO IMINES (β-IMINO KETONES)

SUBMITTED BY DEAN F. MARTIN*† AND EDWARD J. OLSZEWSKI*

The methods of preparation and purification of metal derivatives of 1,3-diketones have been described in a previous volume.[1] Because of the interest in the structure[2–7] and reactions[5] of metal derivatives of β-keto imines, $RCOCH_2C(=NR')R''$, it is desirable to consider the methods of preparation of these compounds. Inasmuch as β-keto imines are closely related to 1,3-diketones and to salicylaldimines, $o\text{-}HOC_6H_4CH=NR$, the methods of preparation show similarities. Although this review is concerned principally with β-keto imines, some comparisons with 1,3-diketones and salicylaldimines are made.

Nomenclature

The nomenclature suggested by the International Union of Pure and Applied Chemistry (I.U.P.A.C.) is usually fol-

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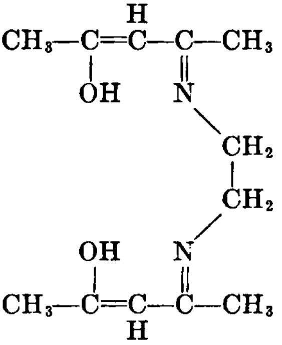
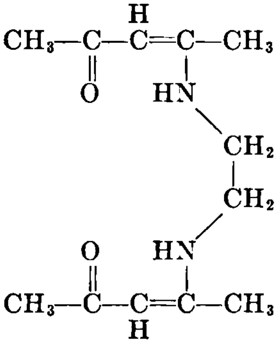
lowed for β-keto imines (β-imino ketones) of the type $RCOCH_2C(=NR')R''$, which can be named in a manner analogous to that used for the 1,3-diketones. Thus, $CH_3COCH_2C(=NH)CH_3$ is named 4-imino-2-pentanone; the nickel(II) derivative, bis(4-imino-2-pentanonato)nickel(II). Alternatively, some workers prefer to indicate that the ligand exists predominately in the keto amine (amino ketone) form,[4,25] in which case the ligand and nickel(II) derivative are named 4-amino-3-penten-2-one and bis(4-amino-3-penten-2-onato)nickel(II), respectively.

Nonsystematic names are commonly used for the condensation products of diamines and 1,3-diketones. Thus, $[CH_3COCH_2C(CH_3)=NCH_2]_2$



Imino enol form

or



Amino ketone form

is often called bis(acetylacetone)ethylenediimine, although the systematic name is 4,4′-(ethylenedinitrilo)di-2-pentanone or 4,4′-(ethylenediamino)di-3-penten-2-one.

A. METAL DERIVATIVES OF β-KETO IMINES

Procedures

1. Direct Reaction of β-Keto Imines with Metal Salts. *In Aqueous Solution.* The direct reaction between a β-keto imine and a salt in water is limited by the slight solubility of most β-keto imines in water and is essentially precluded for some β-keto imines by the ease with which they hydrolyze. Nevertheless, 4,4′-(ethylenedinitrilo)di-2-pentanone [bis(acetylacetone)ethylenediimine] can be crystallized from water,[6] and the preparation of 4,4′-(ethylenedinitrilo)di-2-pentanonatocobalt(II) can be effected by direct reaction in aqueous solution in the presence of an equivalent amount of sodium hydroxide.[9]

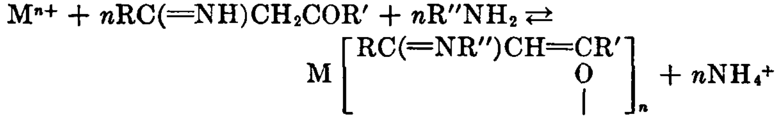
Direct reaction is commonly effected in a mixed-solvent system, frequently by mixing an ethanolic solution of the β-keto imine with an aqueous solution of the metal salt.[4,5] An ammoniacal metal salt solution can be used to prevent hydrolysis and to shift the chelation equilibrium (see synthesis 60). This practice can be very effective, but it has the disadvantage[1] of adding extraneous ions; furthermore, the high concentration of ammonia may result in an undesired amine exchange.[8]

In Nonaqueous Solution. The use of a nonaqueous solvent in which both the metal salt and the β-keto imine are soluble eliminates many of the problems of contamination due to hydrolysis, the presence of extraneous ions, and unfavorable equilibria. Halides such as BCl_3, $AlCl_3$, $SiCl_4$, $GeCl_4$, $ZrCl_4$, $ThCl_4$, $NbCl_5$, and $TaCl_5$, which are soluble in an inactive organic solvent, have been used in the reaction with 1,3-diketones[1] but apparently not with β-keto imines. However, the reaction of metal acetates with β-keto imines has been effected successfully in dioxane,[6] ethanol,[3,10] or methanol.[11]

2. Reaction of a β-Keto Imine with a Metal Hydroxide. This procedure consists of refluxing an acetone solution of the β-keto imine with a freshly prepared metal hydroxide. The product precipitates from solution upon cooling or is obtained by dilution of the acetone solution with water. The method has been used to prepare the copper(II), nickel(II), and cobalt(II) derivatives of a variety of β-keto imines,[3,12] but attempts to prepare zinc and cadmium derivatives were not successful.[12] The advantages of this procedure have been described previously.[1] On occasion, the chelate compound may precipitate during the reaction and thereby make further chelation difficult by coating the metal hydroxide.[12]

3. Direct Combination of a 1,3-Diketone, an Amine, and a Metal Ion. Direct combination is a potentially useful reaction, and it has been used to prepare metal-salicylaldimine compounds. The procedure consists of mixing (and refluxing if necessary) a stoichiometric mixture of salicylaldehyde with an amine, a metal ion, and a base in dilute aqueous methanol.[13–16] This procedure has not been applied commonly to the preparation of metal derivatives of β-keto imines, although the preparation of 4,4′-(ethylenedinitrilo)di-2-pentanonatocopper(II) from 2,4-pentanedione (acetylacetone), ethylenediamine, and copper has been described.[17] Attempts to effect condensation of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hexafluoroacetylacetone) and ethylenediamine by direct combination of the reactants in the presence of copper(II) acetate were unsuccessful.[6]

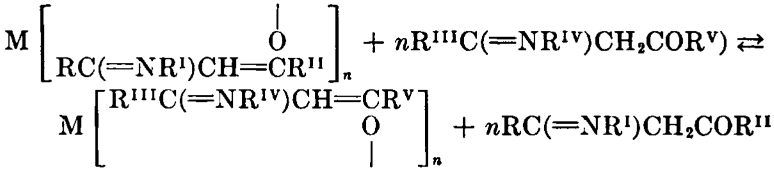
4. Amine Exchange: Reaction of a β-Keto Imine with an Amine in the Presence of a Metal Ion



$$M^{n+} + nRC(=NH)CH_2COR' + nR''NH_2 \rightleftarrows M\left[\begin{array}{l} RC(=NR'')CH=CR' \\ \qquad\qquad\qquad\quad O \\ \qquad\qquad\qquad\quad | \end{array}\right]_n + nNH_4^+$$

This procedure, a variant of method 3, is also potentially a very useful method. An advantage is that the pH of the reaction mixture is controlled by the amount of amine present. In theory, the use of this method would permit the preparation of metal derivatives of a wide variety of β-keto imines and obviate the need for preparation and isolation of the individual ligands. In practice, it appears that of the possible compounds the most stable metal chelate compound is formed. This may not always be the desired compound. Thus, even in the presence of copper(II) ion, the condensation of 4-imino-2-pentanone and trimethylenediamine was not successful, the product isolated being bis(4-imino-2-pentanonato)copper(II).[8]

5. Chelate Exchange. Metal derivatives of β-keto imines can be prepared by a chelate-exchange reaction[5] (synthesis 1).



$$\mathrm{M}\left[\begin{array}{r} | \\ \mathrm{O} \\ \mathrm{RC({=}NR^{I})CH{=}CR^{II}} \end{array}\right]_n + n\mathrm{R^{III}C({=}NR^{IV})CH_2COR^{V}} \rightleftarrows$$

$$\mathrm{M}\left[\begin{array}{r} \mathrm{R^{III}C({=}NR^{IV})CH{=}CR^{V}} \\ \mathrm{O} \\ | \end{array}\right]_n + n\mathrm{RC({=}NR^{I})CH_2COR^{II}}$$

With this method, highly basic conditions no longer exist, an amine-exchange reaction does not occur, and contamination with anions is avoided. An incidental asset is that the two metal derivatives involved usually have different colors, and the extent of reaction can be judged visually. An obvious disadvantage is that the equilibrium may be unfavorable,[13] as was described for the attempted reaction of bis(4-imino-2-pentanonato)copper(II) and 4,4′-trimethylenedinitrilo)di-2-pentanone [bis(acetylacetone)trimethylenediimine]. For successful isolation of a pure product, the metal derivative must be the most insoluble species present; often, this condition is met.

6. Interaction of a Soluble β-Keto Imine Salt and a Soluble Metal Salt. The syntheses of a number of metal derivatives of 1,3-diketones are representative of this method, but the extension to metal β-keto imines has been limited to the synthesis of chromium(III) derivatives. These have been prepared by the interaction of trichlorotris(tetrahydrofuran)chromium(III) and the potassium salt of a β-keto imine.[19] (See synthesis 38.)

7. Template Synthesis. This method consists of using a metal chelate compound as a template to induce ligand molecules to orient in a manner that is favorable for condensation. For example, compounds of the type $\mathrm{Ni[RCOCR'C(R''){=}NCH_3]_2}$ have been prepared by treating an aqueous solution of $\mathrm{[Ni_2(en)_4Cl_2]Cl_2}$ with a catalytic amount of pyridine, followed by a β-diketone. Upon refluxing the mixture, the desired compound precipitated in a very pure state.[20]

8. Miscellaneous Methods. Cobalt(III) derivatives of β-keto imines have been prepared by oxidation (with hydrogen peroxide) of the cobalt(II) derivative, which may[9] or may not[11] be isolated.

Another method which is not included in any of the previous categories is the conversion of a solvated metal chelate compound to the unsolvated form. An interesting example of this is the removal of benzene by heating the benzene complexes of 3,3′-(propylenedinitrilo)bis(1-phenyl-1-butanonato)oxovanadium(IV) [bis(benzoylacetone)propylenediiminooxovanadium(IV)]. The benzene complex is obtained by recrystallizing the metal chelate compound from benzene.[10]

Bis(2,4-pentanedionato)oxovanadium(IV) [vanadium(IV) oxy(acetylacetonate)] has been prepared by direct reaction of 2,4-pentanedione and vanadium(V) oxide.[21] By using the same method, bis(4-imino-2-pentanonato)oxovanadium(IV) has been prepared by substituting acetylacetone imide (4-imino-2-pentanone) for acetylacetone.[22]

Purification

The methods that have been used to purify metal derivatives of β-keto imines are surprisingly limited. Generally, recrystallization has been used, with acetone, ethanol, and benzene as common solvents. Very few quantitative solubility data are available. However, the solubilities of 4,4′-(ethylenedinitrilo)di-2-pentanonatocopper(II) and its 1-hydrate in water and in 12% ethanol have been determined at several temperatures.[23]

On occasion, sublimation has been used as a method of purification: bis(4-methylimino-2-pentanonato)copper(II) sublimes at 120° (2 mm.),[4] and 4,4′-(ethylenedinitrilo)-bis(trifluoro-2-pentanonatocopper(II) at 200°.[10]

B. β-KETO IMINES

The preparation of the β-keto imines is described in several places in the literature in connection with the preparation of the metal derivatives. In addition, Cromwell[24] has discussed the methods of preparation and has summarized the properties of a number of β-keto imines.

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Edited by Henry F. Holtzclaw, Jr.

14. AMMONIUM AZIDE*

$$2NaN_3 + (NH_4)_2SO_4 \rightarrow 2NH_4N_3 + Na_2SO_4$$

Submitted by C. O. Obenland,† D. J. Mangold,† and M. P. Marino†
Checked by T. R. Musgrave‡ and R. N. Keller‡

The preparation of ammonium azide by the interaction of ammonia with hydrazoic acid in ethereal solution has been described by Frierson.[1] A second preparative method using ammonium nitrate or sulfate is also described in the same reference. Both methods have disadvantages, in that the former requires the preparation of hydrazoic acid, whereas the latter is limited to small quantities because of explosion hazards.

Two German patents by Müller[2] describe preparative methods which avoid the use of hydrazoic acid by heating sodium azide with ammonium chloride or sulfate in aqueous solution. A recent Japanese patent[3] describes a reaction between sodium azide and ammonium carbamate in liquid ammonia to give ammonium azide. Evans, Yoffe, and Gray[4] have suggested the reaction of sodium azide with ammonium chloride in *N*,*N*-dimethylformamide. A modification of the last method has been made; it involves the reaction of sodium azide and ammonium sulfate in dimethylformamide to give anhydrous ammonium azide of high purity.

Procedure

Caution. Although this procedure has been repeated many times without requiring special precautions, it is essential that

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* Work sponsored by the Air Force Flight Test Center, Air Research and Development Command, and the United States Air Force.

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‡ University of Colorado, Boulder, Colo.

a safety shield be used during the preparation. The compound is one of the more stable azides, but has been reported as detonating when heated in a sealed tube. No decomposition has been observed under normal laboratory conditions of preparation, handling, and storage.

The apparatus is assembled as shown in Fig. 1. All connections and joints exposed to the corrosive hot vapors of *N*,*N*-dimethylformamide should be of glass. A three-necked 1-l. flask *A* is fitted with a thermowell and thermometer *B* and a motor-driven stirrer *C*. A Dean-Stark trap is attached at *D*, with a water-cooled condenser *G*, the internal diameter of which should be about 10 or 12 mm. At the upper end of the condenser a glass rod *I*, 4 to 5 mm. in diameter, is inserted through a sliding joint *H*. The rod should be of sufficient length to reach to the bottom of the condenser tube. The joint at *H* is made vacuum-tight with a short piece of rubber tubing lubricated with stopcock grease to permit easy movement of rod *I*.

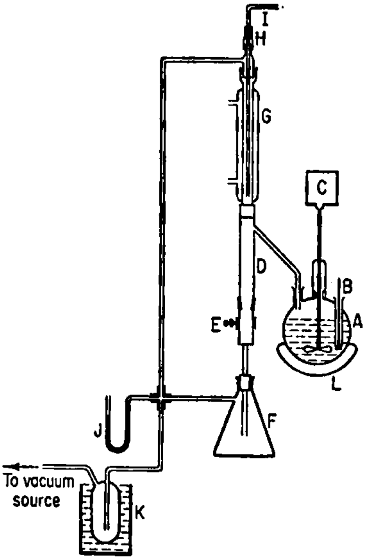

Fig. 1. Apparatus for the preparation of ammonium azide.

The stopper is cut off the lower leg of the Dean-Stark trap, leaving the tube with an opening of about 5 to 6 mm. To the end of this tube is connected a suction flask *F* by means of a short rubber tube. Flow through the tube is controlled by means of a pinch clamp *E*. A vacuum connection is made through trap *K*, which is cooled by an ice-salt mixture. The pressure in the system is determined by means of the mercury-filled manometer *J*.

Sixty-five grams (1.0 mol) of sodium azide, 66.1 g. (0.50 mol) of ammonium sulfate, and 500 ml. of *N,N*-dimethylformamide are placed in flask *A*, the agitator is started, and the mixture is heated by the electric mantle *L*. The system is partially evacuated to a pressure of 70 to 80 mm. Hg. The distillation of solvent and product begins at a pot temperature of 85 to 90°, and this material is collected in trap *D*. The solid contents of trap *D* are periodically drawn off into receiver *F*, while the condensed solvent continually overflows back into flask *A*. Any solid accumulations in the condenser tube are dislodged with rod *I*. Some plugging may occur in the lower end of the condenser depending on cooling-water temperature. Plugging is minimized by using condenser water at a temperature of 20 to 25°. Excessive plugging may occur with colder condenser water. Distillation under reduced pressure is continued until solids are no longer deposited in the trap; this usually requires 5 to 6 hours. At this point, heating is discontinued and the system is brought to atmospheric pressure. Solvent which remains in the leg of the Dean-Stark trap is drained into the product receiver, and the resulting slurry of product and solvent is filtered on a Büchner funnel. The filter cake is washed several times with diethyl ether and dried in a vacuum desiccator. Dilution of the dimethylformamide filtrate with an equal volume of diethyl ether precipitates several grams of additional product. The yield of ammonium azide is 30 to 31 g. (50 to 51%). *Anal.*[5] Calcd. for NH_4N_3: NH_4^+, 30.0; N, 93.3. Found: NH_4^+, 30.2; N, 93.6.

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Properties

The properties of ammonium azide are discussed in Volume II of this series.[1]

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15. PHENYLLEAD(IV) AZIDES

Submitted by Eugene Lieber*† and Francis M. Keane*
Checked by John P. Fackler, Jr.,‡ James Marini,‡ and Victor Wroobel‡

Although satisfactory methods for the preparation of lead(II) azide, $Pb(N_3)_2$, are available in the literature,[1–3] there is no authentic isolation of lead(IV) azide, $Pb(N_3)_4$. The isolation[4] of lead(IV) chloride suggests the existence of lead(IV) azide, but the work of Möller[5] and Lieber[6] has thus far indicated only its qualitative existence without its successful isolation and characterization. Lieber and Keane[7] were the first to attempt the synthesis of lead(IV) azides of the types R_3PbN_3, $R_2Pb(N_3)_2$, and $RPb(N_3)_3$, in which R is a group that can stabilize the lead-nitrogen linkage and thus produce a stable derivative of the azide of tetravalent lead. This expectation was realized for the case in which R is a phenyl group.

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[*] Roosevelt University, Chicago, Ill. Support of this investigation by the Basic Research Group, ERDL, U.S. Army, Corps of Engineers, Fort Belvoir, Va., is gratefully acknowledged.

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A. TRIPHENYLLEAD AZIDE

$$(C_6H_5)_4Pb + HCl \rightarrow (C_6H_5)_3PbCl + C_6H_6$$
$$(C_6H_5)_3PbCl + KOH \rightarrow (C_6H_5)_3PbOH + KCl$$
$$(C_6H_5)_3PbOH + HN_3 \rightarrow (C_6H_5)_3PbN_3 + H_2O$$

Procedure

Caution. Extreme caution must be exercised in working with azide procedures, including use of adequate safety shielding, ready availability of fire extinguishing equipment, and careful attention to directions.

1. **Triphenyllead Chloride.**[8] Tetraphenyllead* (10 g.; 0.193 mol) dissolved in 150 ml. of hot chloroform (15 ml. of chloroform per gram of tetraphenyllead) is placed in a three-necked flask fitted with a gas delivery tube so as to introduce the gas below the level of the chloroform solution. The flask is used as an open system. Dry hydrogen chloride is introduced with constant stirring while the mixture is warmed by means of a water bath to 50 to 60°. The hydrogen chloride is introduced until the appearance of a white precipitate (diphenyllead dichloride) which is similar in morphology to small white satin plates. The mixture is then refluxed for approximately one hour to complete the reaction between the hydrogen chloride and the tetraphenyllead (a shorter reflux time results in low yields). The hot mixture is suction-filtered through a water-heated funnel (55°) using Whatman no. 50 paper. Typical preparations have yielded 1 to 3% of diphenyllead dichloride as a by-product. The solvent is removed from the filtrate by simple distillation, by heating with a water bath. The residue is extracted with portions of hot absolute ethanol. The alcoholic filtrate is cooled to 0° and the precipitate

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* Tetraphenyllead can be made by the procedure of Gilman, Summers, and Leeper;[9] alternatively, the commercial product, available from the Aldrich Chemical Company, Milwaukee, Wis., can be used without further modification.

recovered by suction filtration (chilled apparatus). The yield of triphenyllead chloride averages 6.9 to 7.4 g. (75 to 80%) over several runs. The combined yields are recrystallized from absolute ethanol at 0° for analysis. *Anal.* Calcd. for $(C_6H_5)_3PbCl$: C, 45.61; H, 3.61; Cl, 7.48. Found: C, 45.87; H, 3.20; Cl, 7.50. By checkers: C, 46.80; H, 3.43; Cl, 7.43. The melting point is 207°.*

2. Triphenyllead Hydroxide.[10] In 200 ml. of absolute ethanol, 4.74 g. (0.010 mol) of triphenyllead chloride is dissolved by warming in a water bath. One gram (0.018 mol) of potassium hydroxide is dissolved in 25 ml. of absolute ethanol. The solution is filtered through glass-fiber filter paper, using suction filtration, to remove any carbonate impurity. The titer of the resulting solution is determined by titration of 2-ml. aliquots with 0.100 *N* hydrochloric acid solution to a phenolphthalein end point. On the basis of titer, a volume of the alcoholic potassium hydroxide solution sufficient to provide 0.617 g. (0.010 mol) of potassium hydroxide is added to the warm alcoholic solution of the triphenyllead chloride. The reaction mixture is stirred rapidly for one hour by means of a magnetic stirrer and poured into 400 ml. of warm carbon dioxide–free distilled water. A dense white flocculent precipitate immediately forms. The suspension is stirred for a few minutes and filtered through a large (12.5-cm.) Büchner funnel. The white precipitate of triphenyllead hydroxide is washed with warm carbon dioxide–free distilled water until a negative chloride ion test is obtained with silver nitrate. The residue is dried in a vacuum desiccator over solid sodium hydroxide. The yield is 4.28 g. (0.0094 mol; 94%). *Anal.* Calcd. for $(C_6H_5)_3PbOH$: C, 47.43; H, 3.55. Found: C, 47.49; H, 3.63. By checkers: C, 47.80; H, 3.56. No melting occurs up to about 240°; above 240°, partial liquefaction takes place.

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* All melting points are uncorrected and were determined on a Fisher-Johns melting-point block at a heating rate of 4 to 5° per minute. The checkers obtained a melting point of 208 to 210°.

3. Triphenyllead Azide. At room temperature (25°), 3.87 g. (0.0085 mol) of dry triphenyllead hydroxide is placed in a one-necked 300-ml. reaction flask equipped with a thermometer and a dropping funnel (60-ml.) which has a pressure-equalizing side arm. Two hundred milliliters of absolute ethanol is added, and partial solution is achieved by stirring with a magnetic stirrer. After approximately one hour, 25 ml. of absolute ethanol is placed in the funnel. The system is then closed, and the reaction mixture is stirred vigorously while a chloroform solution of hydrazoic acid, prepared exactly according to the method of Wolff,[11] of sufficient titer to contain 0.368 g. (0.00855 mol) is pipetted slowly over a 15-minute period into the 25 ml. of ethanol. *Care is taken that the temperature of the reaction mixture does not exceed 35°.* The appearance of a white crystalline solid suspended in the reaction mixture is indicative of the presence of triphenyllead azide. After 4 hours of additional stirring, the reaction mixture is transferred to a beaker containing 500 ml. of carbon dioxide–free distilled water. The ethanolic-water suspension is stirred briefly and cooled to 0°. The resulting suspension is filtered by suction, using a large (12.5-cm.) Büchner funnel. The resulting white crystalline mass is washed with 25 ml. of cold aqueous ethanol (1 part ethanol to 3 parts water). The residue is dried in a vacuum desiccator over solid sodium hydroxide. The yield of triphenyllead azide is 3.92 g. (0.00816 mol; 96%). *Anal.* Calcd. for $(C_6H_5)_3PbN_3$: C, 44.98; H, 3.15; N, 8.75. Found: C, 44.90; H, 3.21; N, 8.70. By checkers: C, 45.21; H, 3.22; N, 8.82.

Properties

Triphenyllead azide crystallizes from the cooled ethanolic solution of the reaction medium in the form of small transparent needles. Although insoluble in water, triphenyllead azide has a solubility of 1.39 g./100 ml. of 95% ethanol and 0.12 g./100 ml. of anhydrous diethyl ether. Triphenyllead azide has no true melting point but decomposes on heating. Two milligrams of triphenyllead azide on the tip of a porcelain spatula ignites immediately in the flame of a Meker burner and burns vigorously, leaving behind a deposit of metallic lead. Small crystals observed under a polarizing microscope show loss of birefringence at 159 to 164° when heated at the rate of 4 to 5° per minute on a Kofler hot stage. Samples dried at 160° lose nitrogen. Examination of a 2-mg. sample with the Fisher-Johns melting-point block, by heating at the rate of 4 to 5° per minute, shows a phase change at 186 to 187°. Differential thermal analysis with simultaneous gas profile by the method of Ayres[12] shows an endotherm with gas evolution at 190°. An infrared absorption spectrum in either white oil mull or potassium bromide disk shows the characteristic asymmetric stretching frequencies for the azido group at 2033 cm.$^{-1}$ for the mull and two bands at 2120 cm.$^{-1}$ and 2033 cm.$^{-1}$ for the potassium bromide disk.

B. DIPHENYLLEAD DIAZIDE

$$(C_6H_5)_4Pb + 2HCl \rightarrow (C_6H_5)_2PbCl_2 + 2C_6H_6$$
$$(C_6H_5)_2PbCl_2 + 2KOH \rightarrow (C_6H_5)_2PbO + 2KCl + H_2O$$
$$(C_6H_5)_2PbO + 2HN_3 \rightarrow (C_6H_5)_2Pb(N_3)_2 + H_2O$$

Procedure

Caution. Extreme caution must be exercised in working with azide procedures, including use of adequate safety shielding, ready availability of fire extinguishing equipment, and careful attention to directions.

1. Diphenyllead Dichloride.[8] Tetraphenyllead (10.3 g.; 0.020 mol) is dissolved in benzene by warming to 50° (1 g./10 ml. of benzene) and vigorously stirring in an open reaction flask fitted with a gas inlet tube. Hydrogen chloride gas is introduced slowly to avoid blockage of the protruding tip of the gas inlet tube by the precipitating chloride. The precipitate of diphenyllead dichloride is characterized by the appearance of small shiny white plates. The warm mixture is suction-filtered through a hot-stage (50°) filter. The filtrate is maintained at 50° and returned to the reaction flask for further treatment with hydrogen chloride. Successive treatments require a correspondingly shorter gas-flow interval. When it is observed that the gas-flow interval increases markedly, the hydrogen chloride treatment is discontinued. The precipitate from this treatment contains a small amount of lead(II) chloride. The diphenyllead dichloride is washed with hot benzene and dried in a vacuum desiccator. The yield is 8.25 g. (0.0194 mol; 97%). *Anal.* Calcd. for $(C_6H_5)_2PbCl_2$; C, 33.34; H, 2.33; Cl, 16.40. Found: C, 33.39; H, 2.24; Cl, 16.55. By checkers: C, 33.07; H, 2.30; Cl, 16.52. Diphenyllead dichloride turns from white to yellow at 283 to 286° without melting.

2. Diphenyllead Oxide.[13] To a hot suspension of 4.32 g. (0.010 mol) of diphenyllead dichloride in 300 ml. of absolute ethanol, 20 ml. of 10% absolute ethanolic potassium hydroxide is slowly added with vigorous stirring. The reaction mixture is stirred for an additional 30 minutes after addition is completed. The warm alcoholic suspension is filtered through fine-grade filter paper in a heated funnel (65°). The reaction mixture and filter may be conveniently kept warm with an infrared lamp. The white residue is transferred to a mortar and triturated with hot 95% ethanol. The hot suspension is refiltered through a heated funnel, and the filtrate is tested with aqueous silver nitrate for the absence of chloride ion. The trituration is repeated if necessary. The residue is washed with small amounts of hot carbon dioxide–free distilled water and refiltered. The white amorphous residue is dried in a vacuum desiccator over solid sodium hydroxide. The yield is 3.40 g. (0.0090 mol; 90%). *Anal.* Calcd. for $(C_6H_5)_2PbO$: C, 38.19; H, 2.67. Found: C, 38.16; H, 2.76. By checkers: C, 38.89; H, 2.37. On heating, diphenyllead oxide appears to decompose at 223°.

3. Diphenyllead Diazide. To 3.02 g. (0.0080 mol) of finely ground diphenyllead oxide, 200 ml. of absolute ethanol is added in a one-necked 300-ml. reaction flask at room temperature. The suspension is stirred vigorously for one hour to reduce the particle size of the suspended material. The flask is equipped with a dropping funnel with a pressure-equalizing arm. A chloroform solution of hydrazoic acid, prepared exactly according to the method of Wolff,[11] of sufficient titer to contain 0.723 g. (0.0168 mol) of the acid is pipetted into 25 ml. of absolute ethanol contained in the funnel. The suspension is stirred continuously by a magnetic stirrer while the hydrazoic acid solution is added over a 15-minute interval. The appearance of a white crystalline solid of very small particle size is indicative that the reaction is progressing. The suspension is stirred for an additional 6 hours after addition of the acid is completed (longer stirring results in lower yields). The mixture is filtered by suction, and the resulting white crystalline mass is washed with ethanol. The residue is dried in a vacuum desiccator over solid sodium hydroxide; yield, 3.45 g. (0.0077 mol; 97%). *Anal.* Calcd. for $(C_6H_5)_2Pb(N_3)_2$: C, 32.35; H, 2.26; N, 18.87. Found: C, 32.61; H, 2.46; N, 18.62. By checkers: C, 32.33; H, 2.36; N, 18.66.

Properties

Diphenyllead diazide is obtained from the reaction mixture in the form of very small needle-like crystals. No suitable recrystallizing solvent could be found. Diphenyllead diazide is insoluble in water, 95% ethanol, and anhydrous diethyl ether. Insertion of 2 mg. of substance on the tip of a porcelain spatula into an open flame results in immediate ignition, and burning proceeds with a crackling sound accompanied by flashes of light. A deposit of metallic lead remains when the spatula is cooled. Observation of the thermal characteristics of diphenyllead diazide under silicone oil on a Fisher-Johns block (heating at 5 to

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6° per minute) shows no phase change but rather a browning which begins at 204° and becomes complete at 234°. Gas evolution is noted at 145°. A simultaneous differential thermogram-gas profile shows an endotherm with gas evolution at 190° and an exotherm with marked gas evolution at 210°. The azido groups show strong characteristic absorptions in the infrared.

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16. TETRAPHOSPHORUS HEXAMETHYLHEXAIMIDE

[2,4,6,8,9,10-Hexamethyl-2,4,6,8,9,10-hexaaza-1,3,5,7-tetraphosphaadamantane; Phosphorus(III) Methylimide]

$$4PCl_3 + 18CH_3NH_2 \rightarrow P_4N_6(CH_3)_6 + 12CH_3NH_3{}^+Cl^-$$

Submitted by R. R. Holmes*† and J. A. Forstner*
Checked by C. O. McArthur‡ and R. S. Drago‡

Tetraphosphorus hexamethylhexaimide, $P_4N_6(CH_3)_6$, represents the first isolated member[1,2] of a class of phosphorus-

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nitrogen compounds indicated to be structurally analogous to phosphorus(III) oxide. It is prepared in nearly quantitative yield from the reaction of phosphorus(III) chloride with excess methylamine at low temperature in the absence of solvent, the hydrochloride by-product being readily separated by the use of petroleum ether.

Procedure

The reaction vessel is a 2-l. deep-well all-glass resin kettle* with a removable top section containing ground-glass openings which are fitted with a 125-ml. dropping funnel for the phosphorus(III) chloride, a glass entrance tube for the methylamine, a manually operated stirrer, and a nitrogen entrance (see Fig. 2). A deep-well kettle is found to be most desirable, since white clouds tend to clog the inlet tube of the dropping funnel at the start. A 1-l. three-necked flask is unsatisfactory. The diameter of the kettle is such that the entire assembly can be inserted into the 1-gallon (3.8-l.) Dewar flask used to contain the coolant bath. Before beginning the preparation, a mark should be placed on the wall of the kettle to indicate, as established by experimental trial, when 64.6 ml. of methylamine is present. The stirrer is a strong stainless-steel rod, $\frac{1}{4}$ in. (0.64 cm.) in diameter, bent at the bottom so that it closely follows the curvature of the kettle. Its use is found to be very effective in breaking up the caked white solid mass that forms.

The entire assembly is flushed with nitrogen which has been dried by passage through a drying tower (height of tower, 250 mm.) packed with Drierite. The nitrogen system is so constructed that during the preparation a positive pressure is maintained in the kettle and equalized above the surface of the trichloride in the dropping funnel. Excess pressure is released through a mercury bubbler.

In a typical reaction, 17.5 ml. (0.200 mol) of phosphorus-

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* Available from the Ace Glass Company, Vineland, N.J.

(III) chloride from a freshly opened bottle is placed in the dropping funnel. The reaction kettle then is cooled by lowering it into the gallon Dewar containing a 1:1 mixture (by volume) of carbon tetrachloride and chloroform cooled to −78° with excess Dry Ice.

With nitrogen flowing at a very slow rate but at a slightly greater pressure than for the flow of methylamine, 64.6 ml. (1.60 mols) of anhydrous tank methylamine (to the mark previously placed on the wall of the kettle) is passed through an 18-in. drying tube, constructed from 20-mm. glass tubing and packed with anhydrous barium oxide, and then through an inlet tube which reaches nearly to the bottom of the kettle, where it is condensed. *It is imperative that the pressure in the nitrogen inlet be maintained at a slightly greater level than the pressure in the methylamine inlet in order to prevent the methylamine vapor from reaching the phosphorus(III) chloride.* The inlet tube is then replaced by a glass stopper. At this time, all attachments to the ground-glass

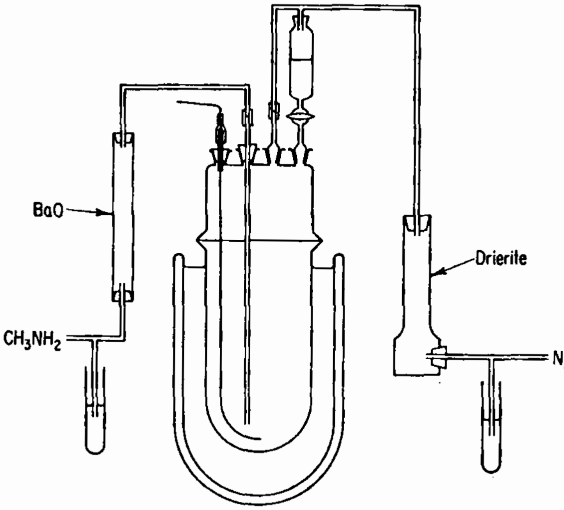

Fig. 2. Apparatus for the preparation of tetraphosphorus hexamethylhexaimide.

joints at the top of the kettle should be secured with spring clips. Thus, any excess pressure developed during the initial reaction will be relieved properly at the mercury bubbler.

The phosphorus(III) chloride is added dropwise during a one-hour period, with occasional stirring. The resulting yellow solid and clear liquid are allowed to stand overnight at −78° and then to warm slowly over a 2-day period to −30°. Above −30° a rock salt–ice mixture is used to maintain the bath temperature.* At this stage of the procedure a yellow-white solid is present in the excess amine. Over the next 2 days the temperature is allowed to rise slowly to room temperature, during which time the solution becomes yellow and viscous. The reaction product is then warmed to 50° and maintained at that temperature for about 4 hours to drive off the excess amine and until a white solid remains. The kettle and product are then placed in a nitrogen-filled dry-box.

Separation of tetraphosphorus hexamethylhexaimide from the methylamine hydrochloride is effected with the use of petroleum ether (30 to 60° fraction, distilled and dried over sodium ribbon).† A 6-g. portion of the product mixture is added to 30 ml. of petroleum ether in an Erlenmeyer flask and the mixture crushed below the liquid level. The Erlenmeyer flask containing the mixture is removed from the dry-box. Separation is achieved in an all-glass apparatus containing a 25-mm. sintered-glass filtering disk of medium porosity to which is attached a removable receiving trap. The latter, in turn, is connected to a liquid-nitrogen trap and pump system. Filtration from the amine hydrochloride is carried out in a nitrogen atmosphere; the appa-

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* The temperature program is essentially governed by heat loss from the original cold baths to the surroundings. It is only necessary to check occasionally to see that the temperature is not rising too rapidly for the time period indicated. If so, more Dry Ice or ice may be added.

† The product dissolves in the ether, while the hydrochloride does not. To avoid use of elaborate filtration equipment, the product mixture is separated in relatively small portions rather than all at once.

ratus is then evacuated cautiously, allowing the petroleum ether to vaporize into the liquid-nitrogen trap.

The product, present in the receiving trap, is a crystalline white solid. Further purification can be effected by sublimation in a vacuum. Assuming no loss in transfer operation, the yield is nearly quantitative. *Anal.* Calcd. for $P_4N_6(CH_3)_6$: C, 24.17; H, 6.08; N, 28.19; P, 41.56. Found: C, 23.92; H, 6.03; N, 28.19; P, 41.32.

Properties[1–3]

Tetraphosphorus hexamethylhexaimide is a moisture-sensitive, white crystalline solid melting at 122 to 123° and boiling at 303 to 304° at 737 mm. It is soluble in a wide variety of organic solvents, including benzene, toluene, *n*-hexane, diethyl ether, acetone, and carbon tetrachloride. It is insoluble in water but dissolves slowly in a hot aqueous ammonia solution.

The solid-vapor equilibrium is represented by the equation:

$$\log p \text{ (mm.)} = -\frac{3191}{T} + 8.476$$

The liquid-vapor equilibrium in the range 128 to 220° is provided by the equation:

$$\log p \text{ (mm.)} = -\frac{3146}{T} + 8.346$$

Molecular weight measurements indicate the molecular formula $P_4N_6(CH_3)_6$. Proton nuclear magnetic resonance data support a cage structure analogous to that of phosphorus(III) oxide, P_4O_6.

The infrared spectrum (Nujol mull) shows the following bands: 4290 (w), 3970 (w), 2860 (s), 2790 (s), 2105 (w), 1540 (m), 1440 (s), 1410 (sh), 1375 (m), 1340 (m), 1260 (m), 1155 (s), 1110 to 1050 (s), and 895 to 850 (s) cm.$^{-1}$. The most intense peaks in the mass spectrum obtained at 250° corre-

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spond to the following unipositive ions: $P_4N_6(CH_3)_6^+$, $P_4N_5(CH_3)_5^+$, $P_4N_6(CH_3)_4^+$, $P_4N_6(CH_3)_2^+$, $P_4N_6^+$, $P_4N_4^+$, $P_3N_3(CH_3)_3^+$, $P_3N_3CH_3^+$, $P_3N_2^+$, $P_2N_2(CH_3)_2^+$, $P_2N_3CH_3^+$, $P_2NCH_3^+$, $PNCH_3^+$, and PN_2^+ (ionizing voltage, 70; ionizing current, 37.5 milliamp.).

Tetraphosphorus hexamethylhexaimide reacts with oxygen at 170° to give $P_2O_2(NCH_3)_3$. With boron fluoride and boron chloride, a variety of substances are formed A water-soluble white solid adduct, $P_4N_6(CH_3)_7I$, forms with methyl iodide. The following reaction proceeds almost quantitatively at −78°:

$$P_4N_6(CH_3)_6 + 18HCl \rightarrow 4PCl_3 + 6CH_3NH_3^+Cl^-$$

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17. DIPHENYL PHOSPHOROCHLORIDITE

(Diphenyl Monochlorophosphite)

$$(C_6H_5O)_3P + CH_3CH_2COCl \rightarrow (C_6H_5O)_2PCl + CH_3CH_2COOC_6H_5$$

Submitted by W. Hewertson,* B. C. Smith,* and R. A. Shaw*
Checked by R. L. Lintvedt†

Diphenyl phosphorochloridite can be prepared from phenol and phosphorus(III) chloride,[1,2] but a mixture of products is produced and the yield of the desired compound is low. Higher yields can be obtained from reaction of triphenyl phosphite with phosphorus(III) chloride, but this method is inconvenient because it involves a reaction which

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must be carried out in a sealed tube.[3] The method of preparation of diphenyl phosphorochloridite described here makes use of the reaction between triphenyl phosphite and an acyl chloride.[4] Propionyl chloride is particularly convenient to use because it reacts readily and, in addition, has a lower boiling point than either of the products of the reaction. Thus, the progress of the reaction can be followed by noting the rise in boiling point of the reaction mixture.

Procedure

The apparatus consists of a 1-l. three-necked flask fitted with a thermometer, a sealed stirrer, and a water-cooled reflux condenser. Before use in the reaction, triphenyl phosphite is freed from phenol by vacuum distillation. During the distillation of the phenol, which comes off first, the condenser should be warmed to about 50° to prevent the material from solidifying before it reaches the receiving flask. Pure triphenyl phosphite distills at 180° and 0.5 mm. pressure.

A nitrogen inlet is connected to the top of the condenser, and the apparatus is flushed with dry nitrogen before adding 92.5 g. (1.00 mol) of redistilled propionyl chloride and 310 g. (1.00 mol) of purified triphenyl phosphite to the reaction vessel. The mixture is stirred and heated for a period of 8 hours. During this period, the temperature of the reaction mixture is increased from about 100° to about 195° at such a rate that boiling is maintained. An estimate of the progress of the reaction can be made by noting the rise in temperature indicated by the thermometer which extends into the flask and is heated by the vapors in the upper portion of the reaction vessel. When the reaction is finished, the mixture is cooled to room temperature, and the apparatus is dismantled and then reassembled as follows: One neck of the flask is closed by a ground-glass stopper; the second is fitted with a drawn-out capillary tube attached to the nitrogen source; and the third neck of the flask is equipped with a heated fractionating column (15 in.) packed with glass rings and topped by a still head, thermometer, and water-cooled condenser equipped with a vacuum adapter. The adapter, in turn, is attached through the ground joint to a Perkin triangle (fraction cutter), or to a "pig" used to collect fractions, and through the vacuum outlet to a three-way stopcock which leads to a nitrogen line and to a vacuum pump protected by a cold trap.

The apparatus is flushed with nitrogen and is then evacuated. Phenyl propionate contaminated with phenyl phosphorodichloridite, $C_6H_5OPCl_2$, distills at about 55° at 0.5 mm. Crude diphenyl phosphorochloridite is obtained at approximately 115° at 0.5 mm. and is followed by unchanged triphenyl phosphite boiling at about 180° at 0.5 mm. After all the triphenyl phosphite has been recovered, the reaction flask is cooled, and the vacuum is broken by passing nitrogen through the three-way stopcock. The residue in the flask is destroyed by pouring it slowly into a large volume of cold water.

The crude product is purified by distillation through an efficient fractionating column. The yield of pure diphenyl phosphorochloridite is 157 g. (62%) *Anal.* Calcd. for $C_{12}H_{10}ClO_2P$: Cl, 14.0. Found: Cl, 13.8.

Properties

Diphenyl phosphorochloridite is a colorless, viscous liquid with a pleasant smell; it shows the following physical properties: b.p. 115° at 0.5 mm.,[4] 147° at 4 mm.,[2] 172° at 11 mm.,[1] and 295° at 731 mm.;[1] $n_D^{25} = 1.5776$;[4] $d_{18}^{18} = 1.221$.[1]

Inasmuch as diphenyl phosphorochloridite disproportionates to triphenyl phosphite and phenyl phosphorodichloridite, it is necessary to distill the product immediately before use:

$$2(C_6H_5O)_2PCl \rightarrow C_6H_5OPCl_2 + (C_6H_5O)_3P$$

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Diphenyl phosphorochloridite hydrolyzes slowly in air and more rapidly in water, but it is less reactive toward nucleophilic reagents than most chlorine derivatives of phosphorus(III). The reaction with alcohols in the presence of a tertiary base is used to prepare diphenyl alkyl phosphites. Addition of sulfur occurs on reaction with thiophosphoryl chloride.

References

1. E. Noack: *Ann.*, **218**, 85 (1883).
2. J. P. Forsman and D. Lipkin: *J. Am. Chem. Soc.*, **75**, 3145 (1953).
3. J. B. Conant, V. H. Wallingford, and S. S. Gandheker: *ibid.*, **45**, 762 (1923).
4. W. Hewertson, R. A. Shaw, and B. C. Smith: *J. Chem. Soc.*, **1962**, 3267.

18. DIPHENYLPHOSPHINIC ACID

$$(C_6H_5)_2PCl + H_2O_2 + 2NaOH \rightarrow (C_6H_5)_2P(O)ONa + NaCl + 2H_2O$$

$$(C_6H_5)_2P(O)ONa + HCl \rightarrow (C_6H_5)_2P(O)OH + NaCl$$

Submitted by L. R. Ocone,* C. W. Schaumann,* and B. P. Block*
Checked by E. N. Walsh†

There are over a dozen different methods in the literature for preparing diphenylphosphinic acid, the first of which[1] was from phenylphosphonous dichloride. By and large they can be divided into one group involving the addition of phenyl groups to phosphorus compounds and into a second group involving the modification of diphenylphosphorus compounds. The latter type is, in general, more con-

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† Victor Chemical Division, Stauffer Chemical Company, Chicago Heights, Ill.

venient provided that a suitable starting material is available. Diphenylphosphinous chloride has been converted to diphenylphosphinic acid by hydrolysis[2] and by oxidation with air[3] or nitric acid.[4] Straight hydrolysis is not satisfactory because one-half of the phosphorus is converted to diphenylphosphine; i.e., a disproportionation is involved. Treatment with hydrogen peroxide in basic solution is a convenient oxidation procedure.

Procedure

The entire reaction is carried out in a 4-l. beaker. A paddle stirrer with a heavy motor is used to mix the reactants, and the temperature is followed with a thermometer. *All operations up to the point where oxidation is complete should be performed in an efficient hood.* Five hundred grams (2.27 mol) of technical-grade diphenylphosphinous chloride* is added dropwise with stirring to 1500 ml. of water at room temperature at a rate of 300 g./hour. After this addition is completed, 190 g. (4.75 mol) of sodium hydroxide pellets is added in small portions with stirring so that the temperature does not exceed 50°. Immediately after the addition of the base, while the temperature of the milky slurry is still above 45°, 20 ml. of 30% hydrogen peroxide is added. The ensuing reaction causes the temperature to rise to about 55°. When the temperature subsides to 45°, an additional 20 ml. of 30% hydrogen peroxide is added. This procedure is repeated until 200 ml. of 30% hydrogen peroxide has been added while maintaining the temperature between 45 and 55°.

After oxidation is complete, and while the solution is still hot, 6 *M* hydrochloric acid is added dropwise to a pH of 2.

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* Available from Victor Chemical Division, Stauffer Chemical Company, Chicago Heights, Ill. This material has a tendency to adhere to equipment, and it cannot be easily flushed away. It can be removed by soaking in concentrated nitric acid.

If the acid is added too rapidly, the resulting precipitate is difficult to filter, but, if the acid is added slowly, the diphenylphosphinic acid precipitates in a filterable microcrystalline form. After acidification, the mixture is cooled, the solid is recovered by filtration, washed thoroughly with dilute hydrochloric acid (10 ml. of concentrated hydrochloric acid per liter), and then with cold water. The wet filter cake is then washed with 250 ml. of benzene to remove the biphenyl which occurs as a by-product. After drying at 110°, the crude product, off-white in color, is obtained in a yield of 90 to 96%. Recrystallization from hot 95% ethanol produces a white crystalline product.* *Anal.* Calcd. for $(C_6H_5)_2P(O)OH$: C, 66.05; H, 5.08; P, 14.20. Found: C, 66.02 ± 0.10; H, 5.08 ± 0.23; P, 14.16 ± 0.23. Calculated formula weight: 218.19. Neutral equivalent determined by titration with standard base in methanol: 219.2 ± 1.4.

Properties

Diphenylphosphinic acid is a white crystalline substance which is fairly soluble in hot ethanol and slightly soluble in cold ethanol. It is insoluble in water and very slightly soluble in benzene and chloroform. The melting point of the material recrystallized from ethanol is 194 to 196°.

References

1. A. Michaelis and F. Graeff: *Ber.* **8**, 1304 (1875).
2. A. Michaelis and L. Gluckmann: *ibid.*, **15**, 801 (1882).

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* The checker reports the following recrystallization procedure. Forty-seven grams of the crude product is recrystallized from 400 ml. of boiling ethanol. On cooling to room temperature, 36.5 g. of product is isolated; m.p. 195 to 196°. The filtrate is concentrated to approximately one-third its volume on a steam bath and a second crop, 6.5 g., is obtained; m.p. 195 to 196°. Evaporating the filtrate yields 4.0 g. of off-white solid (slightly impure product); m.p. 192 to 194°.

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3. A. Michaelis: *ibid.*, **10**, 627 (1877).
4. T. Weil: *Helv. Chim. Acta*, **37**, 654 (1954).

19. (2,2-DIMETHYLHYDRAZINO)-DIPHENYLPHOSPHINE

$$2(CH_3)_2NNH_2 + ClP(C_6H_5)_2 \rightarrow (CH_3)_2NNHP(C_6H_5)_2 + (CH_3)_2NNH_2{\cdot}HCl$$

Submitted by Harry H. Sisler* and R. P. Nielsen*
Checked by T. H. Dexter† and D. J. Jaszka†

(2,2-Dimethylhydrazino)diphenylphosphine may be prepared by the action of *unsym*-dimethylhydrazine‡ on diphenylphosphinous chloride‡ in benzene at temperatures just below room temperature. A 2:1 mol ratio provides an extra mol of the free base to act as a hydrogen chloride acceptor. The *unsym*-dimethylhydrazinium chloride, which is only very slightly soluble in benzene, may be easily removed by filtration. The hydrazinophosphine may then be recovered from the filtrate in good yield by evaporation of the solvent at room temperature under reduced pressure.

Procedure

A 500-ml. three-necked flask is fitted with a pressure-equalizing dropping funnel of about 200 ml. capacity, a glass-joint-type mechanical stirrer, and a desiccant-filled

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† Hooker Chemical Corporation, Niagara Falls, N.Y.

‡ Both reactants are commercially available. Diphenylphosphinous chloride was obtained from the Victor Chemical Division, Stauffer Chemical Company, Chicago Heights, Ill. *Unsym*-dimethylhydrazine was obtained from the Eastman Kodak Company, Rochester, N.Y., but may be obtained from several sources.

drying tube. [Appropriate drying agents include, among others, Drierite (10 to 20 mesh), silica gel, and Linde Molecular Sieve Type 4a.] (*Caution. Desiccants which are strong oxidizing agents should be avoided.*) The apparatus is flushed with dry nitrogen and flamed to ensure dryness. In the flask are placed 100 ml. of anhydrous benzene and 50 ml. (39.2 g.; 0.653 mol) of *unsym*-dimethylhydrazine (dried over calcium hydride). (*Caution. Unsym-dimethylhydrazine is flammable and toxic.*) In the dropping funnel are placed 100 ml. of benzene (dried over calcium hydride) and 50 ml. (59.5 g.; 0.269 mol) of chlorodiphenylphosphine.

Stirring is begun and the flask is cooled in an ice bath. The contents of the addition funnel are added dropwise over a 90-minute period with constant stirring and cooling. When addition is complete, the ice bath is removed and the mixture is stirred for an additional 30 minutes at 40 to 50°. During this period, the crystals of *unsym*-dimethylhydrazinium chloride increase in size and thus become easier to remove by filtration.

After being cooled, the mixture is filtered into a 500-ml. round-bottomed flask through a fritted-glass funnel of medium porosity, using a vacuum-adapter take-off to speed filtration and avoid extended exposure to the atmosphere. The filtrate is evaporated on a rotating vacuum evaporator at room temperature. The yield of dried crude product is 61 g. (92%). The transfer of the solid product should be conducted in a dry-box, or under a flow of dry nitrogen gas, or be carried out very rapidly. The crude product is crystallized by dissolving it in 150 ml. of cyclohexane or *n*-hexane (dried over calcium hydride) at a temperature just below the boiling point and filtering the resulting solution rapidly through coarse filter paper into an Erlenmeyer flask which can be kept closed with a glass stopper. As the solution cools, (2,2-dimethylhydrazino)diphenylphosphine crystallizes. After the solution has stood overnight in a refrigerator, the crystals may be collected and washed with cold hexane. The yield is about 70%; m.p. 66 to 68°.

Additional lower-melting product of 85 to 90% purity can be recovered by evaporation of the hexane mother liquor.

Further purification can be effected by sublimation at 60° at 0.1 mm. of Hg. About 55 g. of purified product melting at 68.5 to 69.5° is normally obtained (84% yield).

Properties

The (2,2-dimethylhydrazino)diphenylphosphine forms colorless needle-like or prismatic crystals. It is soluble in benzene, ether, chloroform, and alcohol. Hydrolysis occurs in water to yield free *unsym*-dimethylhydrazine and diphenylphosphinous acid, which is readily oxidized to diphenylphosphinic acid upon contact with air.

Boiling a solution of (2,2-dimethylhydrazino)diphenylphosphine in benzene overnight in contact with dry air causes precipitation of the oxide, $(C_6H_5)_2P(O)NHN(CH_3)_2$ (m.p. 167 to 168°). Addition of a stoichiometric amount of sulfur to a boiling benzene solution of (2,2-dimethylhydrazino)diphenylphosphine yields, on cooling, the sulfide, $(C_6H_5)_2P(S)NHN(CH_3)_2$ (m.p. 95.5 to 97.0°). Alkylation to $[(C_6H_5)_2(CH_3)PNHN(CH_3)_2]I$ (m.p. 156 to 158°) occurs upon reaction with methyl iodide in ether. Reaction with chloramine in ether yields the aminophosphonium salt, $[(C_6H_5)_2P(NH_2)NHN(CH_3)_2]Cl$ (m.p. 195°). All of the above-described derivatives are colorless solids.

Storage in sealed glass ampuls or in air-tight bottles is recommended.

References

1. R. P. Nielsen and H. H. Sisler: *Inorg. Chem.*, **2**, 753 (1963).
2. R. P. Nielsen, J. F. Vincent, and H. H. Sisler: *ibid.*, **2**, 760 (1963).

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Edited by Henry F. Holtzclaw, Jr.

20. ALKOXY- AND ARYLOXYCYCLOPHOSPHAZENES

(Alkyl and Aryl Phosphonitrilates)

Submitted by B. W. Fitzsimmons* and R. A. Shaw*

A. HEXAETHOXYCYCLOTRIPHOSPHAZATRIENE

(Trimeric Ethyl Phosphonitrilate; 2,2,4,4,6,6-Hexaethoxy-2,2,4,4,6,6-hexahydro-1,3,5,2,4,6-triazatriphosphorine)

$$N_3P_3Cl_6 + 6C_2H_5OH + 6C_5H_5N \rightarrow N_3P_3(OC_2H_5)_6 + 6C_5H_5N\cdot HCl$$

Checked by George M. Nichols†

Hexaethoxycyclotriphosphazatriene may be prepared by the slow addition of dry ethanol to a cold, stirred solution of hexachlorocyclotriphosphazatriene (1,3,5,2,4,6-triazatriphosphorine 2,2,4,4,6,6-hexachloride; phosphonitrile chloride, cyclic trimer) in dry pyridine.[1] The reaction mixture is worked up by the addition of an excess of dry diethyl ether and filtration of the precipitated pyridinium hydrochloride. The solvents are then removed from the washed and dried solution and the product is purified by vacuum distillation.

Procedure

NOTE: For Parts A and B, the pyridine may be conveniently dried by refluxing over, and distillation from, phosphorus(V) oxide. The ethanol may be dried by distillation

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from diethyl phthalate as follows: Diethyl phthalate (10 ml.) and sodium (1 g.) are dissolved in about 2.5 l. of ethanol. The solution is refluxed for 4 hours. The ethanol is then removed by distillation.

Twenty grams (0.057 mol) of hexachlorocyclotriphosphazatriene (1,3,5,2,4,6-triazatriphosphorine 2,2,4,4,6,6-hexachloride; phosphonitrile chloride, cyclic trimer), $N_3P_3Cl_6$,* is dissolved in 82 ml. (80.5 g.; 1.02 mols) of dry pyridine in a 500-ml. two-necked flask. The solution is stirred mechanically and cooled to 0 to 5°. Then 62 ml. (48.7 g.; 1.05 mols) of dry ethanol is added dropwise. The temperature is maintained in the range 0 to 5° throughout the addition and the subsequent stirring, which is continued for 2 hours following the addition of reagent. The mixture is then allowed to attain room temperature and is stored overnight. Dry diethyl ether (300 ml.) is added with stirring, and the precipitated pyridinium chloride is removed by filtration.† The filtrate is washed successively with dilute solutions of hydrochloric acid (5%) and sodium hydrogen carbonate (5%) and with water. The solution is dried over sodium sulfate and the solvent is removed. Purification is effected by vacuum distillation. The first distillation of this compound is sometimes accompanied by extensive decomposition. The difficulty is not usually encountered during the second and subsequent distillations. It is therefore best to carry out the initial distillation in batches of about 10 ml. and to use semimicro distillation apparatus. Two distillations are normally sufficient to give an analytically pure sample of the compound: b.p. 114 to 116° at 0.1 mm. The yield is 8.0 g. (34.4%). *Anal.* Calcd.: C, 35.6; H, 7.4; N, 10.4. Found C, 35.5; H, 7.2; N, 10.6. The compound can be further characterized by its infrared spectrum[2] (see Properties).

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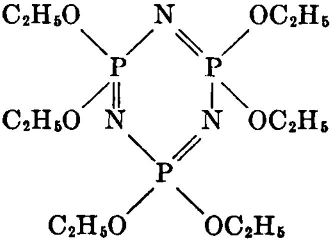
* See procedure by M. L. Nielsen and G. Cranford, INORGANIC SYNTHESES, 6, 94 (1960).

† To obtain a check on the preparation at this stage, the pyridinium chloride can be vacuum-dried and weighed; yield, 99.5%.

Properties

Hexaethoxycyclotriphosphazatriene is a colorless, odorless liquid for which n_D^{24} is 1.4522. The compound is soluble in petroleum ether, benzene, diethyl ether, carbon tetrachloride, or chloroform, but almost insoluble in water. The frequencies of the principal absorption maxima in the infrared spectrum are 3000, 1225, 1170, 1036, 972, 899, 813, 800, and 751 cm.$^{-1}$ The frequency at 1225 cm.$^{-1}$ is characteristic of a six-membered ring in this case.



B. OCTAETHOXYCYCLOTETRAPHOSPHAZATETRAENE

(Tetrameric Ethyl Phosphonitrilate; 2,2,4,4,6,6,8,8-Octaethoxy-2,2,4,4,6,6,8,8-octahydro-1,3,5,7,2,4,6,8-tetrazatetraphosphocine)

$$N_4P_4Cl_8 + 8C_2H_5OH + 8C_5H_5N \rightarrow N_4P_4(OC_2H_5)_8 + 8C_5H_5N{\cdot}HCl$$

Checked by George M. Nichols*

Procedure

Octaethoxycyclotetraphosphazatetraene is prepared by a method exactly analogous to that for hexaethoxycyclotriphosphazatriene (Part A) except that 20 g. (0.043 mol) of octachlorocyclotetraphosphazatetraene (1,3,5,7,2,4,6,8-tetrazatetraphosphocine 2,2,4,4,6,6,8,8-octachloride; phosphonitrile chloride, cyclic tetramer)† requires 130 ml.

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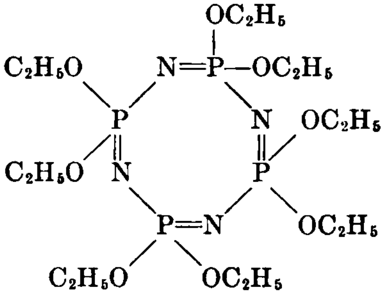
[*] Victor Chemical Division, Stauffer Chemical Company, Chicago Heights, Ill.

[†] See procedure by M. L. Nielsen and G. Cranford: Inorganic Syntheses, **6**, 94 (1960).

(127.6 g.; 1.6 mol) of pyridine for dissolution. The quantity of ethanol utilized is 48.7 g. (1.05 mols). Purification of octaethoxycyclotetraphosphazatetraene is best accomplished by vacuum sublimation. Sublimation is rapid at 60° and 10^{-6} mm. The compound can also be purified by distillation; b.p. 128° at 0.001 mm. If vacuum equipment is not available, purification can be achieved by recrystallization.* The pure compound melts at 45 to 47°. The yield is 16.9 g. (72%), based upon octachlorocyclotetraphosphazatetraene. *Anal.* Calcd. for $N_4P_4(OC_2H_5)_8$: C, 35.6; H, 7.4; N, 10.4. Found: C, 35.4; H, 7.1; N, 10.4.

Properties

Octaethoxycyclotetraphosphazatetraene is soluble in petroleum ether, benzene, diethyl ether, carbon tetrachloride, or chloroform, but almost insoluble in water. The frequencies of the principal absorption maxima in the infrared spectrum are: 3000, 1320, 1160, 1040, 970, 850, 810, and 715 $cm.^{-1}$. The frequency of 1320 $cm.^{-1}$ is characteristic of an eight-membered ring.



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[*] The checker has submitted the following method of purification by recrystallization: To the crude product (which crystallizes to a stiff mush at 25°) is added a small amount of heptane to make a nearly saturated solution at 25°. This solution is cooled to 0° to effect crystallization and is filtered. The filtrate is then cooled to −20°, whereupon a second crop of crystals is obtained. This procedure is repeated until the Dry Ice–acetone temperature is reached or until no further crystallization takes place. The crystal crops are combined and recrystallized in a similar manner to give white granular crystals which melt at 45 to 47°. The yield is 13.6 g. (58%).

C. HEXAPHENOXYCYCLOTRIPHOSPHAZATRIENE

(Trimeric Phenyl Phosphonitrilate; 2,2,4,4,6,6-Hexaphenoxy-2,2,4,4,6,6-hexahydro-1,3,5,2,4,6-triazatriphosphorine)

$$N_3P_3Cl_6 + 6NaOC_6H_5 \rightarrow N_3P_3(OC_6H_5)_6 + 6NaCl$$

CHECKED BY E. H. UHING*

Hexaphenoxycyclotriphosphazatriene may be prepared by the reaction of hexachlorocyclotriphosphazatriene with an excess of sodium phenoxide in dioxane. Sodium phenoxide may be prepared from sodium ethoxide by the exchange reaction:

$$NaOC_2H_5 + C_6H_5OH \rightleftarrows NaOC_6H_5 + C_2H_5OH$$

Alternatively, direct reaction of sodium with a solution of phenol in dioxane may be used. The procedure described in Part C employs the exchange reaction, which is applicable to other high-boiling hydroxy compounds. The more convenient direct method, employed in Part D, requires that the hydroxy compound react readily with sodium.

Procedure

A 500-ml. two-necked round-bottomed flask is attached to a distillation column (25 × 2 cm.) packed with Fenske helixes and fitted with a slow variable-reflux-ratio distillation head. One hundred milliliters of dry ethanol is placed in the flask, and 7.7 g. (0.335 mol) of sodium is added slowly. Then 31.5 g. (0.355 mol) of phenol dissolved in 50 ml. of ethanol is added and the mixture is boiled. The ethanol is

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* Victor Chemical Division, Stauffer Chemical Company, Chicago Heights, Ill.

removed slowly via the distillation take-off head and replaced by 170 ml. of anhydrous dioxane. Fifteen grams (0.043 mol) of hexachlorocyclotriphosphazatriene dissolved in 100 ml. of dioxane is then added during one hour, and the mixture is subsequently boiled for 2 hours. The cold mixture is diluted with 400 ml. of diethyl ether and is placed in a separatory funnel and washed with 120 ml. of water. It is then washed with dilute aqueous solutions of hydrochloric acid and sodium hydrogen carbonate and again with water. The solution is dried over sodium sulfate and the solvent is evaporated. The residual yellow oil is dissolved in about 300 ml. of a 50% benzene–petroleum ether mixture (b.p. 60 to 80°) and the solution is passed through a short column (about 10 × 2 cm.) packed with alumina. The benzene eluate on evaporation crystallizes slowly to give hexaphenoxycyclotriphosphazatriene.[1] The product can be recrystallized from the benzene–petroleum ether mixture to produce crystals which melt at 110 to 111°. The yield is 23 to 26 g. (80 to 90%). *Anal.* Calcd. for $N_3P_3(OC_6H_5)_6$: C, 62.3; H, 4.3; N, 6.1; P, 13.6. Found: C, 62.4; H, 4.3; N, 6.2. By checker: N, 5.9; P, 13.4.

Properties

Hexaphenoxycyclotriphosphazatriene is quite stable and can be kept at 300° for prolonged periods without appreciable decomposition. It is soluble in benzene or chloroform but is almost insoluble in petroleum ether (b.p. 60 to 80°) or in water. It is slowly decomposed by boiling dilute mineral acids. The frequencies of the principal absorption maxima in the infrared spectrum are 3100, 1600, 1495, 1260, 1200, 1190, 1180, 1070, 1020, 1010, 950, 930, 910, 890, 880, 820, 790, 780, 770, 760, 735, and 690 $cm.^{-1}$. The frequency at 1260 $cm.^{-1}$ is characteristic of a six-membered ring in this case, analogous to that of the hexaethoxy compound (see Part A).

D. OCTAPHENOXYCYCLOTETRAPHOSPHAZATETRAENE

(Tetrameric Phenyl Phosphonitrilate; 2,2,4,4,6,6,8,8-Octaphenoxy-2,2,4,4,6,6,8,8-octahydro-1,3,5,7,2,4,6,8-tetrazatetraphosphocine)

$$N_4P_4Cl_8 + 8NaOC_6H_5 \rightarrow N_4P_4(OC_6H_5)_8 + 8NaCl$$

Checked by E. H. Uhing*

Twenty-one grams (0.225 mol) of phenol is dissolved in 150 ml. of dioxane, and 5.1 g. (0.222 mol) of sodium is added. The mixture is boiled under reflux in a 500-ml. round-bottomed flask until all the sodium is dissolved. Ten grams (0.0215 mol) of octachlorocyclotetraphosphazatetraene is added slowly to the cold solution and the mixture is boiled for 3 hours. The cold mixture is diluted with 300 ml. of diethyl ether, then placed in a separatory funnel and washed with 120 ml. of water. It is then washed successively with dilute aqueous solutions of hydrochloric acid (5%) and sodium hydrogen carbonate (5%), and again with water. The solution is dried over sodium sulfate and the solvents are evaporated. The crude product solidifies slowly and melts at about 56°. The yield is 17 g. (85%). Purification is effected by one recrystallization from a benzene–petroleum ether mixture; m.p. 85 to 86°.[1] *Anal.* Calcd.: C, 62.3; H, 4.3; N, 6.1. Found: C, 62.0; H, 4.3; N, 6.0.

Properties

The recrystallization procedure yields one of three solid modifications of this compound which have melting points of 65 to 66°, 70 to 71°, and 85 to 86°, respectively. The three forms have identical infrared spectra and the same composition. They differ in their superficial appearance, as may be seen by examination under a microscope. The form which melts at 65 to 66°, when melted and recrystallized by cooling, yields the modification which melts at 70

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to 71°. This, in turn, with similar treatment yields the modification which melts at 85 to 86°.

Octaphenoxycyclotetraphosphazatetraene is similar to hexaphenoxycyclotriphosphazatriene in solubility and thermal stability. The principal absorption maxima in the infrared spectrum are 3100, 1600, 1495, 1320, 1195, 1160, 1070, 1020, 1010, 950, 900, 830, 770, 710, and 690 cm.$^{-1}$. The frequency at 1320 cm.$^{-1}$ is characteristic of an eight-membered ring analogous to that of the octaethoxy compound (see Part B).

References

1. B. W. Fitzsimmons and R. A. Shaw: *Chem. Ind.* (*London*), **1961,** 109; *J. Chem. Soc.*, **1964,** 1735.
2. B. W. Fitzsimmons and R. A. Shaw: *Proc. Chem. Soc.*, **1961,** 258; B. W. Fitzsimmons, C. Hewlett, and R. A. Shaw: *J. Chem. Soc.*, **1964,** 4459; K. Hess and H. Frahn: *Ber.*, **71,** 2627 (1938).

21. MERCAPTO DERIVATIVES OF CHLOROCYCLOPHOSPHAZENES

(Mercapto Derivatives of Cyclic Phosphonitrile Chlorides)

$$2RSH + 2Na \rightarrow 2NaSR + H_2$$
$$n NaSR + N_3P_3Cl_6 \rightarrow N_3P_3Cl_{6-n}(SR)_n + n NaCl$$

or

$$n NaSR + N_4P_4Cl_8 \rightarrow N_4P_4Cl_{8-n}(SR)_n + n NaCl$$

Submitted by A. P. Carroll* and R. A. Shaw*

From the reaction of the sodium salt of an aliphatic or aromatic mercaptan (thiol) with hexachlorocyclotriphosphazatriene (1,3,5,2,4,6-triazatriphosphorine 2,2,4,4,6,6-hexa-

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* Birkbeck College (University of London), London, England.

chloride; phosphonitrile chloride, cyclic trimer), or octachlorocyclotetraphosphazatetraene (1,3,5,7,2,4,6,8-tetrazatetraphosphocine 2,2,4,4,6,6,8,8-octachloride; phosphonitrile chloride, cyclic tetramer), the mercapto derivatives $N_3P_3Cl_{6-n}(SR)_n$ and $N_4P_4Cl_{8-n}(SR)_n$, respectively, can be prepared. The degree of mercaptalation is dependent on the nature of the mercaptan and the reaction solvent. The replacement of chlorine atoms by these mercapto groups follows a geminal pattern with respect to each phosphorus-substrate center.[1-3] In the compounds E and F below, although the four mercapto groups are known to be attached geminally to two phosphorus atoms, their exact location in the ring has not yet been established.

Because of the heterogeneous nature of the reactions a considerable excess of mercaptide is necessary in order to obtain satisfactory yields. Although all of the reactions described below are carried out under nitrogen, a considerable amount of disulfide is invariably formed. When the products are purified by a series of vacuum distillations, a small amount of decomposition appears unavoidable, especially during the first distillation of the crude reaction product. However, when the compound is pure, no decomposition occurs during distillation and the boiling point, which is constant from distillation to distillation, is considerably lower than that observed in the earlier distillations. The decrease in boiling point is greatest between the first and second distillations.

In order to minimize decomposition and to reduce the temperature required for effective distillation at a given pressure, it is desirable to wrap the distillation assembly with asbestos or other insulating material.

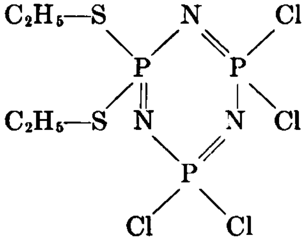
The water content of the solvents used should be less than 0.01%.

Procedure

The following reactions are all carried out under dry nitrogen with the rigorous exclusion of atmospheric moisture. The intermediate mercaptide is prepared *in situ* in a 3-necked flask equipped with dropping funnel, water-cooled condenser, and nitrogen inlet. For the second stage of each reaction the funnel is replaced by a mechanical stirrer.

A. 2,2,4,4-TETRACHLORO-6,6-BIS(ETHYLMERCAPTO)-CYCLOTRIPHOSPHAZATRIENE

[2,2,4,4-Tetrachloro-6,6-bis(ethylthio)-2,2,4,4,6,6-hexahydro-1,3,5,2,4,6-triazatriphosphorine]



Checked by J. A. Kawalko*

Sodium ethyl mercaptide is prepared as a white suspension by the dropwise addition of 13 ml. (10.9 g.; 0.18 mol) of freshly distilled ethanethiol (ethyl mercaptan) to 3.4 g. (0.15 mol) of sodium wire freshly extruded from a sodium press and suspended in 350 ml. of ether contained in a 500-ml. flask.† When mercaptide formation is complete, 6 g. (0.017 mol) of hexachlorocyclotriphosphazatriene $N_3P_3Cl_6$,‡ dissolved in 60 ml. of ether is added and the reaction mixture is stirred continuously for 48 hours at room temperature. Unreacted sodium ethyl mercaptide and the precipitated sodium chloride are filtered out over a mat of kieselguhr on a Büchner funnel. The oil which is obtained from the filtrate by evaporation is purified by

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* Victor Chemical Division, Stauffer Chemical Co., Chicago Heights, Ill.

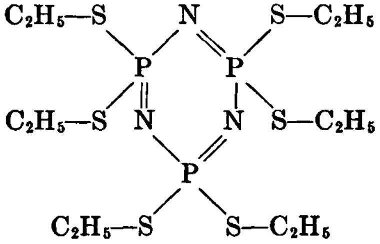
† The checker has found that, if a sodium press is not available, cut sodium can be used effectively.

‡ See procedure by M. L. Nielsen and G. Cranford, Inorganic Syntheses, **6**, 94 (1960).

vacuum distillation. At least three such distillations are usually necessary before a pure product is obtained. The boiling point of the pure compound is 128° at 0.2 mm. The yield is 4.2 g. (62%). *Anal.* Calcd. for $N_3P_3Cl_4S_2C_4H_{10}$: C, 12.0; H, 2.5; Cl, 35.5; S, 16.1; mol. wt., 399. Found: C, 12.0; H, 2.5; Cl, 35.7; S, 16.0; mol. wt., 403. By checker: S, 16.2; b.p., 122 to 124° at 0.01 mm.

B. HEXAKIS(ETHYLMERCAPTO)CYCLOTRIPHOSPHAZATRIENE

[2,2,4,4,6,6-Hexakis(ethylthio)-2,2,4,4,6,6-hexahydro-1,3,5,2,4,6-triazatriphosphorine]



Checked by J. A. Kawalko*

Sodium ethyl mercaptide is prepared by the slow addition of 12 ml. (9.9 g.; 0.16 mol) of ethanethiol to 3.2 g. (0.14 mol) of sodium wire suspended in 200 ml. of tetrahydrofuran in a 500-ml. flask. When all the sodium has reacted, 6 g. (0.017 mol) of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$,† dissolved in 60 ml. of tetrahydrofuran is added. The reaction mixture is boiled under reflux, with continuous stirring, for 25 hours. The suspended sodium chloride and sodium ethyl mercaptide are filtered out over a mat of kieselguhr on a Büchner funnel. When the solvent has been evaporated from the filtrate, a little ether is added to the oily residue, which is again filtered; this ensures the

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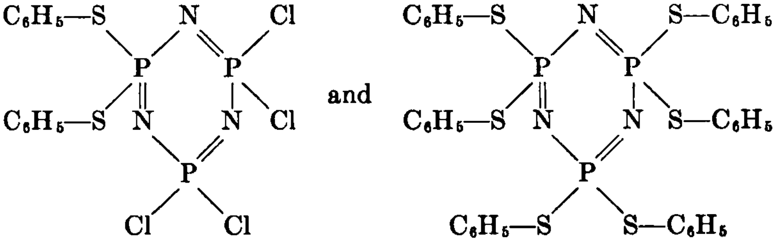
* Victor Chemical Division, Stauffer Chemical Co., Chicago Heights, Ill.

† See procedure by M. L. Nielsen and G. Cranford, Inorganic Syntheses, 6, 94 (1960).

removal of any sodium mercaptide which may have been dissolved in the tetrahydrofuran. The oily material is then dissolved in 25 ml. of petroleum ether (b.p. 60 to 80°) and solidified by chilling to $-78°$ and triturating for 20 to 30 minutes. The solvent is then decanted and fresh petroleum ether added to the residue. This is again chilled and triturated as above. After three or four such coolings with subsequent trituration and decantation of the mother liquor, a solid which does not melt at room temperature is obtained. This solid is recrystallized from ethanol, distilled *in vacuo* (b.p. 196° at 0.06 mm.) and finally recrystallized from light petroleum. The melting point of the pure compound is 35.5°. The yield is 7.8 g., (92%). *Anal.* Calcd. for $N_3P_3S_6C_{12}H_{30}$: C, 28.7; H, 6.0; N, 8.4; P, 18.5. Found: C, 28.7; H, 6.3; N, 8.6. By checker: P, 18.7.

C AND D. 2,2,4,4-TETRACHLORO-6,6-BIS(PHENYLMERCAPTO)CYCLOTRIPHOSPHAZATRIENE AND HEXAKIS(PHENYLMERCAPTO)CYCLOTRIPHOSPHAZATRIENE

[2,2,4,4-Tetrachloro-6,6-bis(phenylthio)-2,2,4,4,6,6-hexahydro-1,3,5,2,4,6-triazatriphosphorine and 2,2,4,4,6,6-Hexakis(phenylthio)-2,2,4,4,6,6-hexahydro-1,3,5,2,4,6-triazatriphosphorine]



Checked by R. B. Fearing*

Sodium phenyl mercaptide is prepared as a white suspension in 500 ml. of ether contained in a 1-l. flask by adding

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* Victor Chemical Division, Stauffer Chemical Co., Chicago Heights, Ill.

45 ml. (48 g.; 0.44 mol) of benzenethiol to 6.9 g. (0.3 mol) of sodium wire. When the last traces of sodium have reacted, 16 g. (0.046 mol) of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$,* dissolved in 80 to 100 ml. of ether is added and the mixture is boiled under reflux for 12 hours. Since the filtering of this reaction mixture—even through a kieselguhr mat—is somewhat tedious, a "wash and decant" method of separation may be employed. The ether washings are then filtered in bulk through a kieselguhr mat. On evaporation, a viscous oil is obtained from the filtrate. This can be solidified by low-temperature trituration as described in Procedure B. The di- and hexamercaptalated products may be obtained by fractional crystallization of this solid from petroleum ether (b.p. 60 to 80°). The hexamercaptalated compound is the less soluble and is recrystallized further from petroleum ether to give a pure compound with m.p. 153.5°. The yield of this compound is 13 g. (35.8%). The dimercaptalated compound is recrystallized from Cellosolve to give a yield of 5 g. (21.5%) of the pure compound with m.p. 107°.

If the reaction mixture is boiled for longer periods, the yield of the hexakis(phenylmercapto)phosphazene increases at the expense of the partially mercaptalated derivative; e.g., if the reaction is allowed to proceed in boiling ether for 3 to 4 days, no bis(phenylmercapto) derivative is detected. *Anal.* Calcd. for $N_3P_3Cl_4S_2C_{12}H_{10}$: C, 29.1; H, 2.0; S, 13.0; Cl, 28.6; mol. wt., 495. Found: C, 29.6; H, 2.2; S, 13.2; mol. wt., 516. By checker: S, 12.9; Cl, 26.3. Calcd. for $N_3P_3S_6C_{36}H_{30}$: C, 54.7; H, 3.8; S, 24.4. Found: C, 54.5, H, 4.2; S, 24.2.

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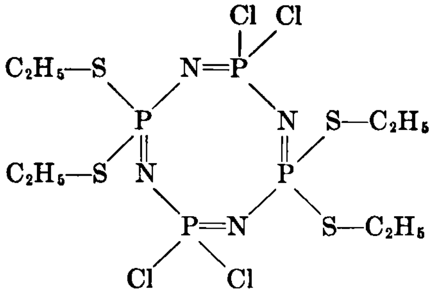
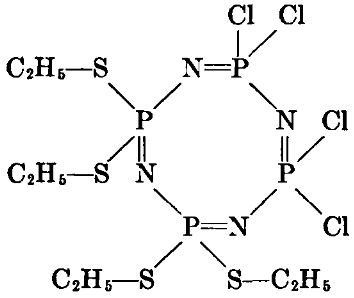
* See procedure by M. L. Nielsen and G. Cranford, INORGANIC SYNTHESES, **6**, 94 (1960).

E. TETRACHLOROTETRAKIS(ETHYLMERCAPTO)CYCLOTETRAPHOSPHAZATETRAENE

[Tetrachlorotetrakis(ethylthio)-2,2,4,4,6,6,8,8-octahydro-1,3,5,7,2,4,6,8-tetrazatetraphosphocine]



or



CHECKED BY G. R. PRICE*

The sodium ethyl mercaptide is prepared from 20 ml. (16.6 g.; 0.27 mol) of ethanethiol and 4.6 g. (0.20 mol) of sodium wire suspended in 280 ml. of ether contained in a 500-ml. flask. To this suspension is added 10 g. (0.02 mol) of octachlorocyclotetraphosphazatetraene (1,3,5,7,2,4,6,8-tetrazatetraphosphocine 2,2,4,4,6,6,8,8-octachloride; phosphonitrile chloride, cyclic tetramer), $N_4P_4Cl_8$, dissolved in 100 ml. of ether. The resulting mixture is stirred continuously for 48 hours at room temperature. The sodium chloride and unreacted sodium ethyl mercaptide are filtered over a kieselguhr mat in a Büchner funnel. The viscous

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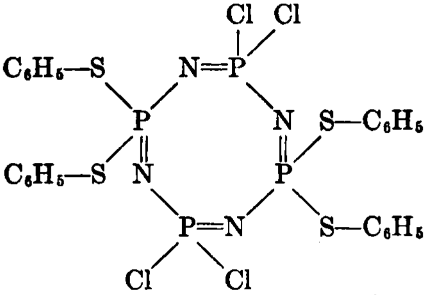
* Victor Chemical Division, Stauffer Chemical Co., Chicago Heights, Ill.

oil which remains on evaporation of the filtrate may be solidified in the usual manner by low-temperature trituration in petroleum ether (b.p. 60 to 80°), as described in Procedure B. The resulting solid is then vacuum-distilled (b.p. 145 to 150° at 0.2 mm.) and subsequently recrystallized from petroleum ether. The pure product melts at 105 to 106.5°. The yield is 7.0 g. (57.3%). *Anal.* Calcd. for $N_4P_4Cl_4S_4C_8H_{20}$: C, 17.0; H, 3.6; P, 21.9; S, 22.7. Found: C, 17.1; H, 3.6; P, 21.8; S, 22.1.

F. TETRACHLOROTETRAKIS(PHENYLMERCAPTO)-CYCLOTETRAPHOSPHAZATETRAENE

[Tetrachlorotetrakis(phenylthio)-2,2,4,4,6,6,8,8-octahydro-1,3,5,7,2,4,6,8-tetrazatetraphosphocine]



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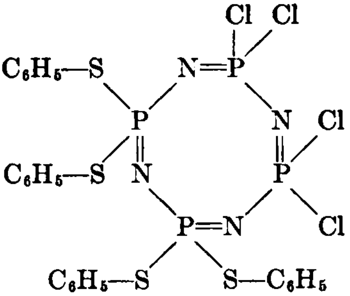

Checked by G. R. Price*

Twenty-four grams (0.18 mol) of sodium phenyl mercaptide, suspended in 275 ml. of ether contained in a 500-ml. flask, is prepared by the method described in Procedure D.

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* Victor Chemical Division, Stauffer Chemical Co., Chicago Heights, Ill.

Eight grams (0.017 mol) of octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$, dissolved in 75 ml. of ether, is added, and the mixture is boiled under reflux for 30 hours with continuous stirring. Insoluble materials are then filtered over a kieselguhr mat. The sticky substance which is obtained by evaporating the filtrate can be solidified by prolonged low-temperature trituration with a small quantity of petroleum ether (b.p. 60 to 80°). Subsequent recrystallizations are also carried out in this solvent. The pure compound melts at 156°. The yield is 8.25 g. (62.9%). *Anal.* Calcd. for $N_4P_4Cl_4S_4C_{24}H_{20}$: C, 38.0; H, 2.66; Cl, 18.7; S, 16.9. Found: C, 38.2; H, 2.8; Cl, 19.1; S, 17.0.

Properties

These mercapto derivatives are all either white crystalline solids or colorless liquids. They are insoluble in water and soluble in the usual organic solvents, and they appear to be quite stable to atmospheric hydrolysis. When pure, they do not decompose below 200°.

References

1. A. P. Carroll and R. A. Shaw: *Chem. Ind.* (*London*), **1962**, 1908.
2. N. Boden, J. W. Emsley, J. Feeney, and L. H. Sutcliffe: *ibid.*, **1962**, 1909.
3. R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith: *Chem. Rev.*, **62**, 247 (1962).

22. (TRICHLOROPHOSPHORANYLIDENE)-AMIDOPHOSPHORYL DICHLORIDE

[Trichlorophosphazophosphorus(V) Oxychloride]

$$2PCl_3 + PCl_5 + 2[H_3NOH]Cl \rightarrow Cl_3P{=}NP(O)Cl_2 + 4HCl + NH_4Cl + POCl_3$$

Submitted by Margot Becke-Goehring* and Ekkehard Fluck*
Checked by Piero Nannelli† and Therald Moeller†

The formation of (trichlorophosphoranylidene)amidophosphoryl dichloride, $Cl_3P{=}NP(O)Cl_2$, was first observed

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* University of Heidelberg, Heidelberg, Germany.
† University of Illinois, Urbana, Ill.

in 1960 in the reaction between phosphorus(V) chloride and hydroxylammonium salts.[1] The same compound is also formed by the reaction of the amides of phosphoric acid with phosphorus(V) chloride[2] or in the reaction of phosphorus(III) chloride with nitrogen(IV) oxide (dinitrogen tetroxide).[3,4] The method of preparation described below is a modified procedure of the reaction first mentioned and leads to a pure product in good yield.

Procedure

In a 2-l. three-necked flask provided with a stirring apparatus, a thermometer, and a reflux condenser fitted with a calcium chloride tube is placed 139 g. (2 mols) of finely powdered hydroxylammonium chloride, $[H_3NOH]Cl$, that has been dried over calcium chloride for 12 hours. To the flask are added 275 g. (2 mols) of phosphorus(III) chloride, 208 g. (1 mol) of phosphorus(V) chloride, and 1700 g. of *sym*-tetrachloroethane. Before use, technical-grade tetrachloroethane is dried and purified by distillation over potassium carbonate at 47° and 12 mm. Hg.

The reaction mixture is stirred and heated to 100° for 4 hours. After the reaction is complete, the ammonium chloride formed is separated from the other reaction products in solution by suction filtration through a sintered-glass plate, care being taken to exclude moisture.

Tetrachloroethane and phosphorus(V) oxychloride, $POCl_3$, are distilled off together at 47° and 12 mm. Hg. The residue is a yellow oil, which may be purified by distillation *in vacuo* at 102° and 1.0 mm. The condenser of the distillation apparatus should be air-cooled rather than water-cooled; indeed, it may even need to be warmed gently with an infrared lamp to prevent premature solidification of the product. The yield of $Cl_3P{=}NP(O)Cl_2$ is about 150 g. (55%). *Anal.* Calcd. for P_2NOCl_5: P, 23.01; N, 5.20; Cl, 65.84. Found: P, 23.5; N, 5.08; Cl, 65.3. By checkers: N, 5.20; Cl, 65.70.

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Properties

The compound consists of colorless crystals which melt at 35.7°. A supercooled melt shows a refractive index $n_D^{25} = 1.5313$. The compound is very sensitive toward hydrolysis. It is readily soluble in benzene, nitrobenzene, and tetrachloroethane.

References

1. E. J. Kahler: U.S. patent 2,925,320 (Feb. 16, 1960); cf. *C.A.*, **54**, 17820b (1960).
2. M. Becke-Goehring, T. Mann, and H. D. Euler: *Chem. Ber.*, **94**, 193 (1961).
3. M. Becke-Goehring, A. Debo, E. Fluck, and W. Goetze: *ibid.*, 1383 (1961).
4. E. Fluck: *ibid.*, 1388 (1961).

23. TRICHLORO[(TRICHLOROPHOSPHORANYLIDENE)AMINO]PHOSPHORUS(V) HEXACHLOROPHOSPHATE

$[Cl_3P{=}N{-}PCl_3][PCl_6]$

Submitted by Margot Becke-Goehring* and Ekkehard Fluck*
Checked by Morris L. Nielsen†

The compound P_3NCl_{12} is easily formed in the reaction between phosphorus(V) chloride and ammonium chloride[1] (Procedure A). It can also be obtained readily by the reaction of phosphorus(V) chloride with hydroxylammonium chloride to produce P_2NCl_7, which subsequently is treated with additional phosphorus(V) chloride to obtain the product[2] (Procedure B).

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* University of Heidelberg, Heidelberg, Germany.
† Monsanto Research Corporation, Dayton, Ohio.

Both methods described below lead to a product of high purity in good yield, but Procedure A is preferred from the standpoint of simplicity.

Procedure A

$$3PCl_5 + NH_4Cl \rightarrow [Cl_3P{=}N{-}PCl_3][PCl_6] + 4HCl$$

NOTE: Water must be carefully excluded throughout the procedure. The product may be conveniently handled and transferred in a polyethylene bag filled with dry nitrogen.

In a 1-l. three-necked flask fitted with a reflux condenser, a stirring apparatus, and gas inlet and outlet tubes 208 g. (1.0 mol) of PCl_5 and 17.8 g. (0.33 mol) of ammonium chloride are suspended in a solution made by mixing 200 ml. of pure, dry *sym*-tetrachloroethane with 150 ml. of pure dry nitrobenzene. The reaction mixture is heated in a bath at 80°, and vacuum is applied until the liquid just begins to boil. During this operation, a stream of dry air is drawn through the reaction mixture in order to remove the hydrogen chloride that is evolved. After about 5 hours, most of the phosphorus(V) chloride should be consumed. The reaction flask is then brought to atmospheric pressure and heated briefly to 140°, and the mixture is then filtered through a warm fritted filter. The filtrate is allowed to cool, whereupon the product, P_3NCl_{12}, separates as needles. These crystals are separated from the mother liquor by filtration. A further fraction of P_3NCl_{12} can be obtained by concentrating the mother liquor and filtering again. Yield, 140 to 150 g. (80 to 85%). The substance can be purified by recrystallization from tetrachloroethane or by sublimation at about 150° and 15 mm Hg. *Anal.* Calcd. for P_3NCl_{12}: P, 17.45; N, 2.63; Cl, 79.92. Found: P, 17.85; N, 2.60; Cl, 79.10. The product is further identified by its nuclear magnetic resonance spectrum.[3]

Procedure B

$$[H_3NOH]Cl + PCl_5 \rightarrow Cl_3P{=}NOH + 3HCl$$
$$Cl_3P{=}NOH + PCl_5 \rightarrow Cl_3P{=}N{-}Cl + HCl + POCl_3$$
$$Cl_3P{=}N{-}Cl + PCl_5 \rightarrow [Cl_3P{=}N{-}PCl_3]Cl + Cl_2$$
$$P_2NCl_7 + PCl_5 \rightarrow P_3NCl_{12}$$

See note at beginning of Procedure A.

Three hundred twelve grams (1.5 mols) of phosphorus(V) chloride and 110 g. (1.58 mols) of hydroxylammonium chloride (which has been pulverized and dried over calcium chloride) are suspended in 1700 ml. of dry *sym*-tetrachloroethane in a 3-l. three-necked flask fitted with a reflux condenser, a stirring apparatus, and a thermometer. A calcium chloride drying tube (2.5 cm. in diameter and 50 cm. in length) is connected to the reflux condenser.

The reaction mixture is heated to 100° by means of a heating mantle within a period of 15 minutes. The evolution of hydrogen chloride and chlorine begins during this operation. As soon as the temperature has reached 100°, the heating mantle is removed and replaced with a water bath at 50°, and the reaction mixture is held at 50° for 2 hours. The mixture is then filtered through a fritted filter, and the filtrate is concentrated to a volume of about 200 ml. by vacuum distillation at a temperature below 47°. The colorless crystals which separate during concentration of the tetrachloroethane solution are filtered in vacuum and are then washed, first with absolute benzene and then with the fraction of petroleum ether boiling at 40 to 60°. Adhering traces of solvent are removed under vacuum. The yield is 63 g. (25.6%) of $P_2NCl_7 \cdot C_2H_2Cl_4$. *Anal.* Calcd. for $P_2NCl_7 \cdot C_2H_2Cl_4$: P, 12.59; N, 2.85; Cl, 79.27. Found: P, 13.0; N, 2.85; Cl, 78.7. The mother liquor consists practically only of P_2NOCl_5 and can be distilled nearly to completion under vacuum at 102° and 1.0 mm. Hg to produce 37. g. of P_2NOCl_5 (see Properties). These products can be identified by their nuclear magnetic resonance spectra.[3]

Sixty-three grams (0.128 mol) of $P_2NCl_7 \cdot C_2H_2Cl_4$ is heated together with 26.7 g. (0.128 mol) of phosphorus(V) chloride in 1700 ml. of tetrachloroethane with stirring until the liquid boils and all solid material has dissolved. The liquid is allowed to cool, whereupon P_3NCl_{12} crystallizes as needles. The yield is 60 g. (83%). *Anal.* Calcd. for P_3NCl_{12}: P, 17.45; N, 2.63; Cl, 79.92. Found: P, 17.0; N, 2.60; Cl, 79.8.

Properties

Trichloro[(trichlorophosphoranylidene)amino]phosphorus hexachlorophosphate is exceptionally sensitive toward hydrolysis. In all operations with this substance, care must be taken to exclude water. The melting point is 310 to 315°.

Both P_3NCl_{12} and $P_2NCl_7 \cdot C_2H_2Cl_4$ react with sulfur dioxide to form P_2NOCl_5 by the following reactions:

$$P_3NCl_{12} + 2SO_2 \rightarrow P_2NOCl_5 + 2SOCl_2 + POCl_3$$
$$P_2NCl_7 \cdot C_2H_2Cl_4 + SO_2 \rightarrow P_2NOCl_5 + SOCl_2 + C_2H_2Cl_4$$

The nuclear magnetic resonance spectrum of a tetrachloroethane solution of P_3NCl_{12} has two peaks at −21.4 and +305.0 p.p.m. (with respect to 85% H_3PO_4) with an intensity ratio of 2:1.[4]

References

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2. M. Becke-Goehring, W. Gehrmann, and W. Goetze: *Z. Anorg. u. Allgem. Chem.*, **326**, 127 (1963).
3. M. Becke-Goehring and E. Fluck: *Angew. Chem., Intern. Ed. Engl.*, **1**, 281 (1962).
4. E. Fluck: *Z. Anorg. u. Allgem. Chem.*, **315**, 181 (1962).

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CHAPTER VIA

See also: Bis(4-imino-2-pentanonato)copper(II) and bis(3-phenylimino-1-phenyl-1-butanonato)copper(II), synthesis 1
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24. HEXAATOMIC SULFUR

$$Na_2S_2O_3 + 2HCl \rightarrow [H_2S_2O_3] + 2NaCl$$
$$6[H_2S_2O_3] \rightarrow S_6 + 6SO_2 + 6H_2O$$

Submitted by Paul D. Bartlett* and William R. Roderick†
Checked by William C. Andersen‡

Hexaatomic sulfur, first isolated in 1891,[1] has been prepared only by the acidification of aqueous solutions of thiosulfates.[1,2] The unstable thiosulfuric acid so generated decomposes to numerous products depending on the concentrations of the reactants and on the temperature.[3–6] Anhydrous solutions of thiosulfuric acid in ether are stable at −78°; at 25° they decompose to hydrogen sulfide and sulfur trioxide.[7] There is evidence for the presence of S_6 in the gas phase of sulfur.[8]

The yield of S_6 is low, being about 4% following the original procedures[1,2] and about 12 to 15% with the procedure described herein. The yield of S_6 has been found to be maximal when the extraction is carried out as the reaction mixture warms to room temperature; later extraction gives less S_6. The yield of S_6 is about the same when acidification occurs at 0°, but the extract appears to contain more S_8 than is obtained at −15°.

Procedure

Two hundred milliliters (2.4 mols) of 12 *N* hydrochloric acid is placed in a 500-ml. three-necked round-bottomed flask fitted with a dropping funnel containing 50 ml. (approximately 0.2 mol) of saturated aqueous sodium thiosulfate (prepared and used at room temperature), an all-

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glass mechanical stirrer, and a thermometer well. The flask is immersed in an ice-methanol bath, and stirring is begun. When the temperature of the acid is −15°, the thiosulfate solution is added rapidly in a total period of approximately 2 minutes. The mixture is stirred for one minute after addition is complete and then is filtered rapidly by suction into a flask cooled in an ice bath.

The clear colorless filtrate is returned to the original reaction flask, after removing the flask from the ice-methanol bath and rinsing with water. Toluene (100 ml.) is added, and the mixture is stirred vigorously for 40 minutes, during which the mixture warms to room temperature and both phases become yellow. After separation of the phases, the toluene extract is dried over magnesium sulfate and refrigerated overnight at −25° to obtain orange-yellow crystals of hexaatomic sulfur in a yield of 700 to 870 mg. (12 to 15%). The octaatomic and other forms of sulfur remain in solution, although occasionally some S_8 may also crystallize, in which case it can be separated manually. Hexaatomic sulfur is most readily identified by molecular weight determination. Freezing point depression measurements in purified benzene show 5.9 to 6.1 sulfur atoms per molecule.

For purification, the crystalline hexaatomic sulfur is dissolved in benzene (approx. 100 mg./l.); toluene is not suitable (see Properties). The benzene solution is extracted with a series of reagents, three or four extractions being made with each reagent except where otherwise indicated. (For 200 ml. of benzene solution, 50-ml. portions of reagent are used). The reagents are employed in the following order: (1) water, (2) 10% aqueous potassium triiodide, until the benzene phase remains colored from iodine, (3) 10% aqueous potassium iodide, (4) water, (5) 5% aqueous lead acetate, twice, (6) water, (7) 5% aqueous potassium hydroxide, once, (8) water. The purified solution is dried over magnesium sulfate and should be used immediately. The approximate concentration of S_6 can be determined spectrophotometrically at 300 mμ (ϵ = 181 l./g.-atom) after suitable dilution of the solution. The absorption curve is rather steep at 300 mμ (although almost linear in the range 280 to 340 mμ),[10] but the concentration can be determined to within ±10% in this manner.

Properties

Crystalline hexaatomic sulfur is orange-yellow in contrast to the lemon-yellow color of the octaatomic form. The crystals have a ragged triangular shape and become cloudy on the surface after a few hours' exposure to air, owing to polymerization. Hexaatomic sulfur has been characterized by determination of its molecular weight,[9] ultraviolet absorption spectrum,[9–11] and crystal structure.[12,13] The S_6 molecule exists as a puckered ring in the chair conformation, with a sulfur-to-sulfur bond length of 2.057 ± 0.018 A and a S–S–S bond angle of 102.2 ± 1.6°.[13]

Hexaatomic sulfur is converted to the more stable octaatomic sulfur by amines in the presence of hydrogen sulfide and/or sulfur dioxide. This reaction has been shown to proceed by way of a polymerization and depolymerization, with the actual catalysts for the conversion being the SH^- and HSO_3^- ions formed by the reaction of the amine with the hydrogen sulfide and/or sulfur dioxide present in the impure S_6.[10,11] The purification procedure given herein is designed to remove these two impurities.[11] Previously employed methods of purification give samples of S_6 which react rapidly and which vary in their rates of polymerization by factors as great as 3000.[10] When solutions of hexaatomic sulfur in benzene are purified as described above and then treated with triethylamine in the absence of oxygen, there is no polymerization for a period ranging from 4000 to 10,000 seconds, following which a slow reaction occurs; purified solutions in toluene show no induction period and undergo rapid polymerization.

Although the purified S_6 can be preserved with only a slight polymerization occurring on standing (in the absence

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of oxygen), the rate of conversion to S_8 on addition of amine increases with age of the sample, indicating formation of sulfur dioxide and/or hydrogen sulfide, which have powerful catalytic effects on the polymerization effected by amines. Hence only freshly purified solutions of S_6 should be employed for studies of chemical properties.

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25. HEPTASULFUR IMIDE

$$S_2Cl_2 \rightarrow S + SCl_2$$
$$S_2Cl_2 + 5S + 3NH_3 \rightarrow S_7NH + 2NH_4Cl^*$$

SUBMITTED BY MARGOT BECKE-GOEHRING† AND EKKEHARD FLUCK†
CHECKED BY AMEDEO FAILLI‡ AND THERALD MOELLER‡

Heptasulfur imide is formed by the reaction of disulfur dichloride with ammonia,[1] the chief by-products being

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* This is a simplified equation. The reaction is complex and leads to several by-products, including sulfur, tetrasulfur tetranitride, and sometimes hexasulfur diimide, $S_6(NH)_2$.

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sulfur (S_8) and tetrasulfur tetranitride. Tetrasulfur tetranitride is difficult to separate from heptasulfur imide; the formation of the former can be suppressed by employing a large excess of ammonia, which binds the tetrasulfur tetranitride as the diammoniate. The latter compound can be destroyed immediately with water.

Procedure

The reaction vessel consists of a 2-l. three-necked flask provided with a stirring apparatus, a gas inlet tube which protrudes almost to the bottom of the flask, and a gas outlet tube which encloses a thermometer extending into the reaction mixture. The outlet tube is connected to a drying tube filled with potassium hydroxide. One liter of *N,N*-dimethylformamide is placed in the flask. This is cooled with an ice-salt mixture, and a very rapid stream of dried ammonia is passed into the vigorously stirred liquid. When the solution has become saturated with ammonia and the temperature has dropped to −5°, a 5-ml. sample of disulfur dichloride is introduced through the gas inlet tube opening with the aid of a syringe pipet. During this manipulation, the stream of ammonia is not interrupted. Upon the addition of disulfur dichloride the temperature of the reaction mixture rises rapidly. The contents of the flask are allowed to cool again to −5°, and a second 5-ml. portion of disulfur dichloride is added. The process is repeated several times. After 100 ml. (1.2 mols) of disulfur dichloride has been introduced in this way, the ammonia stream is maintained for an additional 15 minutes and then shut off. The reaction mixture is allowed to stand for one hour at −5°, and then it is poured into 3 l. of 1% hydrochloric acid, which has previously been cooled to 0°, and mixed with pieces of ice. The mixture is stirred and is neutralized with 10% hydrochloric acid. The reaction product, which consists of sulfur and heptasulfur imide, is allowed to stand. Settling is complete after 2 to 3 hours. The clear liquid is decanted, and the residue is washed with water on a Büchner funnel; it is

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then dried in a desiccator over calcium chloride. The crude product is shaken mechanically with 250 ml. of tetrahydrofuran for 30 minutes and filtered through a fluted filter paper. The tetrahydrofuran in the filtrate is evaporated by means of a water-aspirator vacuum, and the residue is dissolved in hot methanol. Upon cooling, part of the heptasulfur imide crystallizes out of the methanol solution. A further quantity can be obtained by evaporation of the mother liquor. Yield, 16 to 20 g. (32 to 40%). *Anal.* Calcd. for S_7NH: S, 93.72; N, 5.86. Found: S, 93.7; N, 5.8. By checkers: S, 93.57; N, 5.69.

Properties

The compound appears as large yellow crystals, m.p. 111°. With sodium hydroxide in alcohol an intense violet coloration is produced. With formaldehyde and sodium hydroxide in aqueous solution S_7NCH_2OH (m.p. 110.5°) is formed. With acetyl chloride in chloroform in the presence of pyridine reaction occurs at 0° with the formation of yellow needles of S_7NCOCH_3 (m.p. 104.4°).[2]

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26. IMIDODISULFURIC ACID CHLORIDE

$$2PCl_5 + H_2NSO_3H \rightarrow Cl_3P{=}NSO_2Cl + POCl_3 + 3HCl$$
$$Cl_3P{=}NSO_2Cl + ClSO_3H \rightarrow HN(SO_2Cl)_2 + POCl_3$$

Submitted by Margot Becke-Goehring* and Ekkehard Fluck*
Checked by Amedeo Failli† and Therald Moeller†

Imidodisulfuric acid, $HOSO_2NHSO_2OH$, is not stable in the free state, although its salts are well known. Surpris-

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ingly, the acid chloride, $ClSO_2NHSO_2Cl$, can be prepared easily. It is a colorless crystalline material which can be distilled in a vacuum without decomposition. The first step in the synthesis consists of the reaction of sulfamic acid (amidosulfuric acid), $H_2N—SO_3H$, with phosphorus(V) chloride.[1] In the next step, the trichlorophosphazosulfuric acid chloride (trichlorophosphoranylidenesulfamoyl chloride), $Cl_3P{=}NSO_2Cl$, thus formed reacts with chlorosulfuric acid (chlorosulfonic acid), $ClSO_3H$, to form imidodisulfuric acid chloride in good yield.[2]

Procedure

NOTE: It may be necessary, especially in humid climates, to handle and transfer the reagents in a dry-box or a polyethylene bag.

In a 1.5-l. reaction flask provided with a reflux condenser and a drying tube filled with calcium chloride are placed 97 g. (1 mol) of dry pulverized sulfamic acid and 417 g. (2 mols) of dry pulverized phosphorus(V) chloride. The reactants are thoroughly mixed, and the flask is immersed in a steam bath. After about 20 minutes, hydrogen chloride gas begins to be evolved, and after a minimum of about 35 minutes the reaction mixture becomes liquid.* Evolution of gas continues for at least 45 minutes;* when it has ceased, the flask is evacuated to a pressure of 20 mm. Hg and the phosphorus oxychloride (phosphoryl chloride), $POCl_3$, formed during the reaction is distilled from the mixture at a bath temperature of 80°.

The oily residue, which consists essentially of trichlorophosphazosulfuric acid chloride, is transferred to a dry-box and is mixed carefully with 125 g. (1.1 mols) of technical-grade chlorosulfuric acid (a mol ratio of about 1 to 1.1

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* The checkers found that it took 2 hours for the reaction mixture to become completely liquid and more than 5 hours for the reaction to be completed.

should be used). (*Caution. The reaction is very exothermic!*) The reaction vessel is provided with a capillary which permits the introduction of dry nitrogen into the flask. The reflux condenser is connected through a phosphorus(V) oxide drying tube (2.5-cm. diameter, 100-cm. length) and a trap to a water aspirator. The flask is then heated to a temperature of 80° for a period of 8 hours, during which time the system is kept evacuated by means of the water aspirator, and a slow stream of nitrogen is swept through the apparatus. At the end of the reaction period, unchanged chlorosulfuric acid is removed by raising the bath temperature to 120° while maintaining the aspirator vacuum. The residual oil is transferred to a smaller flask, and the reaction product is distilled at a pressure of about 0.03 mm. using a bath heated to 80 to 120°. During this distillation, the condenser should be air-cooled rather than water-cooled. The yield of imidodisulfuric acid chloride is 155 to 170 g. (72 to 80%). *Anal.* Calcd. for $HNS_2O_4Cl_2$: H, 0.47; N, 6.54; S, 29.96; Cl, 33.13. Found: H, 0.6; N, 6.56; S, 30.1; Cl, 33.4. By checkers: N, 6.26; Cl, 32.88.

Properties

Imidodisulfuric acid chloride forms colorless crystals which hydrolyze very rapidly in moist air; they melt at 37°, boil at 115°/4 mm. and at 55°/0.03 mm., and have a refractive index $n_D^{25} = 1.4948$. The compound is readily soluble in organic solvents such as benzene or nitrobenzene. Hydrolysis in alkaline medium leads to imidodisulfate; in acidic medium, sulfamic acid and sulfuric acid are formed.

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27. DIALKYLSULFAMOYL CHLORIDES

$$R_2NH_2Cl + SO_2Cl_2 \rightarrow R_2NSO_2Cl + 2HCl$$

Submitted by Antonio Vandi* and Therald Moeller*
Checked by Elmer Schlemper,† Henry Grote,† and Doyle Britton†

Of the various possible types of *N*-substituted sulfamoyl (sulfamyl) chlorides,[1] the dialkyl compounds are of particular interest because they serve as intermediates in the syntheses of substituted sulfamides (synthesis 28) and of certain of their derivatives (synthesis 29). The dialkylsulfamoyl chlorides have been prepared by the reaction of sulfuryl chloride with an appropriate amine or its hydrochloride,[2-5] by the treatment of secondary *N*-chloroamines with liquid sulfur dioxide,[6] and by the reaction of dialkylaminosulfinic acids with chlorine in carbon tetrachloride.[6] Although either of the first two procedures can be recommended in terms of convenience and yield, the availability of starting materials normally dictates that the first be used. It is of interest that treatment of sulfuryl chloride with either ammonia or ammonium chloride in terms of this procedure does not give the parent sulfamoyl chloride, H_2NSO_2Cl. This compound is obtained in an altogether different way.[7]

Dimethyl- and diethylsulfamoyl chlorides are prepared by heating the corresponding amine hydrochlorides with excess sulfuryl chloride over a steam bath and distilling *in vacuo*. However, the sulfamoyl chlorides of higher-molecular-weight amines are better prepared from the amines themselves, either in the presence or absence of inert solvent and at lower temperatures. The corresponding compounds containing acyl substituents are obtained

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from alkali metal salts of the amides.[8,9] The two procedures given are typical.

Procedure

A. DIMETHYLSULFAMOYL CHLORIDE

Eighty-two grams (1.0 mol) of dimethylamine hydrochloride and 270 g. (2.0 mols) of sulfuryl chloride are mixed in a 500-ml. one-necked flask fitted with a reflux condenser to which a phosphorus(V) oxide drying tube is attached. The flask and its contents are warmed gently until hydrogen chloride gas is evolved rapidly and refluxing begins. Refluxing is continued for some 20 hours, after which time evolution of hydrogen chloride ceases. The refluxing should not be left unattended, because the quantity of heat required decreases as the reaction proceeds. The mixture is then cooled to 0° and treated carefully with a 10% aqueous solution of sodium carbonate to decompose unreacted sulfuryl chloride. The oily layer is separated from the aqueous layer by means of a separatory funnel and washed three times with 200-ml. portions of 10% aqueous sodium carbonate solution. The remaining oil is then extracted with 500-ml. of diethyl ether. The ethereal solution is dried over solid calcium chloride for 24 hours, and the ether is removed *in vacuo* at room temperature. The oily product is purified by fractional vacuum distillation. The yield is 114.0 g. (80%). *Anal.* Calcd. for $C_2H_6ClNO_2S$: C, 16.74; H, 4.21; N, 9.76. Found: C, 16.75; H, 4.20; N, 9.76.

B. 4-MORPHOLINESULFONYL CHLORIDE

Sixty-seven and five-tenths grams (0.5 mol) of sulfuryl chloride is placed in a 500-ml. three-necked flask equipped with a mechanical stirrer,* a reflux condenser with an attached phosphorus(V) oxide drying tube, and a dropping

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* Inasmuch as a large amount of solid is formed, a magnetic stirrer is not a satisfactory substitute.

funnel. The flask is surrounded by an ice-salt bath at approximately −10°. Forty-three and six-tenths grams (0.5 mol) of morpholine is then added dropwise at such a rate that the temperature is maintained at −10 ± 3 to 4°. This amounts to a rate of approximately one drop every 10 seconds, the total addition taking about 2 hours. After addition of the amine is complete, another 67.5 g. (0.5 mol) of sulfuryl chloride is added, and the mixture is cooled to 0° and treated carefully with an aqueous sodium carbonate solution to decompose unreacted sulfuryl chloride. The oily layer is removed by means of a separatory funnel and washed with three 200-ml. portions of 10% aqueous sodium carbonate solution. After the last washing, the product is dissolved in toluene and the solution is dried over solid calcium chloride for 24 hours. After removal of the toluene by evaporation *in vacuo*, the product is purified by fractional vacuum distillation. The yield is 50 g. (54%).[*] *Anal.* Calcd. for $C_4H_8NO_3SCl$: C, 25.88; H, 4.34; N, 7.54. Found: C, 25.99; H, 4.46; N, 7.50.

TABLE I. PROPERTIES OF DIALKYLSULFAMOYL CHLORIDES

Compound	M.p.,[*] °C.	B.p.,[*] °C./mm.Hg	n_D^t
Dimethylsulfamoyl chloride		42/0.6	1.4533^{24}
Diethylsulfamoyl chloride		62/0.02	
Di-*n*-propylsulfamoyl chloride		77/1.5	1.4560^{25}
Di-*n*-butylsulfamoyl chloride		93/1.0	1.4590^{26}
Pentamethylenesulfamoyl chloride		95/1.0	
4-Morpholinesulfonyl chloride		76/0.3	1.4910^{30}
Dicyclohexylsulfamoyl chloride	117–119		

[*] Uncorrected.

Properties

Physical properties of some typical dialkylsulfamoyl chlorides are summarized in Table I. These compounds are

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[*] Lower yields, of the order of 25%, are often obtained first; higher yields may be expected with experience.

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insoluble in water and only slowly hydrolyzed. Hydrolysis is rapid, however, in the presence of alkali. They are uniformly soluble in organic solvents. They are readily converted by ammonia, primary amines, and secondary amines to compounds of the types $R_2NSO_2NH_2$, R_2NSO_2NHR', and $R_2NSO_2NR_2$, respectively (synthesis 28).

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28. *N*- AND *N,N′*-SUBSTITUTED SULFAMIDES

$$R_2NSO_2Cl + 2NH_3 \rightarrow R_2NSO_2NH_2 + NH_4Cl$$
$$R_2NSO_2Cl + 2RNH_2 \rightarrow R_2NSO_2NHR + RNH_3Cl$$
$$R_2NSO_2Cl + 2R_2NH \rightarrow R_2NSO_2NR_2 + R_2NH_2Cl$$

Submitted by Antonio Vandi* and Therald Moeller*
Checked by Elmer Schlemper† and Doyle Britton†

Dialkylsulfamoyl chlorides, R_2NSO_2Cl, have been prepared by the reaction of sulfuryl chloride with the appropriate amine hydrochloride[1,2] (synthesis 27), by the treatment of dialkylaminosulfinic (dialkylamidosulfurous) acids with

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chlorine in carbon tetrachloride,[3] and by the careful addition of amines to an excess of sulfuryl chloride followed by refluxing.[4,5] The dialkylsulfamoyl chlorides are particularly useful in the synthesis of *N*- and *N,N'*-substituted sulfamides since, contrary perhaps to expectation, the direct formation of the latter by the aminolysis of sulfuryl chloride is difficult to control and leads to polymeric products.[6] Reactions of the dialkylsulfamoyl chlorides with ammonia, primary amines, or secondary amines are the bases of the most convenient of the known procedures for preparing, respectively, substances of the types $R_2NSO_2NH_2$, R_2NSO_2NHR, and $R_2NSO_2NR_2$.[7]

These products are obtained in good yields either by treating the sulfamoyl chloride with liquid ammonia or by refluxing it with the appropriate amine in an inert solvent such as chloroform, benzene, or diethyl ether. Reactions with aliphatic amines are usually complete in 12 hours; those with aromatic amines require up to 24 hours. Two typical procedures are given.

The method of synthesis described herein is the best procedure for preparing unsymmetrically substituted sulfamides, but it can be applied also to the symmetrically substituted ones. However, it may be a longer procedure for the latter, although the yields obtained will be consistently higher than those obtained by either direct aminolysis of sulfuryl chloride or deamination of sulfamide. The direct aminolysis of sulfuryl chloride does not work well with aromatic amines, for which ring chlorination is a complication.

Procedure

A. *N,N*-Di-*n*-PROPYLSULFAMIDE

A 500-ml. three-necked flask, equipped with a mechanical stirrer, a dropping funnel, and a reflux condenser with a drying tube filled with potassium hydroxide, is cooled to about −70° in a Dry Ice–acetone bath. Some 300 ml. of liquid ammonia is then condensed into the flask at −70°, and 60 g. (0.33 mol) of di-*n*-propylsulfamoyl chloride[4,5] (synthesis 27) is added from the dropping funnel in small portions and with vigorous stirring.* Stirring is continued at −70° for 6 hours after addition of the chloride is complete. The flask is then allowed to warm to room temperature to remove unreacted ammonia and recooled to −70°. An additional 200 ml. of ammonia is condensed into the flask to complete the reaction, and the flask is rewarmed to room temperature.† The residue in the flask is extracted with three 50-ml. portions of diethyl ether to separate the product from ammonium chloride.‡ The solid obtained upon evaporation of the ether is recrystallized from *n*-heptane (petroleum ether C, b.p. 90 to 100°, is an acceptable substitute) to a white crystalline solid melting at 69°. The yield is 44.0 g. (85%).

B. *N,N*-PENTAMETHYLENE-4-MORPHOLINESULFONAMIDE

[4-(Piperidinosulfonyl)morpholine]

Eight and seventy-one hundredths grams of morpholine (0.1 mol), dissolved in 50 ml. of anhydrous benzene, is placed in a 250-ml. three-necked flask equipped with a mechanical stirrer, a dropping funnel, and a reflux condenser fitted with a drying tube containing calcium chloride. *N,N*-Pentamethylenesulfamoyl chloride (9.18 g.; 0.05 mol) (synthesis 27) dissolved in 50 ml. of anhydrous benzene is added at room temperature in small portions and with stirring. The reaction mixture is then heated for 12 hours with gentle refluxing. The amine hydrochloride formed is

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* Ammonolysis proceeds only when the pure compounds are mixed, and not in the presence of a diluent.

† The second treatment with ammonia improves the yield but is otherwise not necessary. It can be omitted if time is more important than yield.

‡ The di-*n*-propyl, diethyl, dimethyl, and di-*n*-butyl derivatives are all very soluble in cold water. The less soluble morpholine and piperidine derivatives can be freed from ammonium chloride by washing with water.

TABLE I. PROPERTIES AND ANALYSES OF *N*-SUBSTITUTED SULFAMIDES

Compound	Yield, %	M.P.,* °C.	B.P.,* °C./mm. Hg	n_D^t	Carbon		Hydrogen		Nitrogen	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
N,N-Dimethylsulfamide	80	98			19.36	19.38	6.49	6.47	22.58	22.63
N,N-Diethylsulfamide	82	46			31.57	31.49	7.95	7.72	18.41	18.49
N,N-Di-*n*-propylsulfamide	85	69			39.99	40.10	8.95	8.95	15.55	15.50
N,N-Di-*n*-butylsulfamide	87	70			46.15	45.91	9.68	9.83	13.46	13.71
N,N-Pentamethylenesulfamide	73	120			36.57	36.82	7.36	7.31	17.06	16.88
4-Morpholinesulfonamide	60	160–162			28.92	29.05	6.06	5.80	16.86	17.06
N,N-Diethyl-*N'*-cyclohexylsulfamide	60	49			51.28	51.00	9.47	9.40	11.95	11.85
N,N-Diethyl-*N',N'*-di-*n*-butylsulfamide	65		88/0.15	1.4500^{25}	54.53	54.35	10.68	10.65	10.60	10.75
N,N-Diethyl-*N'*-phenylsulfamide	61	31	171/2.5†	1.5260^{26}	52.64	52.48	7.06	7.11	12.28	11.95
N,N-Pentamethylene-*N'*-cyclohexylsulfamide	65	75			53.64	53.62	9.00	8.99	11.37	11.26
N,N-Pentamethylene-*N'*-*m*-tolylsulfamide	70	123–124			56.67	56.83	7.13	7.15	11.02	10.74
N,N-Pentamethylene-*N'*-*o*-tolylsulfamide	62	94			56.67	56.87	7.13	7.11	11.02	10.74
N,N-Pentamethylene-*N'*-*p*-tolylsulfamide	55	97–98			56.67	56.91	7.13	7.20	11.02	10.94
N,N-Pentamethylene-4-morpholinesulfonamide	81	71–72			46.14	46.27	7.74	7.70	11.96	11.93
N,N,N',N'-Dipentamethylenesulfamide (*N,N'*-sulfonyldipiperidine)	77	92–93			51.69	51.60	8.68	8.75	12.06	11.27

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* Melting points and boiling points are uncorrected.

† The checkers recommend distillation at the lowest possible pressure.

removed by filtration and washed several times with benzene. The combined filtrate and washings are freed of solvent by distillation under vacuum. The resulting brown residue is purified by recrystallization from 100 ml. of *n*-heptane (or 150 ml. of petroleum ether C) to a white crystalline product melting at 71 to 72°. The yield is 9.5 g. (81%).

Properties

Analytical, melting point, boiling point, and refractive index data, together with yields, for a series of compounds prepared by procedures of these types are given in Table I. The *N*,*N*-disubstituted sulfamides are white crystalline compounds that dissolve readily in water and many organic solvents. The tri- and tetrasubstituted compounds are either white crystalline solids or colorless oils that dissolve in the common organic solvents but not in cold water. They are only slightly soluble in boiling water.

Recrystallization is best effected from *n*-heptane, carbon tetrachloride, or diethyl ether. The fact that many amines yield sharply melting derivatives with the sulfamoyl chlorides suggests that the latter may be useful in characterizing the former.

The crystal structure of tetramethylsulfamide is consistent with participation of *d* orbitals in sulfur-nitrogen bonding.[8] Data on bond angles and bond lengths significant to this structure are ∠SNC, 119° (av.); ∠CNC, 112.9° (av.); ∠OSO, 119.7°; S–O, 1.445 A. (av.); S–N, 1.623 A.; N–C, 1.476. A. (av.)

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29. DIALKYLAMIDES OF (TRICHLOROPHOSPHORANYLIDENE)SULFAMIC ACID

[*N*,*N*-Dialkyl-*N*′-(trichlorophosphoranylidene)sulfamides; Dialkylamino Trichlorophosphazo Sulfones]

$$R_2NSO_2NH_2 + PCl_5 \rightarrow R_2NSO_2N{=}PCl_3 + 2HCl$$

SUBMITTED BY ANTONIO VANDI* AND THERALD MOELLER*
CHECKED BY SHERMAN THOMAS† AND DOYLE BRITTON†

N,*N*-Dialkylsulfamides, like sulfamide (synthesis 30), react with phosphorus(V) chloride to give the corresponding *N*-trichlorophosphoranylidene derivatives (phosphazo chlorides).[1,2] The reactions are carried out by mixing the reactants in an inert solvent. If the reactants are pure and moisture is excluded, the products are obtained pure and in almost quantitative yields. The synthesis of *N*-(trichlorophosphoranylidene)-4-morpholinesulfonamide is described as typical. The same general procedure is applicable to the preparation of corresponding dialkyl compounds.

Procedure

Eight and three-tenths grams (0.05 mol) of 4-morpholinesulfonamide,‡ 10.4 g. (0.05 mol) of dry pulverized phosphorus(V) chloride, and 50 ml. of dry carbon tetrachloride are placed in a 250-ml. round-bottomed flask fitted with a

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‡ 4-Morpholinesulfonamide is obtained by ammonolysis of the corresponding sulfamoyl chloride (synthesis 28).

reflux condenser carrying a phosphorus(V) oxide drying tube.* The mixture is heated slowly on a steam bath for approximately 5 hours, at the end of which time evolution of hydrogen chloride ceases and a clear solution is obtained. This solution is cooled to 0°. The white crystals that separate are removed by filtration in a dry-box, washed with cold carbon tetrachloride, and dried. The yield is 14.0 g. (93%). *Anal.* Calcd. for $C_4H_8N_2O_3SPCl_3$: C, 15.94; H, 2.67; N, 9.29. Found: C, 16.14; H, 2.76; N, 9.38.

Similarly, the diethyl derivative is obtained in 90% yield, the di-*n*-propyl derivative in 80% yield, and the di-*n*-butyl derivative in 80% yield (see Table I).

Properties

N-(Trichlorophosphoranylidene)-4-morpholinesulfonamide is a white crystalline hygroscopic substance that melts at 94°. It is fairly soluble in most organic solvents. It undergoes rapid hydrolysis in contact with water and is very reactive toward alcohols, amines, and organometallic compounds. When stored in a sealed glass tube, it is stable for a prolonged period.

Several of the dialkylamides of (trichlorophosphoranylidene)sulfamic acid are colorless oils which are obtained from the reaction mixture by evaporation of the solvent and purified by vacuum distillation. The latter is accompanied by some decomposition and a definite reduction in total yield. (*Caution. It is extremely important that air be kept out during the vacuum distillation. Otherwise, decomposition can be vigorous and extensive.*) The chlorine atoms in all of these compounds are highly susceptible to solvolytic attack.

Additional properties and analyses for several of the dialkylamides are summarized in Table I.

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* All weighing and handling operations must be carried out in a dry-box. In humid weather, a calcium chloride drying tube before the phosphorus(V) oxide is desirable.

TABLE I. PROPERTIES AND ANALYSES OF THE DIALKYLAMIDES OF (TRICHLOROPHOSPHORANYLIDENE)SULFAMIC ACID

Compound	Empirical formula	Yield, %	M.p.,* °C.	B.p.,* °C.	n_D^t	Carbon		Hydrogen		Nitrogen	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
N,*N*-Dimethyl-*N*′-(trichlorophosphoranylidene)sulfamide	$C_2H_6N_2O_2PSCl_3$	93	74			9.26	9.75	2.33	2.73	10.80	10.72
N,*N*-Diethyl-*N*′-(trichlorophosphoranylidene)sulfamide	$C_4H_{10}N_2O_2PSCl_3$	90		113/0.2	1.5072^{20}	16.71	16.63	3.50	3.41	9.74	9.91
N,*N*-Di-*n*-propyl-*N*′-(trichlorophosphoranylidene)sulfamide	$C_6H_{14}N_2O_2PSCl_3$	80		113/0.005	1.5010^{20}	22.83	22.99	4.47	4.41	8.87	8.97
N,*N*-Di-*n*-butyl-*N*′-(trichlorophosphoranylidene)sulfamide	$C_8H_{18}N_2O_2PSCl_3$	80		140/0.05	1.4952	27.96	27.75	5.28	5.33	8.15	8.31
N-(Trichlorophosphoranylidene)-4-morpholinesulfonamide	$C_4H_8N_2O_3PSCl_3$	93	94			15.94	16.14	2.67	2.76	9.29	9.38

* Melting points and boiling points are uncorrected.

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30. BIS(TRICHLOROPHOSPHORANYLIDENE)-SULFAMIDE

[Bis(trichlorophosphazo) Sulfone]

$$H_2NSO_2NH_2 + 2PCl_5 \rightarrow Cl_3P{=}NSO_2N{=}PCl_3 + 4HCl$$

Submitted by Antonio Vandi* and Therald Moeller*
Checked by Henry Grote,† George Grimm,† and Doyle Britton†

The syntheses of *N*-trichlorophosphoranylidene derivatives (phosphazo chlorides) by the reaction of phosphorus(V) chloride with acid amides were first described by Kirsanov.[1] When sulfamide is used, bis(trichlorophosphoranylidene)-sulfamide is obtained in nearly quantitative yield.[1,2] The synthesis is effected by causing sulfamide and phosphorus(V) chloride to react in stoichiometric proportions at a controlled temperature and in the absence of a solvent. Better results are obtained, however, if the phosphorus(V) chloride is present in slight excess. If pure starting materials are used, pure bis(trichlorophosphoranylidene)sulfamide is obtained directly from the reaction mixture as a colorless viscous oil that solidifies slowly when cooled to 0°.

Procedure

Caution. Water must be rigorously excluded during all handling or transfer operations. Filtration requires sintered-

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glass apparatus, inasmuch as filter paper is ignited by the product.

Eight grams (0.0832 mol) of dry sulfamide* and 35.2 g. (0.169 mol) of dry, pulverized phosphorus(V) chloride are placed in a dry 250-ml. one-necked flask equipped with a reflux condenser provided with a phosphorus(V) oxide drying tube.† Slow evolution of hydrogen chloride is noted upon mixing the reactants. The mixture is then warmed to 50 to 60° by means of an oil bath and maintained in this temperature range for 6 hours. The reaction is completed by heating at 90° for an additional 3 hours. The reaction ends when evolution of hydrogen chloride ceases and the mixture in the flask turns to a viscous transparent oil. A vacuum of 20 mm. is then applied to the top of the condenser, by means of a mechanical pump,‡ and the flask is heated in the bath at 130°§ for 2 hours at 10 mm. and for 30 minutes at 1 mm. to remove by sublimation unreacted phosphorus(V) chloride. The remaining viscous oil is chilled to 0°, at which temperature it solidifies to a white hard substance. The yield is 30.0 g. (98%). *Anal.* Calcd. for $N_2O_2P_2SCl_6$: N, 7.64; P, 16.90; S, 8.74; Cl, 58.01. Found: N, 7.70; P, 17.17; S, 9.40; Cl, 57.30.

Properties

Bis(trichlorophosphoranylidene)sulfamide is a white, crystalline, highly hygroscopic solid that melts at 40 to 41°. It is readily soluble in benzene, diethyl ether, or carbon tetrachloride, but insoluble in *n*-heptane or petroleum ether

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* Obtainable from General Chemical Company, Morristown, N.J.

† All operations involving grinding the phosphorus(V) chloride and weighing the reactants must be carried out in a dry-box. In addition, a calcium chloride drying tube to protect the phosphorus(V) oxide is desirable when the reaction is carried out in humid weather.

‡ Use of a water aspirator rather than a mechanical pump is discouraged because of the chance of accident. The product reacts with extreme violence when it comes in contact with water.

§ Because decomposition is rapid at higher temperatures, 130° should not be exceeded.

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(b.p. 90 to 110°). Heating with either of the last two solvents causes it to separate as an oily layer. Recrystallization by cooling a saturated solution in ether from room temperature to 0° yields large prisms, but only in 60% yield. Recrystallization always results in substantial losses. Fortunately, the procedure outlined gives the product in sufficient purity that, for most purposes, further purification is unnecessary.

Bis(trichlorophosphoranylidene)sulfamide is extremely reactive. Vigorous reaction occurs with water. Complete replacement of the chlorine atoms is effected by treating with alcohols, phenols, amines, and organometallic compounds.

Bis(trichlorophosphoranylidene)sulfamide is best preserved in sealed glass ampuls, although it can be stored in a vacuum desiccator over concentrated sulfuric acid or phosphorus(V) oxide.

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31. AMINOMETHANESULFONIC ACID

$$HCHO + NaHSO_3 \rightarrow HOCH_2SO_3Na$$
$$HOCH_2SO_3Na + NH_3 \rightarrow H_2NCH_2SO_3Na + H_2O$$
$$2H_2NCH_2SO_3Na + H_2SO_4 \rightarrow 2H_2NCH_2SO_3H + Na_2SO_4$$

Submitted by G. Schlessinger*
Checked by C. J. Nyman†

Aminomethanesulfonic acid,[1-4] a homolog of sulfamic acid, is readily prepared by the interaction of aqueous

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ammonia with sodium hydroxymethanesulfonate. The latter compound is formed almost quantitatively by the reaction of formaldehyde and sodium hydrogen sulfite. Side reactions such as:

$$2HOCH_2SO_3Na + NH_3 \rightarrow HN(CH_2SO_3Na)_2 + 2H_2O$$
$$3HOCH_2SO_3Na + NH_3 \rightarrow N(CH_2SO_3Na)_3 + 3H_2O$$

do not interfere in the synthesis, since the corresponding acids are freely soluble in water.

The amino acid is very easily obtained in a high state of purity, making it suitable for use as a primary standard in the titration of carbonate-free alkali solutions.

Procedure

One hundred and twenty grams (1.15 mols) of sodium hydrogen sulfite (a good technical grade is satisfactory) is slurried well with 120 ml. of water in a 500-ml. Erlenmeyer flask, and 90 ml. of 40% by volume aqueous formaldehyde (0.98 mol) is added with shaking. The temperature of the mixture rises slowly to 65 to 70°, and the formaldehyde odor disappears completely. When the odor of formaldehyde is no longer evident, the vessel and contents are cooled to 50° under running water, and 90 ml. of concentrated aqueous ammonia (about 1.25 mols) is stirred in. This causes a second rise in temperature to 65 to 70°. When the reaction mixture has cooled to 60°, the flask is stoppered loosely and is immersed in a water bath at 60° for one hour with occasional swirling. Alternatively, the flask may be allowed to cool spontaneously immediately after the addition of the ammonia and to stand for one or two days at room temperature.

The solution is filtered by suction through a dense paper to remove small amounts of solid residual material and impurities. An ice-cold mixture of 33 ml. (about 0.6 mol) of concentrated sulfuric acid and 96 ml. of water is added fairly rapidly to the solution of sodium aminomethanesulfonate with good agitation. The acidified liquid is immediately cooled in an ice-water bath to 5 to 10°, during which time the product continuously crystallizes.

The solid is filtered by suction, preferably in a sintered-glass funnel, and drained thoroughly. It is then washed carefully with 25 to 50 ml. of ice water followed by two 100-ml. portions of ice-cold 50% aqueous ethanol. Several final rinsings with 95% ethanol are used to remove all excess sulfuric acid. The white crystalline material is dried *in vacuo;* yield, 60 to 64 g. (54 to 58% based on formaldehyde).

To obtain a more nearly pure product, the acid is recrystallized rapidly from 11 times its weight of water at 70° and dried *in vacuo* after washing with a little ice-cold water. The recovery is 70 to 75% using 50 g. of crude amino acid.

Analysis

Analysis of the product is accomplished by titrating a sample of 0.3 to 0.4 g. to a phenolphthalein end point with carbonate-free 0.1 N sodium or potassium hydroxide. The alkali should be added rather slowly as the end point is approached inasmuch as the neutralization is not quite instantaneous.

The calculated equivalent weight of aminomethanesulfonic acid is 111.1. For the crude material, purity = 98+%. For the recrystallized material, purity values of 99.9 to 100.2% have been consistently obtained.

Properties

Aminomethanesulfonic acid behaves as a weak monoprotic acid in aqueous solution. It reacts with nickel(II), cobalt(II), and copper(II)[5,6] hydroxide gels to form solutions of the corresponding normal salts; the copper(II) compound is only slightly soluble after crystallization. The insoluble barium salt may be formed by conventional metathetical reactions. Both the acid and its salts show a remarkable tendency to form supersaturated solutions.

The acid crystallizes as irregular orthorhombic bipyramids from water and melts at 190° (decomp.). The solubility at 17° is 1.7 g./100 ml. and at 70° about 9 g./100 ml. Boiling in water hydrolyzes the sulfonic group with the liberation of sulfur dioxide and the attendant formation of condensation products of the resultant unstable H_2NCH_2OH.

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CHAPTER VIB

32. ANHYDROUS CHROMIUM(II) ACETATE, CHROMIUM(II) ACETATE 1-HYDRATE, AND BIS(2,4-PENTANEDIONATO)CHROMIUM(II)

Submitted by L. R. Ocone* and B. P. Block*
Checked by James P. Collman† and David A. Buckingham†

Procedures for the preparation of chromium(II) acetate have been presented in three of the preceding volumes of Inorganic Syntheses.[1-3] In Volume VI[3] it is pointed out that the methods described earlier[1,2] require complicated apparatus, whereas a glove box can be used more easily to provide an inert atmosphere. Complete displacement of air from a dry-box, however, often is difficult. A technique has been developed which involves a less cumbersome closed system used in conjunction with a dry-bag for transfers.[4]

More important is the nature of the product prepared. Although the previous procedures for the synthesis of chromium(II) acetate imply that the product is anhydrous, other sources[5,6] indicate that it is hydrated. Thermogravimetric experiments performed on moist fresh products show that the deep red material is the 1-hydrate and that there are no higher hydrates of appreciable stability. The 1-hydrate can be obtained by heating the moist reaction product for about 45 minutes at 58° in a stream of nitrogen flowing at 400 ml./hour or by pumping on the

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sample at 25° for 6 hours. Anhydrous chromium(II) acetate results, on the other hand, at 75° in a nitrogen stream flowing at the rate of 400 ml./hour for 2¼ hours or at 125° in less than 15 minutes. Even at 50° in a vacuum the moist product is converted to the anhydrous acetate within about 28 hours without stepwise dehydration to the 1-hydrate. In Part A, details are presented for the preparation of both the 1-hydrate and the anhydrous acetate. Bis(2,4-pentanedionato)chromium(II) [chromium(II) acetylacetonate] can be made by treating freshly prepared chromium(II) acetate with 2,4-pentanedione (acetylacetone) according to the procedure in Part B.[7]

A. ANHYDROUS CHROMIUM(II) ACETATE AND ITS 1-HYDRATE

$$CrCl_3\cdot aq. + e^- \rightarrow CrCl_2\cdot aq. + Cl^-$$

$$CrCl_2\cdot aq. + 2NaC_2H_3O_2 \rightarrow Cr(C_2H_3O_2)_2\cdot aq. + 2NaCl$$

$$Cr(C_2H_3O_2)_2\cdot aq. \xrightarrow{\text{vacuum}} Cr(C_2H_3O_2)_2\cdot H_2O$$

$$Cr(C_2H_3O_2)_2\cdot H_2O \xrightarrow[100^\circ]{\text{vacuum}} Cr(C_2H_3O_2)_2 + H_2O$$

Procedure

The apparatus is set up as shown in Fig. 3. The Jones reductor *A*, about 40 cm. long and 20 mm. in diameter, is prepared in the usual way by washing granulated zinc with a dilute solution of hydrochloric acid, treating the zinc with a dilute solution of mercury(II) chloride, and subsequently washing with distilled water. The free arm of stopcock *B* is used to drain off the liquid used in preparing the column. The three-necked 500-ml. flask is attached to the lower arm of stopcock *C* by a 2-ft. length of Tygon tubing. This arrangement allows manipulation of the flask together with the attached filter *D* without disturbing the column. The filter chamber *D* is made by attaching a spherical joint* to the mouth of a fritted-glass filter (coarse or medium frits work best), and a vacuum stopcock *F* and small standard-taper joint to the stem. Vacuum stopcocks are necessary at both *F* and *G*.

Before and during reactions, the apparatus is flushed with nitrogen which is purified by treatment with an aqueous chromium(II) chloride solution in a gas-washing bottle. The chromium is kept in the bivalent state by amalgamated zinc in the bottom of the gas-washing bottle. A mercury blow-off should be used to prevent build-up of excessive nitrogen pressure. The fritted disk is normally used as an

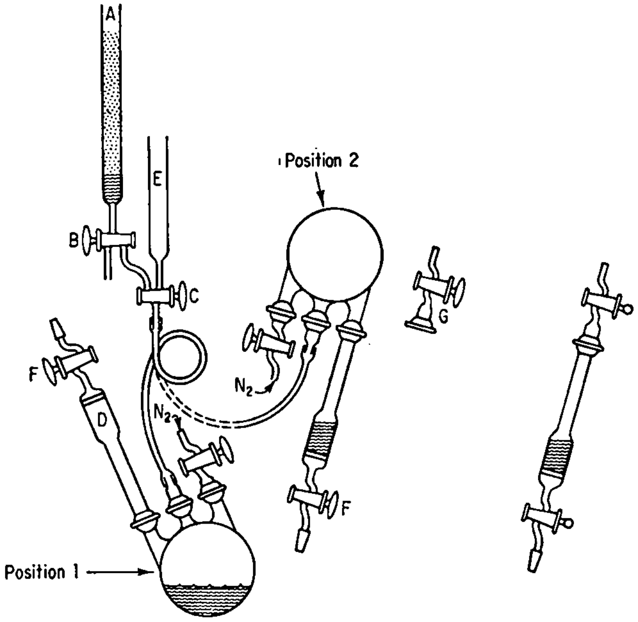

Fig. 3. Apparatus for the preparation of chromium(II) compounds.

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* The checkers report that conventional standard-taper joints on the reaction flask are also satisfactory. The filter chamber *D* is fitted with a male joint (B 34/45), and B 24/40 joints are used for the other two joints on the reaction flask. All joints must be held in place by spring clips or strong rubber bands.

exit for the nitrogen stream, but the reductor and the second addition vessel *E* can be flushed with nitrogen by closing the filter stopcock *F*.

When the apparatus has been flushed, a boiling solution of 16 g. (0.20 mol) of anhydrous sodium acetate dissolved in 35 ml. of water is added through *E*.* A slow nitrogen flow is maintained, and a solution of 9 g. (0.034 mol) of chromium(III) chloride 6-hydrate in 15 ml. of 0.4 *N* sulfuric acid is poured into the top of the reductor. The rate of flow of the chromium solution can be controlled by stopcock *B*. If too fast a rate is used, there is a possibility of incomplete reduction. Distilled water is poured after the chromium chloride until the effluent is only slightly colored by chromium. This requires approximately 125 ml.

The flask is swirled by hand as the blue chromium(II) solution is delivered. A deep red precipitate forms immediately. After a 10-minute period, during which the flask is occasionally swirled, the three-necked flask is rotated to position 2 as shown in Fig. 3. Gravity and the low nitrogen pressure force the liquid to drain through the filter, leaving a solid cake of moist chromium(II) acetate on the frit. Suction may be applied and controlled by the stem stopcock if desired. Wash water may be added through the Jones reductor inasmuch as the zinc column is effective in reducing the dissolved oxygen content of the water, especially when the zinc is contaminated with traces of chromium salts. However, water introduced in this fashion becomes contaminated with zinc, and, if it is desirable to reduce zinc contamination to a minimum, freshly boiled or otherwise deaerated wash water should be added through chamber *E*.

Three 50-ml. portions of water are used for washing. Each wash is allowed to drain slowly through the cake of

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* To ensure the complete absence of oxygen, the checkers find it convenient to boil the sodium acetate solution for about 5 minutes *in the reaction flask* and then cool under a slow nitrogen flow. Exit at this stage is allowed through *F*.

moist chromium(II) acetate. After the last fraction has drained thoroughly, the nitrogen delivery tube is switched rapidly to the stem of the filter chamber so that nitrogen passes through the frit and up through the filter cake. With the moist chromium(II) acetate thus protected, the three-necked flask may be detached from the filter chamber and replaced by the filter chamber cap *G* with its stopcock open. Flushing is continued long enough to purge all the air from the interior of the filter cap, and then both stopcocks on the filter chamber are closed. Pumping on the chamber with a mechanical vacuum pump from 4 to 6 hours at room temperature will dehydrate the sample to the 1-hydrate. The yield is 6.2 g. (96%). *Anal.* Calcd. for $Cr(C_2H_3O_2)_2 \cdot H_2O$: Cr, 27.65; C, 25.54; H, 4.29. Found: Cr, 27.3; C, 25.4; H, 4.3.

The water of hydration can be removed by pumping on the chamber for 2 hours at 100°. The yield of anhydrous compound is 5.5 g. (95% based on $CrCl_3 \cdot 6H_2O$). *Anal.* Calcd. for $Cr(C_2H_3O_2)_2$: Cr, 30.58; C, 28.24; H, 3.56. Found: Cr, 30.7; C, 27.8; H, 3.4.

Properties

Chromium(II) acetate 1-hydrate is a deep red material which is slightly soluble in water and ethanol. It reacts slowly with oxygen when dry and more rapidly when moist. The crystalline 1-hydrate contains dimeric units[8] of the acetate and should, perhaps, be formulated as $Cr_2(CH_3COO)_4 \cdot 2H_2O$. The short intramolecular chromium-to-chromium distance and the low magnetic moment indicate that there is bonding between chromium atoms. Two chromium octahedra are held together (apex-to-apex) by four bridging acetate groups, leaving one position on each chromium atom available for coordination to water (see Fig. 4). The light brown anhydrous chromium(II) acetate is very much more reactive than the 1-hydrate. Exposure to high concentrations of oxygen will cause charring of the material, and very low concentrations cause a noticeable discoloration. The material can be handled only in the complete absence of air.

Chromium(II) acetate is commonly used as a starting material for the preparation of other chromium(II) compounds.

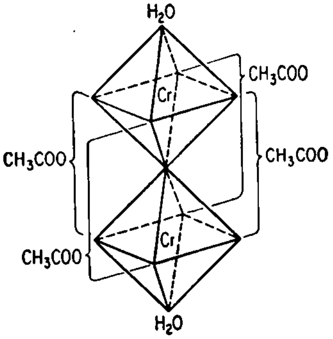

FIG. 4. Dimeric structure of chromium(II) acetate 1-hydrate.

B. BIS(2,4-PENTANEDIONATO)CHROMIUM(II)

$$Cr(C_2H_3O_2)_2{\cdot}aq. + 2C_5H_8O_2 \rightarrow Cr(C_5H_7O_2)_2 + 2HC_2H_3O_2 + aq.$$

Procedure

After the final washing of the chromium(II) acetate precipitated in Part A, a small amount of deaerated water is introduced into the reaction flask, and the cake of washed chromium(II) acetate is broken up and returned to the reaction flask by sloshing the water into the filter chamber. The 2,4-pentanedione [10 ml. (9.76 g. or 0.098 mol) for the quantity of chromium(II) acetate 1-hydrate (6.2 g.) prepared in Part A] is added through chamber *E* and the chamber is rinsed with a small amount of water. A yellow-brown color appears immediately. However, adequate reaction time must be allowed, since the reaction is one between a solid and a liquid which is only partially miscible with water, and the reaction product is a solid. Fifteen minutes with occasional agitation is allowed to ensure complete reaction. The bis(2,4-pentanedionato)chromium(II) thus formed must be recovered and dried as quickly as possible. When freshly precipitated, it has a light yellow-brown color; however, if it is not dried, it slowly turns to a dark brown. After the product is filtered and washed with water, the chamber is disconnected from the flask and capped as described in the procedure for chromium(II) acetate 1-hydrate. The yellow-brown precipitate is vacuum-dried at room temperature until it loses its moist appearance, and then it is heated at 100° for several hours in a vacuum. The yield is 7.65 g. (90% based on $CrCl_3 \cdot 6H_2O$). *Anal.* Calcd. for $Cr(C_5H_7O_2)_2$: Cr, 20.79; C, 48.00; H, 5.64. Found: Cr, 20.3; C, 47.8; H, 5.6.

Properties

Dry bis(2,4-pentanedionato)chromium(II), like the anhydrous acetate, is pyrophoric and can only be handled in the complete absence of oxygen. It is nearly insoluble in water and reacts slowly with it, producing a dark brown solid and gaseous hydrogen. Since the reaction of the acetate with water is extremely slow, the acetylacetonate must be considered a much more active reducing agent. It is slightly soluble in carbon disulfide and has a solubility of 6×10^{-3} mol/l. in ethanol. It decomposes without melting at 218 to 219° and sublimes at 100 to 105° under a pressure of 10^{-2} mm. Hg.

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33. DIPEROXOTRIAMMINECHROMIUM(IV)

$$CrO_3 + 3NH_3 + 3H_2O_2 \rightarrow (NH_3)_3CrO_4 + 3H_2O + O_2\uparrow$$

Submitted by George B. Kauffman[*] and Guillermo Acero[*]
Checked by E. A. V. Ebsworth[†]

Diperoxotriamminechromium(IV) is a good starting material for many triamminechromium(III) complexes. The compound, first discovered by Wiede,[1] may be prepared by the action of aqueous ammonia on red ammonium tetraperoxochromate(V) (K_3CrO_8) or of hydrogen peroxide on ammoniacal solutions of ammonium chromate,[1] ammonium dichromate,[2,3] or chromium(VI) oxide.[4-6] In all cases, the yields obtained are small.

Werner[5] believed that two of the oxygen atoms were bivalent and the other two univalent (peroxidic); he thus formulated the complex as a compound of chromium(VI). Such a compound should be diamagnetic. Inasmuch as the compound has been shown to be paramagnetic with an effective magnetic moment (2.94 B.M.) corresponding closely to that expected for the presence of two unpaired electrons (2.83 B.M.), it is currently believed to involve chromium(IV) coordinated (d^3sp^3) to two peroxide ions and three ammonia molecules.[3]

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[†] University Chemical Laboratory, Cambridge, England.

Procedure

Caution. Inasmuch as the product is a shock-sensitive and heat-sensitive material, shielding must be utilized for protection.

A solution of 20 g. (0.200 mol) of chromium(VI) oxide in 40 ml. of water is added with stirring to a mixture of 70 ml. (1.06 mols) of concentrated aqueous ammonia and 130 ml. of water contained in a 400-ml. beaker. The beaker is allowed to stand in a refrigerator at −30° for about 18 hours to freeze the yellow solution completely. Freezing the solution to a solid mass facilitates the addition of hydrogen peroxide in the next step. Forty milliliters (approximately 0.39 mol) of 30% hydrogen peroxide is added dropwise to the solid mass, which melts by the heat liberated in the reaction. During this time, the temperature is maintained below −6° by means of an ice-salt bath. The deep brown solution is allowed to warm to room temperature by standing for 2 hours, at the end of which time oxygen evolution should have ceased. The solution is then refrozen by returning it to the refrigerator for about 18 hours. The dark brown mass, which now contains a considerable amount of crystallized ammonium dichromate, is slowly heated on a water bath to 50°, taking due care with the effervescence which occurs during heating. The brown solution is maintained at 50° until evolution of oxygen ceases (approximately 30 minutes). The solution is filtered hot, if necessary, and is then again refrozen by allowing it to stand in the refrigerator for about 18 hours. The mixture is then warmed to 10°. The small brown crystals of product are collected on a 5-cm. Büchner funnel and washed with three 10-ml. portions each of 95% ethanol, absolute ethanol, and absolute ether. The crystals are dried first in air and then in a desiccator over potassium hydroxide. *Because of the hazardous nature of the product, the desiccator should be shielded.* (*Caution. Because of the possibility of an explosion, the compound should not be ground in a mortar, nor should it be heated, especially in the presence of organic* *matter.*) The yield is in the range of 1 to 2 g. (4.6 to 9.2% based on H_2O_2). Use of additional hydrogen peroxide does not increase the yield. *Anal.* Calcd. for $(NH_3)_3CrO_4$: Cr, 31.12; NH_3, 30.58. Found: Cr, 31.15; NH_3, 30.55.

Properties[7,8]

Diperoxotriamminechromium(IV) crystallizes in rhombic birefringent prisms of density 1.96 g./ml. (15°),[4] which appear as deep brownish-red to black needles. Although insoluble in most solvents, it may be recrystallized from aqueous ammonia.[4] It is soluble in water with decomposition. The absorption spectra,[9] magnetic susceptibility,[3] and crystal structure[10] of the compound have been measured. A crystallographic study[10] reports the structure as a deformed pentagonal bipyramid. A recent investigation of the infrared spectrum[11] shows the presence of peroxide bands.

When heated, diperoxotriamminechromium(IV) detonates with incandescence and yields chromium(III) oxide. Strong acids liberate oxygen from the compound and form chromium(III) salts; the amount of oxygen evolved depends upon the concentration of the acid. The coordinated ammonia can be replaced by potassium cyanide,[12] ethylenediamine,[13] and hexamethylenetetramine,[13] forming $K_3[CrO_4(CN)_3]$, $CrO_4 \cdot C_2H_4(NH_2)_2 \cdot 2H_2O$, and $CrO_4 \cdot C_6H_{12}N_4$, respectively. Treatment of diperoxotriamminechromium(IV) with hydrochloric acid yields $[Cr(NH_3)_3Cl_3]$[5b] or the three isomers of $[Cr(NH_3)_3(H_2O)Cl_2]Cl$,[14] depending upon the conditions.

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34. TRIS(1,3-DIPHENYL-1,3-PROPANEDIONATO)-CHROMIUM(III)

[Chromium(III) Dibenzoylmethide]

$$[\mathrm{Cr(C_5H_7O_2)_3}] + 3\mathrm{HC_{15}H_{11}O_2} \rightarrow [\mathrm{Cr(C_{15}H_{11}O_2)_3}] + 3\mathrm{HC_5H_7O_2}$$

Submitted by Robert G. Charles*
Checked by R. F. Trimble†

The many satisfactory procedures which have been published for the preparation of metal derivatives of 2,4-pentanedione (acetylacetone) are not always successful when applied to other β-diketones.[1,2] Thus, poor yields of impure product are obtained with attempts to prepare the

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chromium chelate of 1,3-diphenyl-1,3-propanedione (dibenzoylmethane) by reaction with chromium(III) hydroxide[3,4] employing mixed solvents or by reaction with chromium salts in the presence of urea.[5] The method described below, however, conveniently gives high yields of easily purified material. The procedure is based on the replacement of 2,4-pentanedione from the chromium derivative by 1,3-diphenyl-1,3-propanedione. The driving force for the reaction is provided by (1) the volatility of 2,4-pentanedione at the temperatures used and (2) the fact that tris(1,3-diphenyl-1,3-propanedionato)chromium(III) is more stable toward dissociation than is tris(2,4-pentanedionato)chromium(III).[6] The method given here is similar to that used by Wolf, Butter, and Weinelt[7] for the syntheses of the corresponding iron, ruthenium, and rhodium compounds, but the procedure described here does not employ a solvent. It should be useful also for the preparation of other chromium chelates. The principal requirements are that the chelating agent be relatively nonvolatile and that the chelating agent and product be sufficiently heat-resistant.

Procedure

Eleven and two-tenths grams (0.05 mol) of 1,3-diphenyl-1,3-propanedione is ground in a mortar with 5.84 g. (0.017 mol) of tris(2,4-pentanedionato)chromium(III)[5,*] until a fine homogeneous powder is obtained. The mixture is transferred to an Erlenmeyer flask equipped with a gas inlet tube. The flask is heated slowly in an oil bath or with a heating mantle, in a hood, with a slow stream of nitrogen (about 0.5 l./minute) flowing over the mixture. The mixture melts at about 75°; at about 150°, 2,4-pentanedione is

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[*] Tris(2,4-pentanedionato)chromium(III) is available commercially from the MacKensie Chemical Works, Long Island, N.Y., and the Union Carbide Metals Company, Niagara Falls, N.Y.

evolved and evaporates from the flask. The temperature is held at 175 to 180° for 4 hours. The small amount of material which sublimes into the neck of the flask is pushed back into the flask periodically with a stirring rod. The weight of 2,4-pentanedione evolved within 4 hours (5.0 g.) is nearly that calculated.

After cooling, the brown reaction product is broken up, heated briefly with 100 ml. of methanol to extract unchanged starting materials, and cooled to room temperature. The solid is filtered from the extract, washed with 50 ml. of cold acetone, and air-dried at room temperature. The yield is 11 to 11.5 g. (91 to 95%). For purification, the solid is dissolved in 500 ml. of warm benzene. The solution is filtered while warm, and, after cooling, 800 ml. of cyclohexane is added. Tris(1,3-diphenyl-1,3-propanedionato)-chromium(III) slowly separates as a microcrystalline powder. The product is filtered and dried in a vacuum desiccator. Yield, 9 to 9.5 g. (74.4 to 78.6%). *Anal.* Calcd. for $[Cr(C_{15}H_{11}O_2)_3]$: Cr, 7.21; C, 74.88; H, 4.61. Found: Cr, 7.2, C, 74.9; H, 4.2.

Properties

Tris(1,3-diphenyl-1,3-propanedionato)chromium(III) is a red-brown crystalline compound. The density at 30° is 1.32 g./cc. The compound is soluble in benzene, less soluble in acetone, and only very slightly soluble in methanol and in cyclohexane. It is insoluble in water. The visible absorption spectrum in benzene has an absorption peak at 565 $m\mu$ ($\epsilon = 144$). The principal infrared absorption peaks (KBr pellet) are at 6.28, 6.54, 6.75, 6.88, 7.26, 7.60, 8.16, 8.48, 8.87, 9.35, 9.77, 10.62, 12.75, 13.24, 13.83, and 14.58 μ.

When heated in a stream of argon at atmospheric pressure, tris(1,3-diphenyl-1,3-propanedionato)chromium(III) decomposes above 300°.

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35. TRIS(1,1,1-TRIFLUORO-2,4-PENTANEDIONATO)-CHROMIUM(III)

[Chromium(III) Trifluoroacetylacetonate]

$$CrCl_3 \cdot 6H_2O + 3NH_4OH \longrightarrow Cr(OH)_3 + 3NH_4Cl + 6H_2O$$
$$Cr(OH)_3 + 3HC_5H_4O_2F_3 \longrightarrow Cr(C_5H_4O_2F_3)_3 + 3H_2O$$
$$3H_2O + 3CH_3C(OCH_3)_2CH_3 \xrightarrow{[H^+]} 6CH_3OH + 3CH_3COCH_3$$

Submitted by Robert G. Charles*
Checked by Irvin C. Brandt†

Tris(1,1,1-trifluoro-2,4-pentanedionato)chromium(III) has been prepared by heating chromium(III) chloride with 1,1,1-trifluoro-2,4-pentanedione (trifluoroacetylacetone) in an aqueous solution of urea[1,2]‡ and also by the reaction between chromium hexacarbonyl [$Cr(CO)_6$] and 1,1,1-trifluoro-2,4-pentanedione.[3]

The procedure described herein involves the reaction of freshly prepared chromium(III) hydroxide§ with 1,1,1-tri-

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‡ These methods are analogous to that which has been described for the preparation of chromium(III) acetylacetonate [Inorganic Syntheses, **5**, 130 (1957)].

§ The name "chromium(III) hydroxide," used here for convenience, is more properly "hydrous chromium(III) oxide" or "hydrated chromium(III) oxide."

fluoro-2,4-pentanedione in the presence of 2,2-dimethoxypropane at room temperature. The 2,2-dimethoxypropane is a commercially available liquid which is quite useful as a mild dehydrating agent.[4]

Procedure

Freshly prepared chromium(III) hydroxide* is obtained by first dissolving 2.66 g. (0.01 mol) of chromium(III) chloride 6-hydrate in 100 ml. of water. Thirty-five milliliters (0.035 mol) of approximately 1 N aqueous ammonia is added, a little at a time, with shaking. The resulting mixture is allowed to stand 10 minutes and is then filtered by gravity through filter paper. If a significant amount of the finely divided precipitate passes initially through the filter paper, the filtration is repeated with the same filter paper. The precipitate is washed on the filter with 50 ml. of water and allowed to drain for a few minutes.

A solution is prepared in a flask from 5 ml. (an excess) of 1,1,1-trifluoro-2,4-pentanedione† and 100 ml. of 2,2-dimethoxypropane. The moist filter paper containing the chromium(III) hydroxide is transferred intact to this solution. To this mixture is then added, dropwise from a buret, 1.7 ml. (0.03 mol) of glacial acetic acid. The chromium(III) hydroxide slowly dissolves to give a solution which appears red by transmitted light. The flask is stoppered, shaken occasionally, and then allowed to stand overnight at room temperature. Essentially all of the chromium(III) hydroxide reacts in this time.

The red solution is filtered through filter paper. Most of the solvent is evaporated in a stream of nitrogen at room temperature. The remaining acetic acid is removed by drying overnight in a vacuum desiccator. The yield of crude solid is about 4.2 g.

* Chromium(III) hydroxide which has been air-dried and stored does not react satisfactorily.

† 1,1,1-Trifluoro-2,4-pentanedione can be obtained from K & K Laboratories, Plainview, N.Y.

Purification is effected by heating the crude product with 40 ml. of absolute ethanol. The hot solution is filtered through filter paper in a funnel heated to the approximate temperature of the liquid. The filtrate is reheated to dissolve any solid which may separate on cooling, and 125 ml. of *n*-hexane is added to the hot solution. The mixture is cooled, first to room temperature and then in the refrigerator. The pure product crystallizes very slowly on standing. The product is filtered off and dried in a vacuum desiccator. Yield, 2.0 to 2.3 g. (39 to 45%); m.p. 150.0 to 151.5°. *Anal.* Calcd. for $Cr(C_5H_4O_2F_3)_3$: C, 35.25; H, 2.30; F, 33.40. Found: C, 35.39; H, 2.61; F, 33.40. By checker: C, 35.55; H, 2.52; F, 32.58.

Properties

Tris(1,1,1-trifluoro-2,4-pentanedionato)chromium(III) is a red-violet crystalline compound, which is insoluble in water but is readily soluble in benzene, pyridine, acetone, and chloroform. It is less soluble in ethanol and is only slightly soluble in *n*-hexane.

When heated on a thermobalance (2° per minute in flowing argon at atmospheric pressure), the compound sublimes completely in the temperature range 100 to 220° without apparent decomposition.

Principal infrared absorption peaks (Nujol mull) are at 6.19, 6.51, 7.72, 8.14, 8.36, 8.75, 9.92, 10.53, 11.55, 12.49, 12.72, 13.29, and 13.62 μ.

The compound has been separated into cis and trans forms by chromatography on aluminum oxide.[2] Visible and ultraviolet spectra, x-ray diffraction data, and paramagnetic resonance behavior have been studied.[2,3,5]

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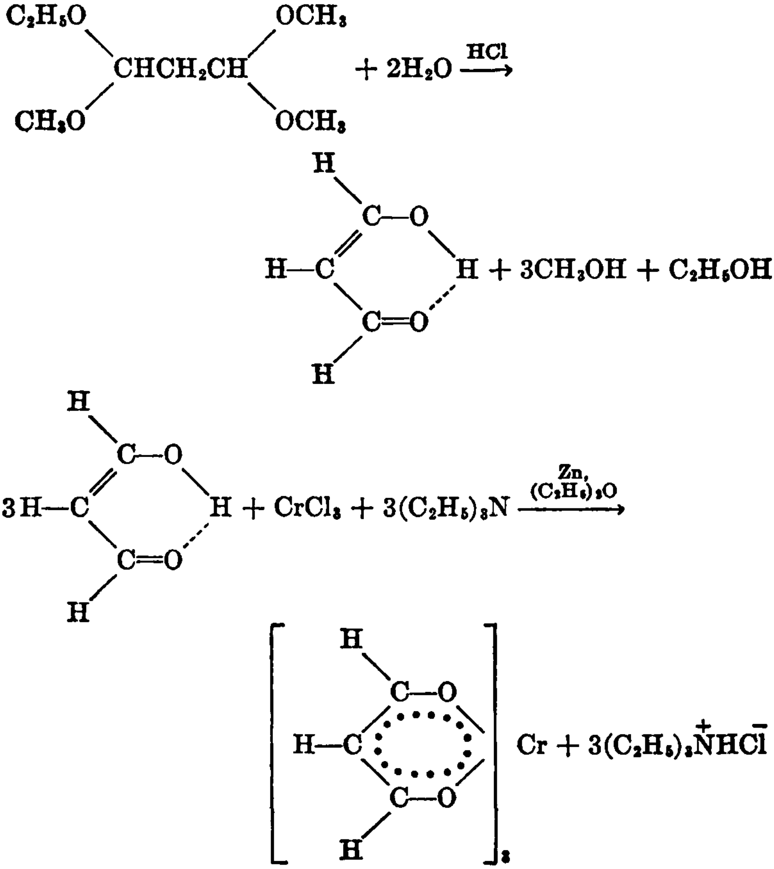
36. TRIS(1,3-PROPANEDIALATO)CHROMIUM(III)



Submitted by James P. Collman,* Edmund T. Kittleman,* William S. Hurt,* and Ned A. Moore*
Checked by Eiichi Sekido†

Chelates of malonaldehyde (1,3-propanedial) can be considered as the parents of 1,3-dicarbonyl chelate ring systems. Because of the great lability of malonaldehyde

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* University of North Carolina, Chapel Hill, N.C. This work was supported by the Petroleum Research Fund, administered by the American Chemical Society.

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toward self-condensation and to oxidation, its chelates are difficult to prepare. The following procedure[1] illustrates the preparation of the chromium(III) chelate of malonaldehyde by means of a complex series of equilibria involving chromium(III) and chromium(II).

Chromium(III) complexes are often difficult to prepare because of the slow rate of ligand exchange with this d^3 ion. Ligands that are sensitive to various side reactions are not easily substituted directly into chromium(III) complexes. Advantage is taken here of the lability of chromium(II) to ligand exchange to catalyze the formation of a chromium(III) complex with a highly reactive ligand, malondialdehyde. Electron-transfer reactions lead to the more stable chromium(III) chelate by way of intermediate chromium(II) complexes.

Procedure

A mixture of 22.0 g. (24 ml.; 0.124 mol) of 1,1,3-trimethoxy-3-ethoxypropane,* 20.0 ml. of water, and 8.0 ml. of 1 *N* hydrochloric acid in a 125-ml. Erlenmeyer flask is swirled on a steam bath until the two-phase system becomes a homogeneous pale yellow liquid. Further heating, which results in a color change to orange-yellow, decreases the yield of final product and hence should be avoided. The solution is cooled to 0° in an ice-salt bath, and then 10.1 g. (0.11 mol) of triethylamine (purified before use by distillation from potassium hydroxide pellets) is added. The resulting red-violet solution is immediately added to a cold (0°) suspension of 5.21 g. (0.04 mol) of anhydrous chromium(III) chloride† and 6.54 g. (0.10 mol) of zinc dust in 400 ml. of ether in a 1000-ml. Erlenmeyer flask. The flask is cooled by an external ice-salt bath and is equipped with a magnetic stirring bar 75 mm. in length. The contents of the

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* Available from Kay-Fries Chemicals, Inc., 180 Madison Avenue, New York. This liquid was purified by vacuum distillation (b.p. 78 to 80° at 18 mm.) before use.

† See INORGANIC SYNTHESES, **2,** 193 (1946); **5,** 154 (1957); **6,** 129 (1960); the compound is also available from Diamond Alkali Co., Painesville, Ohio.

flask are stirred slowly for 30 minutes or until the upper ether layer becomes intensely violet. Then the ether is removed by decantation and replaced by another 400-ml. portion of ether. The stirring is continued, and the ether is replaced every 30 minutes until the ether layer no longer shows any purple color (about 2 to 2½ hours and 4 to 6 portions of ether are required).

The ether solutions are combined, and the solution is dried over 100 g. of calcium chloride for at least 3 hours. The purple solution is filtered and then evaporated in a rotating evaporator to a syrupy residue. The tarry red residue is dissolved in 100 ml. of hot (70°) benzene. The benzene solution is allowed to cool and is then poured onto a chromatographic column (approximately 35 × 300 mm.) packed under benzene with 50 g. of activated aluminum oxide. A dark violet band is rapidly eluted from the column with methylene chloride (dichloromethane). Evaporation of the violet methylene chloride solution yields 2.2 to 2.8 g. of purple crystals (20 to 26%); m.p. 182 to 183°.

The product can be further purified by dissolving it in 40 to 50 ml. of boiling isopropyl alcohol, adding 125 ml. of hot heptane, and storing this solution for 12 hours in a deepfreeze at −10°. The red-violet crystals are collected on a Büchner funnel and air-dried; m.p. 182 to 183°. *Anal.* Calcd. for $C_9H_9O_6Cr$: C, 40.76; H, 3.42. Found: C, 40.80; H, 3.44.

Properties

The chromium chelate of malonaldehyde is a red crystalline solid soluble in benzene and chloroform but insoluble in water. The chelate undergoes nitration and bromination at the central carbon of each chelate ring in the manner of an aromatic system. The infrared spectrum of this substance exhibits major bands at 1600, 1490, 1445, 1375, and 1310 cm.$^{-1}$. The complex undoubtedly exists as a *dl*-racemate, but its resolution has not been achieved.

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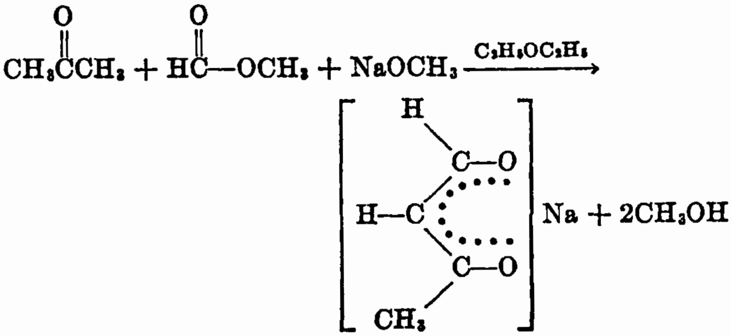
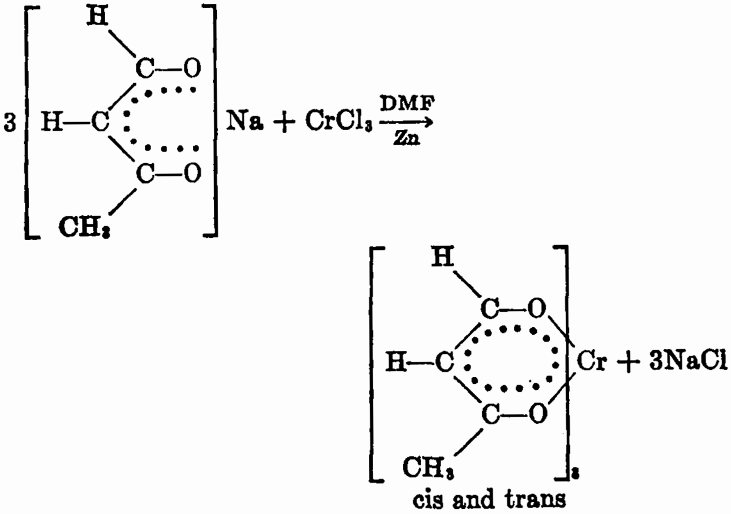
37. *cis*- AND *trans*-TRIS(3-OXOBUTANALATO)-CHROMIUM(III)

A.



B.



Submitted by James P. Collman,* Edmund T. Kittleman,* William S. Hurt,* and Ned A. Moore*
Checked by Glenn Wilkes,† Chin Hsuan Wei,† and Lawrence F. Dahl†

The following procedure is an adaptation of a recently devised method of preparing chromium chelates.[1,2] The

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* University of North Carolina, Chapel Hill, N.C. Work leading to the preparation of these compounds was supported by the Petroleum Research Fund, administered by the American Chemical Society.

† University of Wisconsin, Madison, Wis.

reaction employs a chromium(II)-chromium(III) equilibrium mixture in a nonaqueous medium to prepare the cis and trans chromium(III) chelates of 3-oxobutanal (formylacetone)—the only known examples of a tris-(β-keto aldehyde) complex. The cis and trans isomers are easily separated by column chromatography.

Procedure

A. 3-OXOBUTANALATOSODIUM

With the aid of a dropping funnel, 15 g. (0.26 mol) of dry acetone (water content $<0.5\%$) is added over a period of 30 minutes to a mixture of 13 g. (0.24 mol) of powdered alcohol-free sodium methoxide,* 32 g. (0.53 mol) of methyl formate, and 300 ml. of anhydrous diethyl ether in a 500-ml. flask equipped with a drying tube and a magnetic stirring device. During the addition of the acetone, the temperature of the reaction mixture is maintained below 5° by means of an external ice bath. The magnetic stirrer is conveniently operated through a plastic ice bucket. The mixture is stirred for 4 hours at 0 to 5° and then for an additional 20 hours at room temperature. The pale yellow solid is collected on a suction filter, quickly washed with two 20-ml. portions of anhydrous ether, sucked dry, and then dried overnight in a vacuum at room temperature. A yield of 21.5 to 23 g. (83 to 89%) of the crude, dry, pale yellow 3-oxobutanalatosodium is obtained. This product can be used in Part B without purification.

B. *cis-* AND *trans-*TRIS(3-OXOBUTANALATO)CHROMIUM(III)

A mixture of 0.51 g. (0.0032 mol) of anhydrous chromium(III) chloride,† 0.52 g. (0.008 mol) of zinc powder, and 5 ml. of anhydrous dimethylformamide (DMF), which has been purified by distillation over calcium hydride, is placed in a 125-ml. Erlenmeyer flask fitted with a drying tube and a magnetic stirring bar. The mixture is stirred continuously

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* Available from Matheson Coleman and Bell, East Rutherford, N.J.

† Available from Diamond Alkali Company, Painesville, Ohio.

until the exothermic reaction, which produces a dark green solution, is complete. The solution is then diluted with 15 ml. of anhydrous dimethylformamide and cooled to 0° by means of an external ice-salt bath (again the magnetic stirrer is operated through a plastic ice bucket). To the cold solution are added in separate portions 4.54 g. (0.029 mol) of anhydrous chromium(III) chloride, 0.52 g. (0.008 mol) of zinc powder, and 12.44 g. (0.115 mol) of dry 3-oxobutanalatosodium. In some runs all of the solid does not go into solution. If the solid interferes with the stirrer, an additional 5 or 10 ml. of dimethylformamide is added to complete the solution of the chromium and sodium compounds. The resulting purple mixture is stirred for 90 minutes, during which time the ice of the cooling bath is allowed to melt so that the temperature in the reaction vessel rises to 5 to 10°. The reaction mixture is next combined with 400 ml. of ice water, and the purple slurry is swirled intermittently until an oily, red semisolid substance separates from the mixture. The red semisolid material and the zinc-dust residue are collected on an 11-cm. Büchner suction funnel. The filtrate (referred to later as solution A) is set aside for a subsequent extraction step. The solid residue is washed with 50 ml. of cold water and sucked dry, the wash water being combined with solution A. The solid material from the funnel is spread on a piece of paper and dried with an infrared lamp until all occluded dimethylformamide is expelled, i.e., until the compound is no longer sticky. The granular red precipitate is then treated with 40 ml. of benzene, and the red solution is filtered. The residue on the filter is washed with several small portions of benzene until the washings are colorless. All the benzene filtrates are combined (solution B) and set aside.

Solution A is extracted with two 500-ml. portions of ether. In some runs an emulsion forms at this stage. The extraction can then be carried out by placing the aqueous solution (or the emulsion) in a beaker and extracting six times by adding 100 ml. of ether to the beaker, stirring, and decanting the ether layer. The ether extracts are combined and evaporated to dryness in a rotary flash evaporator at room temperature by using a water aspirator. The solid residue is removed, dried under an infrared lamp, and then dissolved in 40 ml. of benzene. The red solution is combined with solution B. To this solution (approximately 100 ml. in volume) is added 600 ml. of cold (0°) *n*-heptane, and the resulting solution is placed in a freezer maintained at approximately −10°. After 12 hours the purple crystals which have separated from this solution are collected on a filter and sucked dry. The yield is 5.1 g. Concentration of the mother liquor to one-half its volume in a rotary evaporator followed by overnight cooling in the freezer provides an additional 0.2 g. of red crystals. A total yield of 4.9 to 5.3 g. (50 to 54%) of the crude mixture of cis and trans isomers is obtained.*

C. SEPARATION OF THE CIS AND TRANS ISOMERS

The crude product is dissolved in the minimum quantity of benzene and is placed on an alumina-filled column about 60 cm. in length and 5.5 cm. in diameter prepared by packing it, under benzene, with 60 g. of Merck alumina per gram of crude crystalline product. Elution with 1:1 (by volume) methylene chloride (dichloromethane)–benzene mixture removes a red band; a second band is eluted from the column by methanol. Evaporation of the solvent from each of these fractions affords the red crystalline isomers.†

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* The checkers report a total of 6.0 g. (61%) of the crude mixture.

† The checkers report that both the cis and trans isomers may be recrystallized by slow evaporation in air from a mixture of *n*-heptane and methylene chloride having a ratio of 5:2, by volume, to give purple-red crystals. Neither isomer could be recrystallized from benzene.

Recrystallization apparently leads to considerable loss of material without appreciable gain in purity. From a 5.1-g. sample of the crude mixture subjected to both chromatography and recrystallization the checkers isolated 0.72 g. of cis isomer, m.p. 163.4 to 164.0°, and 2.25 g. of trans isomer, m.p. 169.2 to 169.6°.

Band I: Trans isomer, 2.50 to 3.75 g., m.p. 169.0 to 169.5°. *Anal.* Calcd. for $C_{12}H_{15}O_6Cr$: C, 46.89; H, 4.92. Found: C, 46.86; H, 4.91. Band II: Cis isomer, 1.05 to 1.25 g., m.p. 165 to 166°. *Anal.* Calcd. for $C_{12}H_{15}O_6Cr$: C, 46.89; H, 4.92. Found: C, 47.04; H, 5.31.

Properties

The isomers of tris(3-oxobutanalato)chromium(III) are red crystalline compounds soluble in benzene and chloroform and insoluble in water. The purity of the isomers is best determined by chromatography. The infrared spectra of both isomers show major bands at 1585, 1500, 1430, and 1335 $cm.^{-1}$

The cis isomer is defined as that compound in which the three methyl keto groups are on adjacent corners of the octahedral structure; the trans isomer has two of the methyl keto groups on opposite apexes of the octahedron. Both the cis and trans isomers should be *dl*-racemates, but their resolution has not been reported. The structures of the isomers are assigned on the basis of their different chromatographic adsorption (the cis isomer adheres more strongly to alumina) and the ratio of isolated products (the trans isomer predominates) by analogy with the work of Fay and Piper[3] on tris complexes of unsymmetrical 1,3-diketones.

The crude mixture of cis and trans isomers has been nitrated,[1] brominated,[1] and thiocyanogenated[4] at the central carbon of each chelate ring in the manner of a quasi-aromatic system.

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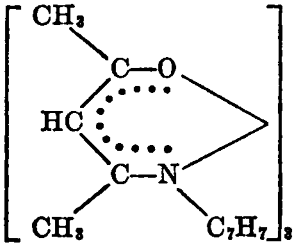
38. TRIS(4-*p*-TOLUIDINO-3-PENTEN-2-ONATO)-CHROMIUM(III)

$$CH_3COCH_2COCH_3 + p\text{-}CH_3C_6H_4NH_2 \xrightarrow{HCl,\ C_6H_6} CH_3COCH{=}C(HNC_6H_4CH_3)CH_3 + H_2O$$

$$3CH_3COCH{=}C(HNC_6H_4CH_3)CH_3 + CrCl_3{\cdot}3C_4H_8O + 3(CH_3)_3COK \xrightarrow{Zn,\ (CH_3)_3COH}$$



$$Cr + 3KCl + 3(CH_3)_3COH + 3C_4H_8O$$

Submitted by James P. Collman* and E. T. Kittleman*
Checked by Norman E. Griswold†

No chromium chelates of α,β-unsaturated β-keto amines (β-amino ketones) have been previously reported, although a wide variety of these ligands are known.[1-7] The following procedure is representative of the preparation of a chromium(III) complex of a hydrolytically unstable ligand under completely anhydrous conditions.‡ This method is general and can be employed in the synthesis of a large number of analogous chromium(III) complexes.[8]

Part A illustrates a general method of preparing α,β-unsaturated β-keto amines (β-keto imines; cf. synthesis 13), a class of weakly acidic bidentate ligands. Part C illustrates the use of chromium(III) chloride–tris(tetrahydrofuran) in the synthesis of a chromium(III) complex under nonaqueous conditions.

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‡ Other amines which have been used are aniline, *o*-toluidine, *o*-chloroaniline, *m*-chloroaniline, *p*-anisidine, benzylamine, β-naphthylamine, and *p*-phenylaniline (4-biphenylamine).

Procedure

A. 4-*p*-TOLUIDINO-3-PENTEN-2-ONE[1]

One hundred fifty milliliters of benzene containing 10 g. (0.10 mol) of 2,4-pentanedione (acetylacetone) and two drops of concentrated (12 *N*) hydrochloric acid is added to 11.0 g. (0.103 mol) of *p*-toluidine in a 300-ml. round-bottomed flask equipped with a Dean-Stark trap[9] (for azeotropic removal of water) and a reflux condenser fitted with a calcium chloride drying tube. Overnight boiling of the reaction mixture results in the separation of 1.6 g. (0.089 mol) of water (89% of the theoretical quantity). The reaction mixture is cooled to room temperature and filtered on a fluted paper filter. The filtrate is then concentrated to an orange oil. Crystallization is induced by allowing a solution of this oil in 20 ml. of ether to remain in a freezer (at about −15°) for 6 hours. The pale yellow solid is removed by suction filtration and air-dried. The crude compound is recrystallized by dissolving it in 35 ml. of boiling heptane followed by chilling the solution in the freezer. After two recrystallizations, the yield of white crystals is at least 11 g. (58%); m.p. 68 to 69°.

B. CHROMIUM(III) CHLORIDE-TRIS(TETRAHYDROFURAN)[10]

A mixture of 1 g. of zinc dust and 20 g. (0.13 mol) of anhydrous chromium(III) chloride* is placed in the thimble of a Soxhlet extraction apparatus. Approximately 218 ml. (2.7 mols) of tetrahydrofuran (freshly distilled from calcium hydride) is placed in a 300-ml. round-bottomed flask and attached to the extraction apparatus; a calcium chloride drying tube is fitted to the reflux condenser. At the end of 4 hours of reflux the reaction is stopped and an additional gram of zinc dust is placed in the thimble. The reflux is then resumed and continued for 8 hours (or until the recycling liquid is colorless). The tetrahydrofuran solution

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* See INORGANIC SYNTHESES, **2**, 193 (1946); **5**, 154 (1957); **6**, 129 (1960); the compound is also available from Diamond Alkali Co., Painesville, Ohio.

is cooled to room temperature and allowed to stand for at least 12 hours (a calcium chloride drying tube protects the solution from atmospheric moisture). Practically all the tetrahydrofuran can be rapidly decanted from the precipitated solvate. The purple crystalline product is dried *in vacuo* at room temperature overnight. The last trace of tetrahydrofuran is removed by pulverizing portions of the product in a mortar under a layer of dry heptane. Suction filtration is used to recover the purple powder. Final drying is effected *in vacuo* at room temperature. The yield is 28.6 g. (60.5%).

C. TRIS(4-*p*-TOLUIDINO-3-PENTEN-2-ONATO)CHROMIUM(III)

To 50 ml. of dry *tert*-butyl alcohol* in a 100-ml. round-bottomed flask fitted with reflux condenser and calcium chloride drying tube is added 0.85 g (0.022 mol) of potassium metal. The mixture is allowed to stand at room temperature for 10 hours, during which time the potassium metal completely dissolves. While this solution is vigorously stirred by means of a magnetic stirrer, an intimate mixture of 3.97 g. (0.021 mol) of 4-*p*-toluidino-3-penten-2-one, 1.37 g. (0.021 mol) of zinc dust, and 2.62 g. (0.007 mol) of chromium(III) chloride–tris(tetrahydrofuran) is added; a gray-colored mass appears within 3 minutes. The reaction mixture is refluxed for 2 hours with continuous stirring. The mixture is cooled to room temperature, poured into 400 ml. of ether, and left in the freezer (−15°) overnight.† The ether-insoluble residue is removed by filtration through a fluted paper filter, and the ether solution is dried over anhydrous magnesium sulfate. The ether–*tert*-butyl alcohol solution is concentrated to a volume of 45 ml.‡

Dilution of this solution with 45 ml. of 95% ethanol is

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* The *tert*-butyl alcohol is dried by refluxing over calcium hydride and then distilling into the reaction vessel.

† This procedure facilitates the following filtration step.

‡ Concentration of all solutions is conveniently accomplished on a rotating evaporator using a water aspirator.

followed by concentration to a viscous red oil. An additional 45 ml. of 95% ethanol is added, and the mixture is concentrated to a red grease. Finally, 45 ml. of 95% ethanol is added and the mixture is concentrated to a sticky red solid. This red solid is dissolved in 10 ml. of benzene and introduced into a 4-in. column (1-in. diam.) of aluminum oxide in benzene. Elution from the column is effected with an 80:20 (by volume) benzene-heptane mixture. The eluate is dried over magnesium sulfate and concentrated to a red grease. Crystallization is effected by a combination of the following steps. The grease is swirled for 5 minutes with 5 ml. of 95% ethanol. An additional 10 ml. of 95% ethanol is added, and the mixture is swirled for 5 minutes in a water bath at 70° before transferring to a beaker. The flask is rinsed with 5 ml. of 95% ethanol, which is added to the solution in the beaker. The ethanol solution is allowed to stand overnight in a freezer at about $-18°$. Additional crystals may be obtained by allowing the ethanol solution to stand at room temperature in contact with air for several days, crystals being filtered off every other day. (The checker obtained more nearly pure, more sharply melting crystals with each of three such successive crystallizations.) Total yield after filtration of each crystal crop is at least 1.51 g. (35%) of red crystals, m.p. 179 to 181°.* *Anal.* Calcd. for $Cr(C_{12}H_{14}NO)_3$: C, 70.11; H, 6.87; N. 6.81. Found: C, 70.18; H, 6.68; N, 6.90. By checker: C, 70.13, 69.91; H, 7.28, 7.42; N, 6.78, 6.62.

Properties

Tris(4-*p*-toluidino-3-penten-2-onato)chromium(III) is a dark red crystalline material which is soluble in common organic solvents. It shows no tendency to sublime at 100°

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* The checker noted several wide melting ranges for some of the crystal crops. After the crystals stood for 2 days in a desiccator, the melting range lessened. These observations may probably be accounted for by the initial presence of the less stable cis isomer or by some residual solvent.

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and 8 mm. (drying conditions for the pure material). The infrared spectrum of 4-*p*-toluidino-3-penten-2-one exhibits strong absorption bands at 1600, 1550, and 1265 cm.$^{-1}$, whereas that of the chromium chelate exhibits major bands at 1572, 1501, and 1400 cm.$^{-1}$.

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39. TRIS(2,4-PENTANEDIONATO)-MOLYBDENUM(III)

[Molybdenum(III) Acetylacetonate]

$$K_3[MoCl_6] + 3C_5H_8O_2 \rightarrow Mo(C_5H_7O_2)_3 + 3HCl + 3KCl$$

Submitted by Melvin L. Larson* and Fred W. Moore*
Checked by James Waller† and Burl E. Bryant†

The first mention of tris(2,4-pentanedionato)molybdenum(III) in the literature is a report of some of the cell constants and of the paramagnetic resonance.[1] It has been

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synthesized by the neutralization of an aqueous solution of diammonium pentachloroaquomolybdate(III) and 2,4-pentanedione (acetylacetone).[2] Other methods include the use of the Mo^{3+} cation produced *in situ* by electrolytic reduction and the reaction of molybdenum hexacarbonyl with 2,4-pentanedione under reflux.[3]

Procedure

Caution. Tris(2,4-pentanedionato)molybdenum(III) reacts vigorously with air, sometimes bursting into flame.

A 1-l. two-necked round-bottomed flask, to the side of which is sealed a draining stopcock, is equipped with a reflux condenser and a coarse-frit gas-dispersion tube positioned to project beneath the surface of the liquid. A magnetic stirrer driving a Teflon-coated stirring bar is utilized for stirring. An immersion thermometer is suspended in the reflux condenser. Into the flask is placed 650 ml. of distilled water. Prepurified cylinder nitrogen (0.002 to 0.004% oxygen) is bubbled into the water with stirring while the liquid is heated to 55° with a heating mantle. The exit gases are passed through the reflux condenser to a bubbler in order to assure a constant nitrogen pressure. Into this flask is pipetted 102.5 ml. (100 g.; 1.0 mol) of 2,4-pentanedione, which dissolves completely. The deaeration of the solution is continued while the mixture is heated to 75°, and this temperature is maintained for 30 minutes. The solution is cooled to 30°, and 42.6 g. (0.1 mol) of potassium hexachloromolybdate(III)[4,*] is added while the nitrogen flow is continued. The material dissolves completely, forming a dark red solution. The solution is heated to 50° with rapid stirring over a period of one hour. The solution is maintained at 50° for 30 minutes and is then allowed to

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[*] The checkers report that 39.94 g. (0.1 mol) of potassium pentachloroaquomolybdate(III)[4] can be used instead of potassium hexachloromolybdate(III), following the other portions of the procedure exactly. With this modification, a yield of 23.8 g. (60%) is obtained.

cool slowly for a 2-hour period, during which an abundant crop of dark purple crystals precipitates.

The reaction apparatus is prepared so that the filtration and washing operation can be conducted under prepurified nitrogen. The two-necked flask is rotated so that the draining stopcock is at the bottom. By use of a rubber stopper, the draining stopcock is attached to a medium-frit filter tube, which is in turn connected by a ground-glass joint to one neck of a 2-l. three-necked round-bottomed flask. The other two necks of the 2-l. flask are equipped with stopcock valves, one for evacuation and the other for introduction of nitrogen. Under prepurified nitrogen the reaction mixture is filtered, and the crystals are washed with several volumes of deaerated distilled water. The filter tube containing the wet crystalline product is evacuated at room temperature for 4 hours, always destroying the vacuum, whenever necessary, with prepurified nitrogen. The product is then transferred to a vacuum desiccator (Drierite desiccant) inside a nitrogen box with oxygen content 0.02% or less. The desiccator is evacuated to dry the product to a constant weight. The yield is 33 g. to 37 g. (85 to 95%). *Anal.* Calcd. for $Mo(C_5H_7O_2)_3$: C, 45.81; H, 5.38; Mo, 24.40. Found: C, 45.68; H, 5.20; Mo, 24.65. By checker: 24.56.

Properties

Tris(2,4-pentanedionato)molybdenum(III) is a dark purple crystalline solid, m.p. 228 to 230°. It reacts rapidly with atmospheric oxygen to form a diamagnetic brown product, m.p. 284 to 285° (decomp.), containing pentapositive molybdenum. This oxidation state is determined by dissolution in concentrated hydrochloric acid to produce a solution which has the same absorption spectrum in the visible region as green oxopentachloromolybdate(V),[5] by cerimetric titration of this concentrated hydrochloric acid solution after chloroform extraction of the liberated 2,4-pentanedione, and by independent synthesis from a brown aqueous solution of 2,4-pentanedione and $(NH_4)_2[MoOCl_5]$. Hydrolysis of $[MoOCl_5]^{2-}$ gives a brown diamagnetic dimeric species believed to have the oxygen-bridged $[O{=}Mo{-}O{-}Mo{=}O]^{4+}$ structure.[5] It is therefore proposed that the brown molybdenum product produced in air contains an oxygen bridge with the simplest empirical formula of $[(C_5H_7O_2)_2Mo{=}O]_2O$.* The diamagnetism probably results from $d\pi$-$p\pi$ interaction along the proposed Mo—O—Mo group.[6] Above the melting point, tris(2,4-pentanedionato)molybdenum(III) loses one 2,4-pentanedione group. However, the compound can be sublimed readily in a vacuum (less than 1 mm.) at 170 to 180°. It is readily soluble in benzene, and ebullioscopic molecular weight determination on this solution demonstrates that it is not associated. Calcd.: mol. wt., 393. Found: mol. wt., 393. Although it is soluble in carbon tetrachloride, refluxing of this solution causes replacement of 2,4-pentanedione by chlorine. The compound is soluble in benzophenone, pyridine, and triphenylphosphine without reaction. It is insoluble in and unattacked by boiling water. The infrared absorption spectrum of the solid has the following distinct peaks in the 1650- to 750-$cm.^{-1}$ region: 1550 (s,sh); 1527 (s); 1429 (m); 1370 (s); 1274 (s); 1193 (w); 1020 (m); 930 (m); 778 (m) (s, strong; sh, shoulder; m, medium; w, weak absorption). These peaks are very similar to those described for acetylacetonates of other trivalent metal ions.[7]

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* The checkers report a molybdenum analysis of 29.40%; calculated per cent Mo for $[(C_5H_7O_2)_2Mo{=}O]_2O$, 30.17.

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40. POTASSIUM TETRAOXALATOURANATE(IV)

$$U(C_2O_4)_2 \cdot 6H_2O + 2K_2C_2O_4 \cdot H_2O \rightarrow K_4U(C_2O_4)_4 \cdot 5H_2O + 3H_2O$$

Submitted by Frederic A. Johnson* and Edwin M. Larsen†
Checked by Carl L. Rollinson‡ and Betty Wallace‡

The procedure described below represents an improvement in the synthesis of Marchi, published in an earlier volume of Inorganic Syntheses.[1] The earlier procedure produces a product which has a C_2O_4:U ratio of about 3.75. An analysis of a typical preparation is: Calcd.: U, 28.46; C_2O_4, 42.08. Found: U, 29.73, 29.63; C_2O_4, 40.76, 40.43. A purer product can be obtained by dissolving the initial product in a solution of potassium oxalate and oxalic acid, followed by precipitation with ethanol. The concentration of alcohol specified below does not cause precipitation of potassium oxalate, potassium hydrogen oxalate, or oxalic acid.

Procedure

Eight grams of the product obtained in the original procedure[1]§ is dissolved in a hot solution made by stirring 1 g. of potassium oxalate 1-hydrate and 0.4 g. of oxalic acid 2-hydrate into 40 ml. of water. Forty-two milliliters of 95% ethanol is added in 10- and 20-ml. increments from a dropping funnel to the clear dark green solution while the solution is stirred with a magnetic stirrer. The first 10-ml. portion may be added rapidly; the second 10-ml. increment should be added slowly and with rapid stirring to promote the deposition of a granular product and to avoid the forma-

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‡ University of Maryland, College Park, Md.

§ It should be noted that 6 g. of $U(C_2O_4)_2 \cdot 6H_2O$ is 0.0115 mol, instead of 0.014 mol as stated in the original procedure.

tion of an oily layer. The final 20-ml. quantity may be added rapidly. The pale gray-green precipitate is then filtered on a small Büchner funnel, washed with 15 ml. of absolute ethanol, and then washed with 25 ml. of diethyl ether. The yield is about 7.2 g. (90% based on the initial product). *Anal.* Calcd. for $K_4U(C_2O_4)_4{\cdot}5H_2O$: U, 28.46; C_2O_4, 42.08; H_2O, 10.75. Found: U, 28.77, 28.56, 28.67; C_2O_4, 42.30, 42.27, 42.27; H_2O, 9.32, 9.35. Low results for water were always encountered. Analyses of products precipitated with alcohol and dried with ether customarily indicate 4.3 to 4.8 mols of water per mol of uranium. The density of the hydrated salt is 2.57 g./cc. as determined pycnometrically in benzene at 25.0 ± 0.1°.

An anhydrous preparation is obtained by heating the product for 4 hours at a maximum temperature of 185°. Additional heating at 190° causes no further change in weight. This seemingly is in contradiction to the statement by Marchi[1] that heating at 200° yields the 1-hydrate. *Anal.* Calcd. for $K_4U(C_2O_4)_4$: U, 31.89; C_2O_4, 47.17. Found: U, 32.03, 31.92; C_2O_4, 46.75, 46.68.

Properties

The properties of potassium tetraoxalatouranate(IV) are described in Volume III.[1]

Reference

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CHAPTER VIIA

See also: Dichloro(2,2′-iminodipyridine)zinc, diacetato(2,2′-iminodipyridine)zinc, and dicyano(2,2′-iminodipyridine)zinc, synthesis 3
Dichlorobis(2,4-pentanedionato)titanium(IV), synthesis 10
Tris(2,4-pentanedionato)zirconium(IV) chloride, synthesis 11
Phenyllead(IV) azides (includes triphenyllead chloride and diphenyllead dichloride), synthesis 15
Diphenyl phosphorochloridite, synthesis 17
Mercapto derivatives of chlorocyclophosphazenes, synthesis 21
(Trichlorophosphoranylidene)amidophosphoryl dichloride, synthesis 22
Trichloro[(trichlorophosphoranylidene)amino]phosphorus(V) hexachlorophosphate, synthesis 23
Imidodisulfuric acid chloride, synthesis 26
Dialkylsulfamoyl chlorides, synthesis 27
Dialkylamides of (trichlorophosphoranylidene)sulfamic acid, synthesis 29
Bis(trichlorophosphoranylidene)sulfamide, synthesis 30
Tris(1,1,1-trifluoro-2,4-pentanedionato)chromium(III), synthesis 35
Bis(ethylenediamine)dioxorhenium(V) chloride, bis(ethylenediamine)oxohydroxorhenium(V) perchlorate, and bis(ethylenediamine)dihydroxorhenium(V) hexachloroplatinate(IV), synthesis 44
Nitrosylpentaamminecobalt(II) chloride, synthesis 49
cis-Bromoamminebis(ethylenediamine)cobalt(III) bromide, *cis*- and *trans*-aquoamminebis(ethylenediamine)cobalt(III) bromide, and *cis*- and *trans*-aquoamminebis(ethylenediamine)cobalt(III) nitrate, synthesis 51
Dichlorotetracarbonyldirhodium, synthesis 55
Chlorocarbonylbis(triphenylphosphine)rhodium and chlorocarbonylbis(triphenylarsine)rhodium, synthesis 56
Sodium hexachlororhodate(III) 2-hydrate and potassium hexachlororhodate(III) 1-hydrate, synthesis 57
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Resolution of the tris(1,10-phenanthroline)nickel(II) ion, synthesis 59

Tetraamminepalladium(II) tetrachloropalladate(II) and *trans*-dichlorodiamminepalladium(II), synthesis 61
Tris(ethylenediamine)platinum(IV) chloride, synthesis 62
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Introduction to the chemistry of compounds of the noble gases, synthesis 65
Xenon tetrafluoride, synthesis 66
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41. SULFUR CHLORIDE PENTAFLUORIDE

$$ClF_3 + Cl_2 \rightarrow 3ClF$$
$$3ClF + 3SF_4 \rightarrow 3SF_5Cl$$

Submitted by F. Nyman,* H. L. Roberts,* and T. Seaton*
Checked by John W. George†

The first reported preparations of sulfur chloride pentafluoride involved the fluorination of sulfur(II) chloride,[1] the chlorination of disulfur decafluoride,[2] and the electrolysis of sulfur(II) chloride–hydrogen fluoride mixtures.[3] Newer methods utilize the reaction between chlorine monofluoride and sulfur(IV) fluoride[4] or the reaction between chlorine, cesium fluoride, and sulfur(IV) fluoride.[5] The directions described here for the reaction between chlorine monofluoride and sulfur(IV) fluoride are for the preparation of substantial quantities; if only a 1- or 2-g. sample is required, the modifications described in the last paragraph of the Procedure section may be employed or a batch pro-

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† University of Massachusetts, Amherst, Mass.

cedure similar to the continuous-flow method described may be utilized.

Procedure

Caution. The reagents and products are extremely toxic, particularly sulfur chloride pentafluoride and disulfur decafluoride.

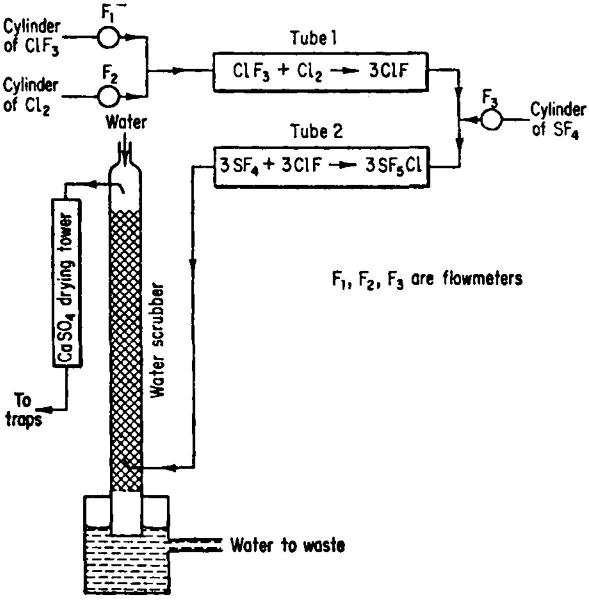

FIG. 5. Apparatus for the preparation of sulfur chloride pentafluoride.

The starting materials, chlorine, chlorine trifluoride, and sulfur(IV) fluoride can be purchased in cylinders and can be used as received.

The required apparatus (Fig. 5) consists of two flowmeters suitable for use with easily hydrolyzed fluorine compounds,[6] one capillary or Rotameter flowmeter for chlorine, two nickel tubes 4 ft. long × 2½ in., and two tube furnaces capable of heating the tubes to 400 ± 5°. Metal tubing is recommended for all lines which carry either chlorine trifluoride or sulfur(IV) fluoride.[7]

Chlorine trifluoride (0.18 l./minute) and chlorine (0.22 l./minute) are mixed together at a T-junction and passed through the first nickel tube, which is maintained at 350°. The gases emerging from this tube are mixed with sulfur(IV) fluoride (0.54 l./minute) and passed into the second reactor, the optimum temperature for which is 375°. Lower temperatures result in incomplete conversion; higher temperatures cause the following side reaction to become increasingly important:

$$SF_4 + 2ClF \rightarrow SF_6 + Cl_2$$

The desired reaction will often be just maintained without the application of additional heat at the flow rates and for the tube sizes quoted. The side reaction is more exothermic than the one desired, and it may cause an accelerating temperature rise. If this is observed, the supply of reagents should be shut off and nitrogen passed through the apparatus to reduce the temperature. If the temperature should drop, as occurs when the reaction is carried out on a smaller scale, heat must be supplied to make up for the loss.

It is advisable to monitor the product emerging from the second reactor by gas chromatographic analysis, for which a column packed with a chlorofluorocarbon grease on a firebrick support is suitable. The retention times on such a column are SF_6, 1; SF_4/SOF_2, 1.4; SF_5Cl, 2.7; $Cl/ClF/ClF_3$, 3.2. This provides a more sensitive means of adjusting to optimum conversion than reliance on flowmeters alone.

The gas emerging from the second reactor will usually contain some sulfuryl fluoride, sulfur(IV) fluoride, and chlorine. These are removed by passing the gases up a packed tower (2-in.-diam. glass tubing), down which a rapid stream of water is flowing. After this treatment, the product is dried over calcium sulfate (*not* calcium chloride) and condensed in a trap cooled by an acetone–Dry Ice mixture. At this stage, depending on the degree of temperature control, the product may contain up to 10% sulfur(VI) fluoride, SF_6. For further chemical reactions this is of no importance. However, the hexafluoride can be removed easily by preparative scale chromatography or by distillation at a pressure sufficient to ensure that the hexafluoride is liquid at its distillation temperature (>2 atmospheres). The yield for a 4-hour reaction time is 660 g. (85%) based on 520 g. (4.9 mol) of sulfur(IV) fluoride fed into the reaction vessel. The infrared spectrum[8] has principal bands at 920, 856, 805, 706, 602, and 578 cm.$^{-1}$

For a smaller-scale preparation, the following modifications in apparatus and method, suggested by the checker and approved by the authors, may be utilized:

Two nickel tubes 4 ft. long × 1 in. o.d. are used. They are coated with alundum cement and wound with 18-gage Chromel wire which is in turn covered with cement and with 2 in. of rock-wool insulation. The pipes are provided with threads to accommodate nickel caps in which are placed brass flare fittings for the $\frac{1}{4}$-in. copper tubing connecting the reactors. The gas cylinders are joined by copper and Teflon tubing to flowmeters. Fisher-Porter Tri-Flat Pyrex Flowrator Tubes with sapphire floats function satisfactorily as flowmeters for chlorine and chlorine trifluoride if moisture is rigorously excluded; for sulfur(IV) fluoride, Matheson 601 Pyrex tubes with stainless-steel and Pyrex floats are recommended. A 1-in.-diam. scrubbing column about 30 in. high is adequate. The calcium sulfate column is 1 in. in diameter and 16 in. long. Two Dry Ice–trichloroethylene cold traps are employed in series to condense volatile products. Flow rates used, with the smaller reactor dimensions, are 29, 35, and 87 ml./minute for chlorine trifluoride, chlorine, and sulfur(IV) fluoride, respectively. At the end of a preparation, all gas input lines are flushed with nitrogen. Temperatures employed are the same as for the larger-scale preparation. However, when using the smaller quantities, external heating must usually be continued while the reaction is in progress, in order to maintain a constant temperature. A typical yield for the smaller-scale preparation is approximately 2 g. (50%), based on sulfur(IV) fluoride.

Properties

Sulfur chloride pentafluoride is a colorless, highly toxic gas. It condenses to a colorless liquid at −19.1° and freezes to a white solid at −64°. Its vapor pressure over the range −60 to −20° may be calculated from the equation:

$$\log P_{\text{mm}} = 7.145 - \frac{1083}{T\ (^\circ\text{K})}$$

The density of the liquid, in grams per milliliter, is given by:

$$1.861 - 0.0016t \qquad \text{where } t = {}^\circ\text{C.}$$

The compound is stable toward dilute acids and water but is rapidly hydrolyzed by dilute alkali:

$$SF_5Cl + 8KOH \rightarrow 5KF + KCl + K_2SO_4 + 4H_2O$$

Sulfur chloride pentafluoride can be reduced photochemically[9] to the very toxic S_2F_{10} and can be oxidized photochemically[10] to a mixture of SF_5OSF_5 and SF_5OOSF_5. With olefins, it reacts to form a variety of organic sulfur pentafluorides.[11] The ultraviolet irradiation of a mixture of sulfur chloride pentafluoride and dinitrogen tetrafluoride yields SF_5NF_2.[12]

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42. TRIFLUOROMETHYL HYPOFLUORITE

$$CO + F_2 \rightarrow COF_2$$
$$COF_2 + F_2 \rightarrow CF_3OF$$

Submitted by George H. Cady*
Checked by Saadideen I. Khayat† and K. S. Willson†

Trifluoromethyl hypofluorite, CF_3OF, is formed by the reaction of fluorine in excess with carbon monoxide, carbon dioxide, methanol, or other compounds containing both carbon and oxygen.[1,2] In the procedure described below, carbon monoxide first reacts with an excess of fluorine to give largely carbonyl fluoride. The mixture is then passed through a hot tube where nearly all of the carbonyl fluoride reacts with fluorine to give trifluoromethyl hypofluorite. It is desirable to use somewhat more than two volumes of fluorine per volume of carbon monoxide. If this is not done, much perfluorodimethyl peroxide [bis(trifluoromethyl) peroxide] is formed by the combination of carbonyl fluoride with trifluoromethyl hypofluorite by the reaction:

$$CF_3OF + COF_2 \rightarrow CF_3OOCF_3$$

Apparatus

Two flowmeters are used—one to measure the flow of carbon monoxide, the other the flow of fluorine. One of the meters measures the pressure drop when carbon mon-

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† The Harshaw Chemical Company, Cleveland, Ohio.

oxide flows through a piece of capillary glass tubing;* the other, the pressure drop when fluorine flows through a pinhole in a small sheet of platinum, the drop in pressure being measured in a manometer which contains Kel-F oil [poly(chlorotrifluoroethylene)]. The gases flow from cylinders of commercial-grade carbon monoxide and fluorine, the flow rates being controlled by hand-operated valves. A nickel diaphragm valve of the 413 type made by Hoke, Inc., is suitable to control the flow of fluorine. The flowmeter for fluorine is calibrated by establishing a fixed flow of fluorine and collecting a measured sample of the gas over Kel-F oil, using a stopwatch to determine the time required.†

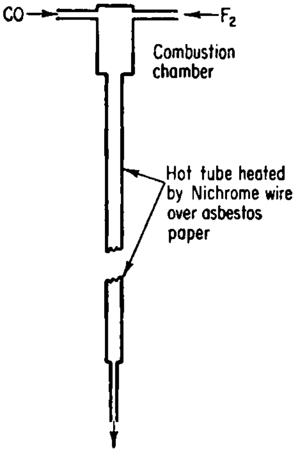

FIG. 6. Reaction vessel for preparation of trifluoromethyl hypofluorite.

A satisfactory reaction vessel made from copper tubing and fabricated by using silver solder is shown in Fig. 6. The tubing for introducing and leading away gases is 0.63 cm. o.d. The combustion chamber for carbon monoxide and fluorine is 4.5 cm. o.d. and 9 cm. long. The electrically heated tube is 17 mm. o.d. and 80 cm. long and

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* The checkers used a calibrated bubble counter.

† The checkers used a fluorine generator of calibrated output.

is covered with asbestos paper over which 9.2 meters of Nichrome heating wire (2.28 ohms resistance per meter) is wound with uniform spacing between turns. This in turn is covered with more asbestos paper. The combustion chamber is not insulated, because it is desirable at this part of the system to allow heat to escape to prevent ignition of the copper vessel.*

When in operation, the heated tube should be at about 350°. This condition can be established by using a thermometer or thermocouple inserted into a well (not shown in Fig. 6) or by applying the proper voltage to the heating coil to give a temperature of 350°. This voltage can be established, before using the apparatus for the preparation of trifluoromethyl hypofluorite, by applying various voltages and reading the resulting temperatures as indicated by a thermometer inserted in the heated tube.

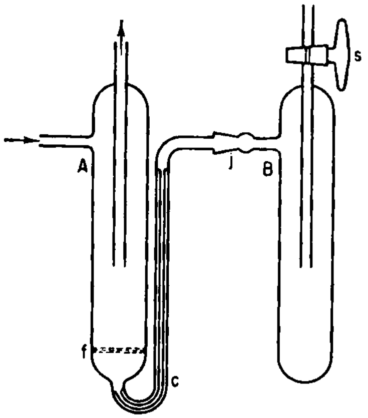

Fig. 7. Low-temperature filter.

Traps of Pyrex glass for collecting and handling the product are shown in Fig. 7. Trap *A* is about 23 cm. in length and 3 cm. in diameter. In the figure, the letter *f* indicates a medium-porosity sintered-glass filter; *j* repre-

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* The checkers added a cooling coil to the combustion chamber.

sents a ground joint lubricated with Kel-F grease; *s* stands for a stopcock with a Teflon plug or a glass plug lubricated with Kel-F grease.

Procedure

Caution. Fluorine presents some, though not an extreme, hazard because of its toxicity. It ignites combustible materials spontaneously and may start laboratory fires. Waste fluorine from the reaction should be discharged into a hood, and the waste vent should not be close to materials which will burn. Fluorine in high concentration burns human skin. The burn seems to be caused at least as much by heat as by the hydrogen fluoride produced by the reaction.

Liquid oxygen also may cause bad fires or explosions. Care should be taken to avoid handling combustible materials in traps cooled by liquid oxygen, and combustible solvents should be kept at least several feet away. Liquid oxygen and Dry-Ice–acetone should not be used at the same time as coolants on a single vacuum rack.

In operation, the gases enter at diametrically opposite sides of the cylindrical combustion chamber. It is here that much carbonyl fluoride is formed and much heat is liberated. If flow rates are too high, the heat of the reaction may ignite copper in contact with fluorine. The capacity of the apparatus to produce trifluoromethyl hypofluorite appears to be limited by the rate of removal of heat from this reactor. A mixing chamber made from copper, nickel, Monel metal, or other fluorine-resistant metal should be satisfactory, provided that adequate provision is made for removal of heat. Suitable rates of flow for the apparatus described are: fluorine, about 5 l./hour; carbon monoxide, about 2 to 2.3 l./hour. The limiting rates have not been established.* It is important that the ratio by volume of fluorine to carbon monoxide be somewhat more than 2:1.

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* The checkers used flow rates of 7 l. of fluorine and 3 l. of carbon monoxide per hour.

The stream of mixed gases passes from the mixing chamber through the electrically heated copper tube, held near 350° by controlling the electrical current in the coil of resistance wire. Temperatures in excess of about 400° must be avoided because of the possibility that fluorine may ignite the copper vessel.

Gas from the hot tube is passed through glass trap *A* (Fig. 7), which is immersed in liquid oxygen (not nitrogen) up to the level of the letter *A* on the diagram. Most of the gas condenses as liquid CF_3OF, solid COF_2, and solid CF_3OOCF_3. Enough fluorine condenses to cause the liquid to be yellow. Much of the excess fluorine passes from the trap as gas which escapes into a fume hood. If liquid nitrogen is used as the refrigerant for trap *A*, all of the excess fluorine condenses together with a large quantity of air.

After the desired volume of liquid has condensed in trap *A*, the flow of gas is cut off. Trap *B* is immersed in liquid oxygen up to the level of the letter *B* on the diagram; then gas is pumped from the system through stopcock *s*. This causes liquid to flow from trap *A*, through filter *f* and capillary tube *c*. Solids are held back on the filter. After the liquid has been transferred, pumping is stopped and the traps are separated at *j*. A ground-glass plug greased with Kel-F grease is inserted in the socket part of *j*. The pumping of gas through *s* is then resumed until all fluorine has been removed from the liquid, as shown by the disappearance of the yellow color. Liquid remaining in trap *B* is substantially pure trifluoromethyl hypofluorite. It may be subjected to fractional distillation, but for most purposes this is unnecessary.

Removal of the fluorine by pumping offers some experimental difficulty. The gas ignites pump oil and causes vanes in oil pumps to stick. It also ignites rubber tubing. The latter difficulty can be overcome by using copper or glass tubing. A simple connection of two pieces of the hard tubing may be made by inserting them into a short length of rubber tubing so that the pieces of hard tubing are in contact with each other. A water aspirator, operating in a fume hood, can be used to remove most of the fluorine. The remainder of the fluorine can be pumped away by using an oil pump (preferably an old pump because of the abusive service required in pumping fluorine). *The gas is drawn through a bed of granular soda lime to remove most of the fluorine before it gets to the pump.*

Yields of trifluoromethyl hypofluorite may run as high as 90% of that theoretically obtainable from the carbon monoxide.

Properties

Trifluoromethyl hypofluorite is a colorless or nearly colorless substance which boils at −95.0°. The freezing point is not known, but the liquid can exist at −215°. It is a highly poisonous substance and is a very strong oxidizing agent. It hydrolyzes rapidly in basic solutions to give carbonate and fluoride ions. With water at 25° the hydrolysis is very slow, if it occurs at all. The gas decomposes reversibly into carbonyl fluoride and fluorine at temperatures above 370°. It is in general a very reactive substance.[3–6] Under the influence of ultraviolet light it combines with ethylene to give $CF_3OCH_2CH_2F$.[5] Some of its reactions are explosive.

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CHAPTER VIIB

43. AMMONIUM PERRHENATE

$$HReO_4 + NH_3 \rightarrow NH_4ReO_4$$

Submitted by Richard J. Thompson*
Checked by Tung-ch'ing Wang,† Jacob Kleinberg,† George M. Adams,‡ and Burl E. Bryant‡

Rhenium is commonly separated as the heptasulfide and isolated as potassium perrhenate, a substance which is sparingly soluble in water.[1] The ammonium salt, which is desirable for the preparation of pure rhenium[2–4] and rhenium compounds,[4,5] is less readily obtained than is the potassium salt because of the pronounced solubility of ammonium perrhenate in water.[1] Ammonium perrhenate can be obtained readily by neutralizing a solution of perrhenic acid with ammonia.

Procedure

A perrhenic acid solution is obtained from 10.0 g. (0.036 mol) of potassium perrhenate by the method of Watt and Thompson.[6]§ The perrhenic acid solution is concentrated

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‡ North Texas State University, Denton, Tex.

§ Dowex 50-WX2 (but not Dowex 50-WX8) may be used in the ion-exchange column instead of Dowex 50-WX1, which is no longer available. The use of an ion-exchange column coated with "Instatherm," fabricated by the Ace Glass Co., Inc., Vineland, N.J., has been found to facilitate the conversion of potassium perrhenate to perrhenic acid. Thereby, the column can readily be held at a temperature of 95°, at which the potassium perrhenate will remain in solution (solubility,[7] about 80 g./l. at 95°).

at 90° to as low a volume as possible without decomposition (about 5 ml.). If the concentration of the solution is continued until darkening occurs (at about 3 to 4 ml.), the color should be removed by adding one drop of 30% hydrogen peroxide solution.* The solution is cooled to 0°. To the stirred, chilled solution is slowly added a chilled mixture of 15 ml. of 2-propanol (saturated with gaseous ammonia) and 50 ml. of diethyl ether. The chilled mixture is allowed to stand for one hour, after which the white crystals are transferred onto the sintered-glass disk of a crucible, washed with three 10-ml. portions of 2-propanol–diethyl ether (1 part of 2-propanol to 9 parts of diethyl ether by volume), freed of solvent *in vacuo* and dried at 110°. The yield is 8.9 g. (96%). *Anal.* Calcd. for NH_4ReO_4: Re, 69.4; N, 5.23. Found: Re, 69.7; N, 5.20. By checkers: N, 5.53; per cent purity, 99.4, 99.95 (by titration with standard base after passage of water solutions of two weighed samples through acid ion-exchange resin).

Properties

Ammonium perrhenate is a white salt which has a solubility of 17 g./l. at 0° and 162 g./l. at 50.2°.[1] Its density is 3.53 g./cc. The compound decomposes at 365°.

Ammonium hexahalorhenate(IV) compounds can readily be made by substituting ammonium perrhenate for the potassium salt in procedures such as those for the synthesis of potassium hexabromorhenate(IV) and potassium hexachlororhenate(IV).[8]

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* When the solution is concentrated to a volume of 5 ml. or lower, the yield will be well over 90%. With higher volumes the yield is decreased markedly (65 to 70% yield with a 10-ml. volume, for example).

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44. BIS(ETHYLENEDIAMINE)DIOXORHENIUM(V) CHLORIDE, BIS(ETHYLENEDIAMINE)OXOHYDROXORHENIUM(V) PERCHLORATE, AND BIS(ETHYLENEDIAMINE)DIHYDROXORHENIUM(V) HEXACHLOROPLATINATE(IV)

Submitted by R. Kent Murmann*
Checked by C. J. L. Lock† and G. Wilkinson†

Compounds of rhenium containing coordinated amines are uncommon and are generally difficult to prepare. Exceptions are found in compounds containing the ion $[Re(en)_2O_2]^+$, which have been described by Lebedinsky and Ivanov-Emin.[1] These compounds are readily prepared by air oxidation of $[ReCl_6]^{2-}$ in the presence of 90% ethylenediamine.

Procedure

A. BIS(ETHYLENEDIAMINE)DIOXORHENIUM(V) CHLORIDE

$$4K_2ReCl_6 + 8C_2H_4(NH_2)_2 + O_2 + 6H_2O \rightarrow 4[Re(en)_2O_2]Cl + 8KCl + 12HCl‡$$

Five grams (0.0105 mol) of potassium hexachlororhenate(IV)[2] is ground to a fine powder and quickly added to 25 ml.

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† Imperial College of Science and Technology, London, England.

‡ This reaction will proceed without oxygen, probably with oxidation by the ethylenediamine. However, the yields in the absence of oxygen are lower.

(0.40 mol) of 90% ethylenediamine contained in a 100-ml. Erlenmeyer flask. Reaction starts after a few minutes, and the mixture becomes warm. After 15 minutes of vigorous hand stirring, a very slow stream of air is passed into the solution for 12 hours. Then 50 ml. of ice-cold acetone is added with stirring (heat evolved), and the mixture is added to 500 ml. of cold acetone in a 1-l. flask. After 10 minutes of stirring, the crude product is collected by vacuum filtration* and washed five times with 100-ml. portions of acetone. The precipitation flasks are rinsed with a total of 50 ml. of water, and the crude product is dissolved in the rinsings. After filtration, 500 ml. of acetone is added and the product is collected on a filter. The yield is 3.1 g. (80%). The product at this stage is sufficiently pure to use for subsequent preparations. Recrystallization is accomplished by dissolving the product in the minimum quantity of warm (65°) water containing 2 drops of 1 *N* hydrochloric acid, adding 35 ml. of absolute methanol, and cooling to 0°. After 2 hours at 0°, the brownish-green crystalline product is collected on a filter, washed with absolute methanol, and dried under vacuum at 58°. The yield is 2.62 g. (67%). *Anal.* Calcd. for $ReC_4H_{16}N_4O_2Cl$: Re, 49.81; Cl, 9.50; C, 10.2; H, 4.3; oxidation state change for $[Re(en)_2O_2]^+ \rightarrow ReO_4^-$, 2.0. Found: Re, 49.5; Cl, 9.32; oxidation state change, 1.97. By checkers: C, 10.0; H, 4.1.

B. BIS(ETHYLENEDIAMINE)OXOHYDROXORHENIUM(V) PERCHLORATE

$$[Re(en)_2O_2]Cl + 2HClO_4 \rightarrow [Re(en)_2O(OH)](ClO_4)_2 + HCl$$

Caution. Bis(ethylenediamine)oxohydroxorhenium(V) perchlorate explodes violently upon drying at temperatures above room temperature. The compound is also somewhat sensitive to shock. Although no explosions have occurred below 40° in the author's laboratory unless the compound was

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* Some of the product is oily and sticks to the sides of the flask.

struck with a heavy object, temperatures above 25° are not considered safe. The checkers report that carbon-hydrogen and nitrogen analyses have frequently resulted in shattered combustion tubes. Extreme care must always be exercised with respect to temperature and mechanical shock when working with the dry compound.

One gram (0.0027 mol) of $[Re(en)_2O_2]Cl$ is dissolved in 7.0 ml. of water, and a mixture of 1.0 ml. of 60% $HClO_4$ (0.012 mol) and 2.0 ml. of water is quickly added. After cooling in an ice bath for 25 minutes, the purple needles are collected on a filter and dried under vacuum *at room temperature.* (*See Caution at beginning of this section.*) The yield is 1.10 g. (76%). *Anal.* Calcd. for $ReC_4H_{17}N_4O_{10}Cl_2$: Re, 34.60; N, 10.4; ClO_4, 36.96. Found: Re, 34.48. By checkers: N, 10.7; ClO_4, 36.77.

C. BIS(ETHYLENEDIAMINE)DIHYDROXORHENIUM(V) HEXACHLOROPLATINATE(IV)

$$2[Re(en)_2O_2]Cl + 3H_2PtCl_6 \rightarrow [Re(en)_2(OH)_2]_2(PtCl_6)_3 + 2HCl$$

One gram (0.0027 mol) of $[Re(en)_2O_2]Cl$ is dissolved in 10 ml. of concentrated hydrochloric acid at room temperature. To this solution is added 5 ml. of a solution of H_2PtCl_6 in concentrated hydrochloric acid (about 0.2 g. Pt/ml.; 0.0051 mol Pt in 5 ml.) After cooling at 0° for 15 minutes, the gray-green crystals are collected on a sintered-glass filter, washed with concentrated hydrochloric acid, and dried under vacuum at 50 to 70°. The yield is 2.0 g. (80%). *Anal.* Calcd. for $Re_2C_8H_{36}N_8O_4Pt_3Cl_{18}$: Re, 19.56; C, 5.04; H, 1.9; O, 3.4. Found: Re, 19.82. By checkers: C, 5.0; H, 2.0; O, 3.5.

Properties

Bis(ethylenediamine)dioxorhenium(V) chloride consists of brown-green plates which dissolve in water to give a yellow-green solution with an absorption maximum at 440 mμ and a molar absorbancy of 20.1. In water or dilute acid the compound is stable, but it decomposes in alkaline media. It is insoluble in absolute methanol and acetone and forms sparingly soluble iodide, perchlorate, and hexachloroplatinate(IV) salts. It is diamagnetic and has an electrical conductivity corresponding to a 1:1 electrolyte. In neutral or slightly basic solution, the oxygen atoms are slow to exchange with the solvent.[3] Its infrared spectrum is almost identical with that of *trans*-$[Co(en)_2Cl_2]Cl$ except that most peaks are shifted to higher frequencies. This, coupled with the fact that attempts to resolve it into optical isomers with the *d*-3-bromo-8-camphorsulfonate ion have failed, suggests that the oxygen atoms are trans to each other. Quantitative oxidation of $[Re(en)_2O_2]Cl$ takes place with Ce^{4+} in acid and with bromine in basic solution.

Bis(ethylenediamine)oxohydroxorhenium(V) perchlorate consists of purple needles which dissolve in water or acids to give a purple solution. It is acidic, with a dissociation constant of 5×10^{-4}. In water it partially reverts to the dioxo form but is stable in dilute acid. It is insoluble in absolute methanol and acetone. An absorption maximum at 487 mμ, molar absorbancy of 19.1, is observed together with a weak absorption at 650 mμ.

Bis(ethylenediamine)dihydroxorhenium(V) hexachloroplatinate(IV) occurs in the form of small gray-green crystals which are unstable in water. The $[Re(en)_2(OH)_2]^{3+}$ ion is a very strong acid which has a deep blue color with absorption maxima at 610 and 840 mμ with molar absorbancies of 20.8 and 8.5, respectively. The chloride salt is soluble in concentrated hydrochloric acid.

The analogous forms of each of these complexes may be prepared with 1,2- and 1,3-propanediamine but not with *N*-alkylethylenediamines.

Analysis

Except in the presence of perchlorate, rhenium is determined gravimetrically by oxidation with hydrogen peroxide in a dilute nitric acid medium followed by precipitation of the perrhenate ion with "Nitron" or with $(C_6H_5)_4As^+$. *In the presence of* ClO_4^-, rhenium is determined colorimetrically by using furil dioxime and tin(II) ion.[4] With this method, the complex must first be oxidized to ReO_4^- by fuming it with nitric acid and the excess acid evaporated. The oxidation state is determined by oxidation to ReO_4^- with cerium(IV) ion in a dilute sulfuric acid solution. The titration is followed potentiometrically by using platinum and calomel electrodes. Chlorine is determined by silver chloride precipitation from dilute nitric acid.

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CHAPTER VIII

See also: Complex carbonates of beryllium, synthesis 2
Bis(ethylenediamine)dioxorhenium(V) chloride, bis(ethylenediamine)oxohydroxorhenium(V) perchlorate, and bis(ethylenediamine)dihydroxorhenium(V) hexachloroplatinate(IV), synthesis 44

45. DIIRON ENNEACARBONYL

$$2Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9 + CO$$

Submitted by E. H. Braye* and W. Hübel*
Checked by Marvin D. Rausch† and Thomas M. Wallace†

Speyer and Wolf[1] obtained diiron enneacarbonyl, $Fe_2(CO)_9$, by exposing an acetic acid solution of iron pentacarbonyl to sunlight. The yield of 30% claimed by these authors is reached only under the ideal conditions of bright sunshine and low temperatures. The modified procedure which is described here is based on the use of artificial light and water cooling of the reaction mixture; it gives consistently high yields of diiron enneacarbonyl.

Procedures

Two different procedures are given; the choice between them will depend upon the availability of the special equipment required. *Caution. Regardless of the procedure*

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* Union Carbide, European Research Associates, S. A., Brussels, Belgium.
† Monsanto Company, St. Louis, Mo.

chosen, the reaction must be run in a hood inasmuch as the iron carbonyls and carbon monoxide are highly toxic.

Procedure A

A three-necked 1-l. Pyrex flask equipped with an efficient stirrer, gas inlet, and mercury valve is flushed with nitrogen and charged with 100 ml. (146 g.; 0.746 mol) of iron pentacarbonyl and 200 ml. of glacial acetic acid.* The reaction vessel is placed in a 5-l. silvered Dewar flask† and is cooled continuously by running water.‡ The reaction mixture is irradiated by a 125-watt high-pressure mercury lamp. A suitable lamp circuit, constructed to avoid contact of the cooling water with the lamp, is made up with a quartz tube (about 30 cm. long and 1.7 cm. i.d.). The tube, which is closed at one end, contains a Philips mercury-vapor lamp (HPK 125 W, type 57203B) to which extension wires insulated with porcelain beads have been attached. The lamp assembly is placed in the water of the bath as close to the reaction flask as possible. Efficient stirring of the reaction mixture is necessary in order to avoid reduction of the light intensity owing to deposition of diiron enneacarbonyl on the walls of the reaction vessel; if deposition should occur, the reaction may be interrupted from time to time in order to remove the diiron enneacarbonyl which has formed. The filtrate is then reintroduced into the reaction vessel after it has been flushed with nitrogen once more. After

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* If the acetic acid contains more than 5% of water, the reaction yields only a brown pyrophoric powder.

† Both the authors and the checkers have successfully substituted for the silvered Dewar flask a plastic pail carefully lined on sides and bottom with aluminum foil and provided with an improvised aluminum foil lid having holes for the clamps and stirrer. The pails used varied in size from 8 to 13 l.; a hole was cut near the top, a metal spout inserted in the hole, and a drain hose attached to the spout. A hose inserted to the bottom of the pail delivered cooling water to the system and provided the means of keeping the temperature of the reaction mixture between 20 and 25°.

‡ The reaction rate, as well as the yield of the reaction, appears to be fairly independent of temperature up to 25°.

24 hours of irradiation, the precipitated diiron enneacarbonyl is filtered from the solution, is washed first with ethanol and then with ether, and is dried *in vacuo*. The yield is 100 to 122 g. (74 to 91% based on iron pentacarbonyl; the yield of 74% is obtained when using a silvered Dewar without a lid, and the 91% yield is obtained when using the plastic pail completely lined with aluminum foil and with a lid of the same material). *Anal.* Calcd. for $Fe_2(CO)_9$: Fe, 30.71; C, 29.70; O, 39.59. Found: Fe, 30.58; C, 29.95; O, 39.78.

Procedure B

The lamp described in Procedure A is a variety that is not readily obtainable in the United States; a suitable alternative is a 100-watt General Electric mercury lamp (H-100-A4/T).

The General Electric lamp is connected by an extension cord to a General Electric Autotransformer (Model No. 9T64Y3518), a transformer especially designed for 100-watt Type H-4 mercury-vapor lamps. After the lamp has been suspended in a quartz tube (approximately 34 cm. long and 5.0 cm. i.d. and rounded and closed on one end), the assembly is ready to be inserted into the cooling bath for use in the irradiation step.

With the exception of the irradiation time, which should be increased to 34 hours owing to the lower light intensity provided by the General Electric lamp, all experimental details given in Procedure A are pertinent and may be followed exactly. The yield is 97 g. (72%) for 30 hours' irradiation and 100 g. (74%) for 35 hours' irradiation.

Properties

Diiron enneacarbonyl is obtained as shiny orange hexagonal leaflets having a density[2] of 2.08 g./cc. The com-

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pound decomposes at 100 to 120°. It is practically insoluble in all organic solvents and is slowly decomposed in tetrahydrofuran and methylene chloride. It can be stored for long periods of time in the dark in an inert atmosphere, preferably carbon monoxide. Aged diiron enneacarbonyl, which may be contaminated with pyrophoric materials, is readily purified by washing it under nitrogen with 25% hydrochloric acid, water, ethanol, and finally ether, and drying it *in vacuo.*

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46. TRIIRON DODECACARBONYL

$$3Fe(CO)_5 + NR_3 + 2H_2O \rightarrow [R_3NH][HFe_3(CO)_{11}] + 2CO_2 + 2CO + H_2$$

$$12[R_3NH][HFe_3(CO)_{11}] + 18HCl \rightarrow 11Fe_3(CO)_{12} + 15H_2 + 3FeCl_2 + 12R_3NHCl^*$$

Submitted by W. McFarlane† and G. Wilkinson†
Checked by W. Hübel‡

Triiron dodecacarbonyl can be used with advantage in place of iron pentacarbonyl in many syntheses because it often reacts under milder conditions and is easier to handle. The compound was originally prepared[1] by treating the solution obtained by dissolving iron pentacarbonyl in

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* This is a probable equation. The stoichiometry has not yet been uniquely proved.

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aqueous alkali with manganese(II) oxide and then acid; directions for this procedure have been given by King and Stone.[2] The purpose of the manganese(II) oxide is somewhat obscure, but it is believed[3,4] that it accelerates the polymerization of pale yellow $[HFe(CO)_4]^-$ ion to the dark red species $[HFe_2 CO)_8]^-$ and $[HFe_3(CO)_{11}]^-$, the latter giving $Fe_3(CO)_{12}$ on acidification. It has been found[4,5] that aqueous strongly basic organic amines react readily with iron pentacarbonyl to give the polynuclear ion which on acidification gives $Fe_3(CO)_{12}$ almost quantitatively. The German workers[5] used formic acid, but hydrochloric acid as used herein is satisfactory. The following procedure, adapted from this work, gives high yields of the carbonyl with little manipulation and is satisfactory for large-scale operation.

Procedure

Caution. The preparation should be performed in an efficient hood because iron pentacarbonyl is highly toxic.

First, 240 ml. of air-free water is placed in a 1-l. nitrogen-filled three-necked flask equipped with a stirrer and a reflux condenser. Then, 110 ml. (160 g.; 0.82 mol) of iron pentacarbonyl and 83 ml. (60 g.; 0.59 mol) of triethylamine are added, and the mixture is stirred and heated at 80° under nitrogen for 10 hours or overnight, whichever is more convenient. It is important that the proper temperature be maintained, because below 75° the reaction is incomplete and above 90° decomposition of the iron complex occurs.

The triethylammonium hydrogen undecacarbonyltriferrate, $[Et_3NH][HFe_3(CO)_{11}]$, formed in this reaction is a deep red oil at 80° but solidifies when the mixture is cooled. The air-stable solid is washed several times with water* and then dissolved in about 600 ml. of methanol.

* Some care should be exercised here because some unchanged iron pentacarbonyl may still remain. Washings should not be disposed of by drains unless bromine water has been added to destroy any carbonyl.

To the methanol solution is added slowly 1 l. of 1:1 hydrochloric acid–water mixture, and the solution is heated on a steam bath for several hours until the solution is colored pale green and the iron dodecacarbonyl is floating on the surface. The product is removed, washed several times with water, methanol, and petroleum ether (boiling range 40 to 60°) in succession, and dried *in vacuo*. It sometimes happens that iron dodecacarbonyl made in this way is so finely divided as to be pyrophoric when dry; this danger is avoided if the crude product is placed in the thimble of a Soxhlet apparatus and extracted with petroleum ether (boiling range 40 to 60°). Comparatively large crystals are then obtained and the effect upon the yield (90 to 96 g.) is negligible. The precise yield is somewhat variable and rather sensitive to the conditions.

Properties

Triiron dodecacarbonyl is a very dark green dense solid which normally appears black. It is slowly attacked by atmospheric oxygen; if it is to be stored for more than a few days, air should be excluded. Although it is but sparingly soluble in most common organic solvents, its solutions in them are intensely colored and deposit iron mirrors on glassware on standing in the air or on boiling. The structure is unknown but x-ray work[6] on the analogous osmium dodecacarbonyl makes it probable that the view that the compound contains bridging carbonyl groups is incorrect.

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47. TRICARBONYL(CYCLOOCTATETRAENE)IRON

$$Fe_3(CO)_{12} + 3C_8H_8 \rightarrow 3C_8H_8Fe(CO)_3 + 3CO$$

Submitted by W. McFarlane* and G. Wilkinson*
Checked by W. Hübel†

The three reported preparations[1–3] of tricarbonyl(cyclooctatetraene)iron involve the interaction of cyclooctatetraene with iron pentacarbonyl. Although the yields are good, considerable amounts of $C_8H_8[Fe(CO)_3]_2$ and $C_8H_8Fe_2(CO)_7$ are often obtained as well. The reaction between cyclooctatetraene and triiron dodecacarbonyl takes place more rapidly and gives a product of better purity.

Procedure

Caution. This preparation should be performed in a hood inasmuch as small amounts of iron pentacarbonyl are occasionally formed in the reaction.

Eight and four-tenths grams (0.017 mol) of triiron dodecacarbonyl (synthesis 46), 6 ml. (0.057 mol) of cyclooctatetraene, and 30 ml. of petroleum ether (boiling range 120 to 130°) are placed in a 100-ml. flask equipped with a reflux condenser. The mixture is gently refluxed under nitrogen until the color changes from deep green to brown (about 30 minutes), and it is then filtered in the air. The solvent is removed from the clear brown solution under reduced pressure, and the product is recrystallized from the minimum volume of hot ethanol. The tricarbonyl(cyclooctatetraene)iron obtained in this way is fairly pure but may be further purified from the last traces of $C_8H_8[Fe(CO)_3]_2$ by subliming the product at 50° and 0.01 mm. pressure onto a water-cooled cold-finger. The yield is somewhat variable, ranging from about 7 to 11 g. (56 to 88%).

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Properties

Tricarbonyl(cyclooctatetraene)iron forms red-brown air-stable crystals which melt at 94°. It is insoluble in water but dissolves readily in organic solvents. It is easily sublimed. X-ray studies[4] indicate that the metal is bound to two double bonds only, and the unsaturation is also shown by the protonation in concentrated sulfuric or other strong acid solutions to give the tricarbonylbicyclo[5.1.0]-octadieniumiron ion, $C_8H_9Fe(CO)_3^+$, and by the formation of a Diels-Alder adduct with tetracyanoethylene.[5]

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48. IRON CARBONYL COMPLEXES OF TRIPHENYLPHOSPHINE, TRIPHENYLARSINE, AND TRIPHENYLSTIBINE

$$[Fe(CO_4)_3 + 3(C_6H_5)_3M \rightarrow 3[Fe(CO)_4\{(C_6H_5)_3M\}]$$

$$(M = P, As, Sb)$$

$$Fe(CO)_5 + (C_6H_5)_3M \rightarrow [Fe(CO)_4\{(C_6H_5)_3M\}] + CO$$

$$[Fe(CO)_4\{(C_6H_5)_3M\}] + (C_6H_5)_3M \rightarrow [Fe(CO)_3\{(C_6H_5)_3M\}_2] + CO$$

Submitted by A. F. Clifford* and A. K. Mukherjee*
Checked by Donald C. Jicha† and Forrest C. Hentz, Jr.†

Iron carbonyl phosphines were first mentioned by Reppe and Schweckendiek[1] as products of the direct reaction

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* Purdue University, Lafayette, Ind. This work was performed under a subcontract with the U.S. Borax Research Corporation and is part of a program supported by Materials Central, Wright Air Development Division, under Contract AF 33 (616)-5931.

† University of North Carolina, Chapel Hill, N.C.

between triphenylphosphine and iron pentacarbonyl. However, no details were given.

Later, Hallam and Pauson[2] prepared $[Fe(CO)_3\{(C_6H_5)_3P\}_2]$ by heating triphenylphosphine in an autoclave with an equimolecular amount of $[Fe(CO)_2C_5H_5]_2$ or $[FeCl(CO)_2C_5H_5]$, or by treating $[FeI_2(CO)_3\{(C_6H_5)_3P\}]$ with cyclopentadienylsodium in tetrahydrofuran. Recently, Cotton and Parish[3] obtained the phosphine derivatives by heating triphenylphosphine and iron pentacarbonyl in a Carius tube. It has been found possible to prepare both mono- and diphosphine derivatives, as well as the corresponding arsines and stibines, much more simply by reaction in an appropriate solvent.[4]

Procedure

A. TETRACARBONYLMONO(TRIPHENYLPHOSPHINE)IRON AND TRICARBONYLBIS(TRIPHENYLPHOSPHINE)IRON

Method 1

Two grams (0.007 mol) of triphenylphosphine is dissolved in 100 ml. of dioxane or tetrahydrofuran. One gram (0.0020 mol) of triiron dodecacarbonyl (synthesis 46) is added, and the mixture is stirred in an atmosphere of nitrogen at a temperature of about 70° for 45 minutes, or until the green color of the solution completely disappears. The mixture is then cooled to room temperature, filtered, and the brown residue washed with dioxane or tetrahydrofuran. The solvent is removed from the filtrate and washings by distillation under vacuum and the residue treated with 50 ml. of methanol or ethanol and cooled. A yellow crystalline product is obtained. The crystals are filtered, washed with two 10-ml. portions of petroleum ether, and sublimed under vacuum at 180°. The sublimate consists of $[Fe(CO)_4\{(C_6H_5)_3P\}]$, which melts at 201 to 203° with decomposition. The residue from the sublimation is dissolved in a minimum amount of benzene, and the solution is filtered. The filtrate is then diluted with about 4 to 6 times its own volume of petroleum ether and cooled to give yellow crystals of $[Fe(CO)_3\{(C_6H_5)_3P\}_2]$, which melt at 272° with decomposition. Another fraction of the products can be isolated from the brown residue by extraction with benzene followed by filtration. Benzene is distilled from the yellow filtrate under vacuum, and the products are separated and isolated from the residue by vacuum sublimation as described above. The final yield is 0.88 g. of $[Fe(CO)_4\{(C_6H_5)_3P\}]$ (34%) and 1.1 g. of $[Fe(CO)_3\{(C_6H_5)_3P\}_2]$ (27%). If, however, excess triphenylphosphine is used, only $[Fe(CO)_3\{(C_6H_5)_3P\}_2]$ is obtained.

METHOD 2

The compounds may also be prepared by using iron pentacarbonyl as the starting material. Two milliliters (0.015 mol) of iron pentacarbonyl and 5 g. (0.02 mol) of triphenylphosphine are placed in about 100 ml. of freshly distilled cyclohexanol, and the mixture is refluxed for about one hour in an atmosphere of nitrogen. It is then diluted with an equal volume of petroleum ether and cooled. The resulting yellow precipitate, consisting of a mixture of $[Fe(CO)_4\{(C_6H_5)_3P\}]$ and $[Fe(CO)_3\{(C_6H_5)_3P\}_2]$, is then filtered, washed with petroleum ether, and dried. The two compounds are then separated by vacuum sublimation. The yield is 0.98 g. of $[Fe(CO)_4\{(C_6H_5)_3P\}]$ (15%) and 1.2 g. of $[Fe(CO)_3\{(C_6H_5)_3P\}_2]$ (15%).

B. TETRACARBONYLMONO(TRIPHENYLARSINE)IRON AND TRICARBONYLBIS(TRIPHENYLARSINE)IRON

A mixture of 6 g. (0.016 mol) of triphenylarsine and 2 g. (0.004 mol) of triiron dodecacarbonyl (synthesis 46) is either refluxed in 150 ml. of tetrahydrofuran or heated at 80 to 90° in dioxane in an atmosphere of nitrogen for 45 minutes. The mixture is then cooled and filtered. The residue is rejected. It contains very little product, inasmuch as the arsine complexes are more soluble than the phosphine derivatives in dioxane or tetrahydrofuran. From the filtrate the products are separated by evaporation of the solvent and isolated by vacuum sublimation at 2 to 5 mm. pressure, first at 100° to remove unreacted triphenylarsine and then at 160° in the same manner as for the phosphine compounds in Part A. The yield of $[Fe(CO)_4\{(C_6H_5)_3As\}]$ (monoclinic needles; m.p. 178° with decomposition) can be up to 1.0 g. (17.5%), and the yield of $[Fe(CO)_3\{(C_6H_5)_3As\}_2]$ (m.p. 193 to 195° with decomposition) up to 1.8 g. (20%). However, yields are likely to be erratic because of the varying extents to which decomposition of the mixture may occur during sublimation. *Anal.* Calcd. for $[Fe(CO)_4\{(C_6H_5)_3As\}]$: C, 55.71; H, 3.19; Fe, 11.77; mol. wt., 474. Found: C, 55.56; H, 3.29; Fe, 11.26; mol. wt., 466 (determined cryoscopically in benzene). Calcd. for $[Fe(CO)_3\{(C_6H_5)_3As\}_2]$: C, 62.26; H, 4.02; Fe, 7.42; mol. wt., 752. Found: C, 62.55; H, 4.02; Fe, 7.16; mol. wt., 767.

C. TETRACARBONYLMONO(TRIPHENYLSTIBINE)IRON AND TRICARBONYLBIS(TRIPHENYLSTIBINE)IRON

A mixture of 6 g. (0.017 mol) of triphenylstibine and 2 g. (0.0040 mol) of triiron dodecacarbonyl (synthesis 46) is refluxed in tetrahydrofuran or heated in dioxane at 90 to 95° in an atmosphere of nitrogen for one hour and filtered. The mixed products are then isolated from the filtrate by removing the solvent under vacuum and treating the residue with methane. The compounds are then separated from each other by fractional crystallization from benzene and methanol. The less soluble fraction gives $[Fe(CO)_3\{(C_6H_5)_3Sb\}_2]$ (m.p. 196° with decomposition). The yield is 1.3 g. (13%). From the more soluble fraction the pure mono derivative, $[Fe(CO)_4\{(C_6H_5)_3Sb\}]$, is obtained (m.p. 136°, sharp). The yield is 1.2 g. (20%). *Anal.* Calcd. for $[Fe(CO)_4\{(C_6H_5)_3Sb\}]$: C, 50.61; H, 2.90; Fe, 10.72; mol. wt., 521. Found: C, 50.60; H, 2.60; Fe, 10.49; mol. wt., 523. Calcd. for $[Fe(CO)_3\{(C_6H_5)_3Sb\}_2]$: C, 55.37; H, 3.57; Fe, 6.60; mol. wt., 846. Found: C, 55.00; H, 3.93; Fe, 6.41; mol. wt., 838.

Similar treatment of triiron dodecacarbonyl solutions with triphenylbismuthine and triphenylamine gives no isolable products. In the former case, the original green color of the solution is discharged in about 2 hours and an unidentifiable, brown, amorphous, uncrystallizable solid precipitates. In the latter case, a brown solid which contains no nitrogen is obtained. The triphenylamine is recovered unchanged.

Properties

All of these compounds are soluble in most organic solvents. They are very stable to air and light, although on long exposure to daylight tricarbonylbis(triphenylphosphine)iron has been observed to darken on the exposed surface. The corresponding tricarbonyl-*o*-phenylenebis(dimethylarsine)iron and carbonylbis[*o*-phenylenebis(dimethylarsine)]iron are reported[5] to darken gradually on standing, although they are more stable to light than is iron pentacarbonyl. As compared with the great stability of both $[Fe(CO)_4\{(C_6H_5)_3Sb\}]$ and $[Fe(CO)_3\{(C_6H_5)_3Sb\}_2]$, the antimony trichloride substitution compound, $[Fe(CO)_3(SbCl_3)_2]$,[6] is quite unstable and photosensitive. A series of substitution products of nitrosyldicarbonyliron[7] with triaryl phosphites, phosphines, arsines, and stibines has been prepared; all of these are oxidized spontaneously in air when not perfectly dry and also when stored at low temperatures, whereas the compounds listed in Table I are all stable to

TABLE I*

Compound	Color	M.p., °C. (with decomp.)
$[Fe(CO)_4\{(C_6H_5)_3P\}]$	Pale yellow	201–203
$[Fe(CO)_3\{(C_6H_5)_3P\}_2]$	Yellow	272
$[Fe(CO)_4\{(C_6H_5)_3As\}]$	Yellow	178
$[Fe(CO)_3\{(C_6H_5)_3As\}_2]$	Yellow	193–195
$[Fe(CO)_4\{(C_6H_5)_3Sb\}]$	Yellowish brown	136†
$[Fe(CO)_3\{(C_6H_5)_3Sb\}_2]$	Yellowish brown	196

* From *Inorganic Chemistry*, **2**, 151 (1963); reprinted by permission.
† Sharp, no decomposition.

air, light, and water. The compound $[Fe(CO)_3\{(C_6H_5)_3P\}_2]$ is not attacked by hot alcoholic alkali or by cold concentrated acids, and it remains unchanged even when heated at 110° for 24 hours. The compound is, however, slowly cleaved by potassium in boiling dioxane, one of the products being $(C_6H_5)_2PK$. It reacts with iodine in ether to give $[FeI_5(CO)_2\{(C_6H_5)_3P\}_2]$. The bis derivatives are always more stable than the mono ones and, in either type, the stability decreases from phosphine to arsine to stibine compounds. Thus, both the monophosphine and monoarsine compounds can be sublimed in a vacuum, but the monostibine compound decomposes under these conditions. Another notable feature of the complexes is the stability of the carbon monoxide–metal bond. The direct replacement of carbon monoxide by pyridine in these complexes does not appear to be possible.

TABLE II*

Compound	Medium†	CO-stretching frequency, cm.$^{-1}$		
$[Fe(CO)_4\{(C_6H_5)_3P\}]$	Nujol	2050	1970	1930
	CCl_4	2055.0	1978.0	1943.0
	CCl_4‡	2059	1984	1946
	$CHCl_3$‡	2059	1978	1938
	CS_2‡	2063	1982	1943
$[Fe(CO)_3\{(C_6H_5)_3P\}_2]$	Nujol		1890	
	CS_2		1884.8	
	CS_2‡		1886	
	$CHCl_3$‡		1887	
$[Fe(CO)_4\{(C_6H_5)_3As\}]$	Nujol	2063	1985	1946
	CCl_4	2053.7	1977.1	1945.3
$[Fe(CO)_3\{(C_6H_5)_3As\}_2]$	Nujol		1894	
	CS_2		1884.3	
$[Fe(CO)_4\{(C_6H_5)_3Sb\}]$	Nujol	2058	1985	1946
	CCl_4	2048.0	1975.3	1942.3
$[Fe(CO)_3\{(C_6H_5)_3Sb\}_2]$	Nujol		1873	
	CS_2		1882.0	

* From *Inorganic Chemistry,* **2,** 151 (1963); reprinted by permission.

† The spectra in Nujol were obtained with an Infracord with NaCl optics. The spectra in CCl_4 and CS_2 were obtained with a Perkin-Elmer Model 421 grating instrument.

‡ Cotton and Parish, ref. 3.

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The infrared spectra in the carbonyl-stretching regions for these compounds are presented in Table II. The data of Cotton and Parish[3] for $[Fe(CO)_4\{(C_6H_5)_3P\}]$ and $[Fe(CO)_3\{(C_6H_5)_3P\}_2]$ are also included for convenient comparison.

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49. NITROSYLPENTAAMMINECOBALT(II) CHLORIDE

Submitted by Ole Bostrup*
Checked by R. S. Tobias,† Sister Sigrid Hutcheson, O.S.B.,† and W. H. Englemann†

The black crystalline compound $[Co(NH_3)_5(NO)]Cl_2$ can be prepared in pure form by saturating an ammoniacal solution of cobalt(II) chloride with nitrogen(II) oxide. Previously reported methods of preparation[1–4] result in a product contaminated with hexaamminecobalt(II) chloride, which is only slightly soluble in the solutions used and precipitates together with the black chloride. It should be noted that analysis for cobalt, chlorine, or nitrogen cannot reveal the presence of as much as 10% $[Co(NH_3)_6]Cl_2$ in a sample of $[Co(NH_3)_5(NO)]Cl_2$. The best tests for purity are microscopic examination or magnetic measurements.[5]

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[*] Frederiksborg Statsskole, Hillerød, Denmark. Appreciation is expressed to Prof. R. W. Asmussen, Technical University of Denmark, for his help and to Statens Almindelige Videnskabsfond for financial support.
[†] University of Minnesota, Minneapolis, Minn.

In order to avoid this contamination, the procedure described herein utilizes a somewhat higher temperature and a lower concentration of ammonia than has previously been suggested.[1–3] The formation of the pink precipitate of hexaamminecobalt(II) chloride is thereby completely eliminated. An additional advantage of the procedure is that no special apparatus is required.[2,3,5]

A. NITROGEN(II) OXIDE

Although cylinder nitrogen(II) oxide provides a convenient source for preparations, often it is desirable to obtain the gas quickly in fairly large quantities in the laboratory. The preparation suggested by Blanchard,[6] utilizing the reduction of sodium nitrite by means of iron(II) sulfate, is more difficult than the procedure described below, in which sodium nitrite is treated with dilute sulfuric acid.[7,8] The product thus obtained is suitable for use in the preparation of such compounds as $Fe(NO)_2Br$,[9] $Co(NO)_2Br$,[9] and $[Co(NH_3)_5(NO)]Cl_2$.[5]

Procedure

$$3NaNO_2 + H_2SO_4 \rightarrow Na_2SO_4 + NaNO_3 + 2NO + H_2O$$

(1) In a 2-l. Kipp generator, 69 g. (1 mol) of sodium nitrite in stick form is treated with 2 *M* sulfuric acid. Thereby, a readily controlled flow of nitrogen(II) oxide is produced.

(2) Alternatively, in a 1-l. flask fitted with a dropping funnel, 69 g. (1 mol) of powdered sodium nitrite is treated dropwise with 300 ml. of 2 *M* sulfuric acid.

In either case, the gas is purified by bubbling it through two washing bottles containing 30% (10 *M*) sodium hydroxide. The gas can be further purified and dried by passing it through a tower containing glass wool and solid sodium hydroxide.

The yield is 16 g. (80%).

B. NITROSYLPENTAAMMINECOBALT(II) CHLORIDE

$$CoCl_2 \cdot 6H_2O + 5NH_3 + NO \rightarrow [Co(NH_3)_5(NO)]Cl_2 + 6H_2O$$

A 1-l. flask is fitted with a three-hole stopper, to which are attached an inlet tube for gases, a dropping funnel, and an exit tube for gases. The inlet tube should be about 15 mm. in diameter to avoid plugging during the reaction. Eight hundred milliliters (5.6 mols) of 12.5% ammonia solution is placed in the flask, which is cooled in an ice bath. The apparatus is flushed for 30 minutes with nitrogen, after which time a solution of 30 g. (0.125 mol) of cobalt(II) chloride 6-hydrate in 40 ml. of water is added to the cold ammonia solution. Nitrogen(II) oxide is substituted for the nitrogen flow, and the solution is treated with the nitrogen(II) oxide gas for 3 hours. During this period, the solution darkens and black crystals are precipitated.

The nitrogen(II) oxide atmosphere is again replaced by one of nitrogen, and the mother liquor is decanted off. A 100-ml. sample of ethanol is added to the slurry, whereupon the black crystals settle to the bottom and the cobalt(II) ammines are suspended in the alcohol, making it milky. The milky phase is removed by decantation. This flotation process is repeated twice more with ethanol and once with ether. The black shiny crystals are then filtered by means of a sintered-glass crucible, washed with ether, and dried in a vacuum desiccator.

The yield is about 3 g. [10%, based on cobalt(II) chloride]. *Anal.* Calcd. for $[Co(NH_3)_5(NO)]Cl_2$: Co, 24.1; NH_3, 34.8; Cl, 28.9. Found: Co, 24.0; NH_3, 34.5; Cl, 28.8. By checkers: Co, 23.9; Cl, 28.8.

Analysis

Gravimetric Analysis of Cobalt as $CoSO_4$. Approximately 200 mg. of the sample is decomposed in a crucible with concentrated sulfuric acid in slight excess. The crucible is heated first with an infrared lamp and finally in an electric furnace at 520°. The cobalt(II) sulfate which forms is then weighed.

Spectrophotometric Analysis of Cobalt as $[CoCl_4]^{2-}$. A 20-mg. sample is dissolved in 100 ml. of concentrated hydrochloric acid, and the optical density is measured at 660 and 670 mμ.

Chloride. Chloride is determined gravimetrically as silver chloride.

Ammonia. Ammonia is determined acidimetrically. A 100-mg. sample is dissolved in dilute sulfuric acid, and the mixture is heated until it is free from nitrogen(II) oxide. The solution is then transferred to a standard Kjeldahl apparatus and made alkaline with 30% sodium hydroxide, and the ammonia is distilled over into 25 ml. of 0.1 *M* hydrochloric acid.

Properties

The black chloride is a lustrous crystalline solid. It is stable when perfectly dry. It cannot be dissolved in water (even at 0°) without decomposition to yield basic cobalt(II) chlorides. Treatment with concentrated hydrochloric acid yields $[CoCl_4]^{2-}$ in solution,[5] and neither the red isomer[3] nor the chloropentaammine chloride[4] can be obtained. If air is allowed to come in contact with basic solutions of the compound, oxidation to cobalt(III) ammines occurs. Treatment with concentrated ammonia solution (in a nitrogen atmosphere) yields $[Co(NH_3)_6]^{2+}$.[5]

The pure compound has no unpaired electrons,[5,10] contrary to the results obtained in earlier investigations[2,11–14] on impure samples.

If either $[Co(NH_3)_5(NO)]Cl_2$ or $[Co(H_2O)_6]Cl_2$ is treated first with 10 ml. of 50% ammonium thiocyanate and then with 50 ml. of acetone and finally diluted to 100 ml. with water, blue solutions with identical absorption spectra are formed.[15]

From all the evidence stated above, it is concluded[15] that from a chemical standpoint the black chloride can best be classified as a cobalt(II) complex with neutral nitrogen(II) oxide as ligand.

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Edited by Henry F. Holtzclaw, Jr.

50. *cis*-DINITROBIS(ETHYLENEDIAMINE)-COBALT(III) NITRITE AND NITRATE

$$trans\text{-}[Co(en)_2Cl_2]Cl + 3NaNO_2 \xrightarrow{-12°} cis\text{-}[Co(en)_2(NO_2)_2]NO_2 + 3NaCl$$

$$2\ cis\text{-}[Co(en)_2(NO_2)_2]NO_2 + 2HNO_3 \rightarrow 2\ cis\text{-}[Co(en)_2(NO_2)_2]NO_3 + NO_2 + NO + H_2O$$

Submitted by Edward P. Harbulak* and Marvin J. Albinak*†
Checked by Richard L. Lintvedt,‡ Robert C. Henney,‡ and Henry F. Holtzclaw, Jr.‡

Several preparations of salts of the *cis*-dinitrobis(ethylenediamine)cobalt(III) ion have been reported in the literature. The most usual is that of Werner,[1] modified by Holtzclaw, Sheetz, and McCarty,[2] beginning with potassium hexanitrocobaltate(III). However, this method makes use of a starting material which is difficult to prepare in high purity and to dry thoroughly, involves critical temperature control, and produces a yield of about 15%. The following procedure,[3] which utilizes *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride as the starting material, provides a 60% yield of *cis*-dinitrobis(ethylenediamine)cobalt(III) nitrite. The nitrite is then easily converted to the nitrate.

trans-Dinitrobis(ethylenediamine)cobalt(III) nitrate can be prepared in good purity and in 84% yield by the method of Holtzclaw, Sheetz, and McCarty.[2]

Procedure

Thirty grams (0.105 mol) of *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride[4] is dissolved in 150 ml. of cold

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water with the aid of a magnetic stirrer. After all of the green *trans*-dichloro salt has dissolved, the solution is cooled in an ice-salt bath maintained at −12°. Some freezing takes place, during which the temperature of the solution adjusts to about −3°. One hundred and fourteen grams (1.65 mols) of powdered sodium nitrite is added to the cold solution over a period of 1 to 2 minutes while stirring moderately rapidly with a magnetic stirrer. The solution turns from green to red and, before all of the nitrite has been added, to bright orange-brown with the appearance of a precipitate of *cis*-dinitrobis(ethylenediamine)cobalt(III) nitrite. The mixture is allowed to remain in the ice-salt bath with constant stirring for an additional 30 minutes, following which the precipitate is immediately filtered. The filtered precipitate is washed once with 20 to 30 ml. of cold water, twice with 20- to 30-ml. portions of absolute ethanol, twice with similar portions of ether or acetone, sucked dry on the funnel, and air-dried. The yield of *cis*-dinitrobis(ethylenediamine)cobalt(III) nitrite is at least 20 g. [60% based on *trans*-dichlorobis(ethylenediamine)-cobalt(III) chloride]. The small amount of contaminating sodium nitrite and sodium chloride is removed by converting to the nitrate salt with concentrated nitric acid.[2] The resulting compound then gives no chloride test with silver nitrate.

Properties are reported in Volume IV.[2]

Analysis

The *cis*-dinitrobis(ethylenediamine)cobalt(III) nitrate may be analyzed electrolytically or volumetrically for cobalt. Calcd. for $[Co(en)_2(NO_2)_2]NO_3$: Co, 17.69. Found: Co, 17.6. By checkers: Co, 17.76, 17.80. The qualitative test for the cis isomer described by Holtzclaw, Sheetz, and McCarty[2] and infrared analysis confirmed that the product is the correct isomer. As a final check, the compound was resolved according to the method of Dwyer;[5] the specific

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rotation of the bromide salt is −0.45° (previously reported, −0.44°).

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51. *cis*-BROMOAMMINEBIS(ETHYLENEDIAMINE)-COBALT(III) BROMIDE, *cis*- AND *trans*-AQUOAMMINEBIS(ETHYLENEDIAMINE)-COBALT(III) BROMIDE, AND *cis*- AND *trans*-AQUOAMMINEBIS(ETHYLENEDIAMINE)-COBALT(III) NITRATE

SUBMITTED BY M. L. TOBE* AND DEAN F. MARTIN†
CHECKED BY A. A. THELEN,‡ L. HILO,‡ GEORGE GLOVER,‡ AND JOHN P. FACKLER, JR.‡

Several methods are available for the preparation of *cis*-bromoamminebis(ethylenediamine)cobalt(III) bromide. These include the reaction of *trans*-dibromobis(ethylenediamine)cobalt(III) bromide with concentrated aqueous ammonia;[1] treatment of *cis*-nitroamminebis(ethylenediamine)cobalt(III) bromide or *cis*-aquoamminebis(ethylenediamine)cobalt(III) bromide with concentrated hydrobromic acid;[2] and reaction of concentrated ammonium bromide with bis[bis(ethylenediamine)cobalt(III)-μ-dihy-

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droxo]diaquocobalt(II) sulfate ("pink sulfate").[3] The procedure presented here is a modification of the last method. The conversion of the *cis*-bromoamminebis(ethylenediamine)cobalt(III) bromide to the *cis*- and *trans*-aquoamminebis(ethylenediamine)cobalt(III) bromide and nitrate salts is a modification of a procedure of Werner.[4]

Procedure

A. *cis*-BROMOAMMINEBIS(ETHYLENEDIAMINE)-COBALT(III) BROMIDE

$$6(CoSO_4 \cdot 7H_2O) + 10(en) + O_2 \rightarrow 2[Co(H_2O)_2\{(HO)_2Co(en)_2\}_2](SO_4)_2 \cdot 7H_2O + 18H_2O + 2(en) \cdot H_2SO_4$$

$$[Co(H_2O)_2\{(HO)_2Co(en)_2\}_2](SO_4)_2 \cdot 7H_2O + 6NH_4Br \rightarrow [Co(H_2O)_6]SO_4 + 2[Co(en)_2(NH_3)Br]Br_2 \cdot H_2O + (NH_4)_2SO_4 + 2NH_3 + 5H_2O$$

To a solution of 145 g. (0.52 mol) of cobalt(II) sulfate 7-hydrate in 180 ml. of water contained in a 1-l. beaker is added 300 ml. of 10% ethylenediamine (0.50 mol). The mixture is stirred for 10 minutes and is allowed to oxidize by standing undisturbed and exposed to air. A dark red-brown precipitate begins to form within a few hours. The reaction mixture should be allowed to stand undisturbed for three or four days. The product is filtered, washed successively with water (until the washings are pink), ethanol, and ether, and then air-dried. The yield is usually 25 to 31 g. (17 to 21%) of the "pink sulfate"; yields as high as 50 to 60% have sometimes been obtained. A suspension of 18 g. of the "pink sulfate" (0.022 mol) and 50 g. of ammonium bromide (0.51 mol) in 50 ml. of water is warmed (about 50°) until all of the complex dissolves. The deep purple solution is allowed to cool in the refrigerator overnight. The purple crystalline solid which precipitates is filtered, washed with ethanol, and air-dried. The yield of crystalline 1-hydrate is 12 to 18 g. (60 to 90%, based upon "pink sulfate"). The product is crystallized from a minimum amount of hot (approximately 70°) solution prepared by adding 4 ml. of concentrated hydrobromic acid to 50 ml. of water. Typically, 40 ml. of solution per 20 g. of crude complex is required. Recovery is about 60 to 70%. *Anal.* Calcd. for $[Co(en)_2(NH_3)Br]Br_2 \cdot H_2O$: Br, 52.8; N, 15.4. Found: Br, 51.8. By checkers: N, 15.0.

The anhydrous compound is obtained when a saturated solution is treated with a large excess of concentrated hydrobromic acid. *Anal.* Calcd. for $[Co(en)_2(NH_3)Br]Br_2$: C, 11.0; H, 4.4; N, 16.1; Br (ionic), 36.7; Br (total), 55.0. Found: C, 11.2; H, 4.7; N, 16.1; Br (ionic), 36.8; Br (total), 55.6.

B. *cis*- AND *trans*-AQUOAMMINEBIS(ETHYLENEDIAMINE)-COBALT(III) BROMIDE

$$cis\text{-}[Co(en)_2(NH_3)Br]Br_2 \cdot H_2O + LiOH \rightarrow cis\text{- and } trans\text{-}[Co(en)_2(NH_3)(OH)]Br_2 + LiBr + H_2O$$

$$cis\text{- and } trans\text{-}[Co(en)_2(NH_3)(OH)]Br_2 + HBr + H_2O \rightarrow cis\text{- and } trans\text{-}[Co(en)_2(NH_3)(H_2O)]Br_3 \cdot H_2O$$

Twenty-six grams (0.057 mol) of recrystallized *cis*-bromoamminebis(ethylenediamine)cobalt(III) bromide 1-hydrate is mixed with 30 g. (0.125 mol) of filtered 10% (by weight) aqueous lithium hydroxide. The purple crystals dissolve gradually as the mixture is shaken and a red solution is obtained. The solution is filtered and cooled in an ice bath. The filtrate is acidified to a pH of 4 with concentrated hydrobromic acid, using a pH meter. The resulting orange crystals of *trans*-aquoamminebis(ethylenediamine)cobalt(III) bromide are filtered, air-dried (yield: 2 to 3.5 g.; 7 to 13%), and recrystallized from a water-ethanol mixture containing a trace of hydrobromic acid. The temperature should be maintained below 50°. If the pure trans isomer is desired, recrystallization should be repeated until a constant spectrum[6] is obtained. If this is done, the yield of purified trans isomer is about 1 to 3%. However, the preparation of the trans nitrate from mixtures of cis and trans bromide (Procedure C) affords a better separation than by recrystallization of the bromide.

The cis isomer (yield: 14 to 18 g.; 52 to 67%) is obtained by treating the cooled mother liquors with 1 to 4 ml. of concentrated hydrobromic acid or by permitting the mother liquors to stand in the refrigerator for a few days. Purification of the cis isomer* is effected by recrystallization from a water-ethanol mixture at 40°. *Anal.* Calcd. for *cis*-$[Co(en)_2(NH_3)(H_2O)]Br_3 \cdot H_2O$: Br, 50.8; H_2O, 7.6; Found: Br, 51.0; H_2O, 7.2.

C. *trans*- AND *cis*-AQUOAMMINEBIS(ETHYLENEDIAMINE)-COBALT(III) NITRATE

trans- (or *cis*-) $[Co(en)_2(NH_3)(H_2O)]Br_3 \cdot H_2O + 3HNO_3 \rightarrow$
trans- (or *cis*-) $[Co(en)_2(NH_3)(H_2O)](NO_3)_3 + H_2O + 3HBr$

A solution of 5 g. (0.011 mol) of singly recrystallized *trans*-aquoamminebis(ethylenediamine)cobalt(III) bromide 1-hydrate in 15 ml. of water is well cooled in ice and is treated dropwise with 3 ml. of concentrated nitric acid. The orange platelets that form are filtered, washed with a little cold water, and air-dried (yield: 1.8 to 2.5 g.; 42 to 59%). The crude material is recrystallized from the minimum amount of water or from a water-ethanol mixture at 40°. *Anal.* Calcd. for $[Co(en)_2(NH_3)(H_2O)](NO_3)_3$: Co, 14.7; C, 12.0; H, 5.3; N, 28.0. Found: Co, 14.7; C, 12.6; H, 5.8; N, 28.2.

The preparation of the *cis*-aquoamminebis(ethylenediamine)cobalt(III) nitrate is effected by treating a well-cooled, saturated solution of *cis*-aquoamminebis(ethylenediamine)cobalt(III) bromide with concentrated nitric acid. However, the cis nitrate crystallizes very slowly and, if the solution is left too long, bromine, hydrogen bromide, and nitric acid are formed.

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* If the cis isomer is not desired, it may be converted to *cis*-bromoamminebis(ethylenediamine)cobalt(III) bromide by warming a saturated solution that contains an excess of concentrated hydrobromic acid.

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Properties

The *cis*-bromoamminebis(ethylenediamine)cobalt(III) bromide crystallizes in purple platelets. The compound has been resolved,[5] and the kinetics of the reactions of hydroxide ion with the *d*- and *l*-isomers in water have been determined.[6] The red-orange crystals of *cis*-aquoammine-bis(ethylenediamine)cobalt(III) bromide are compact and almost cubic, in contrast to the orange needle-plates of the trans isomer. The crystals of *trans*-aquoamminebis(ethylenediamine)cobalt(III) nitrate are orange platelets. The isomerism and water exchange of the aquoammine complexes have been studied.[7]

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52. SODIUM TRICARBONATOCOBALTATE(III) 3-HYDRATE

$$2[Co(NO_3)_2 \cdot 6H_2O] + H_2O_2 + 10NaHCO_3 \rightarrow 2\{Na_3[Co(CO_3)_3] \cdot 3H_2O\} + 4NaNO_3 + 4CO_2 + 12H_2O$$

Submitted by H. F. Bauer* and W. C. Drinkard†
Checked by Richard J. Thompson‡

The formula $Co_2(CO_3)_3$ was initially assigned to the product obtained from the oxidation of cobalt(II) salts by

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hydrogen peroxide in the presence of sodium hydrogen carbonate.[1] Subsequently it was shown that oxidation of cobalt(II) nitrate under these conditions results in a compound which is represented by the formula $Na_3[Co(CO_3)_3]\cdot 3H_2O$ or $Na_3[Co(HCO_3)_3(OH)_3]$.[2] No direct evidence which will allow a selection between the two structures is available.

The compound is of particular interest because it contains six base equivalents per mol. Addition of ligands in their acid form results in the displacement of carbon dioxide and water with the formation of the cobalt(III) complex of the ligand. This procedure is especially useful for the formation of cobalt(III) complexes of easily oxidized ligands. The excellent stability of $Na_3[Co(CO_3)_3]\cdot 3H_2O$ makes it a logical intermediate for the preparation of a variety of cobalt(III) complexes.[2]

Procedure

A solution of 29.1 g. (0.10 mol) of cobalt(II) nitrate 6-hydrate and 10 ml. of 30% hydrogen peroxide (excess) in 50 ml. of water is added dropwise with stirring to an ice-cold (0°) slurry of 42.0 g. (0.50 mol) of sodium hydrogen carbonate in 50 ml. of water.* The mixture is stirred for one hour at 0°. The olive-green product is filtered, washed on the filter with three 10-ml. portions of cold water, then thoroughly washed with absolute ethanol and dry ether. The product is further dried in a desiccator over phosphorus(V) oxide. The product must be thoroughly dry if it is to be stored. Small amounts of water cause decomposition to a black solid. The yield is 26.7 g. (74%). *Anal.* Calcd. for $Na_3[Co(CO_3)_3]\cdot 3H_2O$: C, 9.95; H, 1.66; Co, 16.3. Found: C, 8.72, 9.03; H, 1.39, 1.69; Co, 16.2. By checker: C, 9.98; H, 1.73; Co, 16.1, 16.2.

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* When too little of this reagent is present, or if a temperature higher than 0° is used, a black precipitate, probably cobalt(III) oxide, is formed.

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Properties

Sodium tricarbonatocobaltate(III) 3-hydrate is an olive-green powder insoluble in water. When completely dry, it is stable indefinitely if stored at room temperature in a closed bottle. It decomposes at 93° without melting. Addition of the acid form of a complexing agent results, in many cases, in the formation of the cobalt(III) complex of the ligand with evolution of carbon dioxide.

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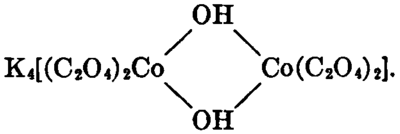
53. POTASSIUM TETRAOXALATO-DI-μ-HYDROXODICOBALTATE(III) 3-HYDRATE (DURRANT'S SALT) AND SODIUM TETRAOXALATO-DI-μ-HYDROXODICOBALTATE(III) 5-HYDRATE

Submitted by A. M. Sargeson* and I. K. Reid*
Checked by John H. Boughton† and R. N. Keller†

Durrant[1] first prepared the potassium salt, to which he assigned the formula $[K_2Co(C_2O_4)_2(H_2O)_2]_2O$, from cobalt(II) oxalate, potassium oxalate, and hydrogen peroxide. Percival and Wardlaw,[2] from freezing-point measurements, subsequently suggested that the compound is a binuclear complex containing five ions:



$$K_4[(C_2O_4)_2Co\overset{OH}{\underset{OH}{\diamond}}Co(C_2O_4)_2].$$

The published yields of the poorly soluble dark green potassium salt[3,4] are rather low (30 to 40%). However, the method below gives an almost quantitative yield, based

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on the cobalt used. The conversion of the potassium salt to the very insoluble barium compound and thence to the more soluble sodium salt is also described. Because of its greater solubility, the latter compound can be more readily split into two $[Co(C_2O_4)_2(H_2O)_2]^-$ ions than the potassium salt. This has prompted its use in the preparation of dioxalato cobalt(III) complexes containing ligands such as acetylacetone and glycine.[5]

Procedure

A. POTASSIUM TETRAOXALATO-DI-μ-HYDROXODICOBALTATE(III) 3-HYDRATE

$$2[Co(C_2H_3O_2)_2 \cdot 4H_2O] + 4[K_2C_2O_4 \cdot H_2O] + H_2O_2 \rightarrow K_4[Co_2(C_2O_4)_4(OH)_2] \cdot 3H_2O + 4KC_2H_3O_2 + 9H_2O$$

A mixture of 20.0 g. (0.08 mol) of cobalt(II) acetate 4-hydrate, 50.0 g. (0.27 mol) of potassium oxalate 1-hydrate, and 0.5 ml. of glacial acetic acid in 150 ml. of water is placed in a beaker protected from light and is stirred mechanically and heated to 55°, whereupon a clear solution results. Sixty milliliters of 6% hydrogen peroxide is added dropwise from a buret over a 15-minute interval. The temperature is kept at 55 to 56° by the addition of small pieces of ice as the reaction proceeds. The dark green product is filtered off at room temperature, washed well with ice water, methanol, and finally acetone, and dried in the dark at 40°; yield, 27.1 g. (94%). *Anal.* Calcd. for $K_4[Co_2(C_2O_4)_4(OH)_2] \cdot 3H_2O$: C, 13.45; H, 1.12. Found: C, 13.44; H, 1.05.

B. SODIUM TETRAOXALATO-DI-μ-HYDROXODICOBALTATE(III) 5-HYDRATE

$$K_4[Co_2(C_2O_4)_4(OH)_2] \cdot 3H_2O + 2Ba(C_2H_3O_2)_2 \rightarrow Ba_2[Co_2(C_2O_4)_4(OH)_2] \cdot 3H_2O + 4KC_2H_3O_2$$

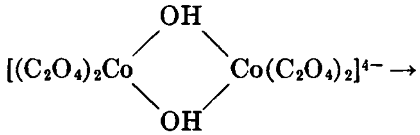
$$Ba_2[Co_2(C_2O_4)_4(OH)_2] \cdot 3H_2O + 2[Na_2SO_4 \cdot 10H_2O] \rightarrow Na_4[Co_2(C_2O_4)_4(OH)_2] \cdot 5H_2O + 2BaSO_4 + 18H_2O$$

Twenty-seven grams (0.038 mol) of potassium tetraoxalato-di-μ-hydroxocobalate(III) 3-hydrate is suspended in 300 ml. of water at room temperature in a stoppered 500-ml. Erlenmeyer flask protected from light. The mixture is shaken vigorously with 23.25 g. (0.087 mol) of barium acetate for 15 minutes. The very insoluble green product is collected, washed well with water, methanol, and finally acetone, and dried in the dark at 40°; yield, 29.2 g. (92%). Because of its insolubility the barium complex cannot be recrystallized.

Twenty-eight grams (0.034 mol) of the barium salt is suspended in 500 ml. of water in an Erlenmeyer flask protected from light and shaken vigorously with 30.0 g. (0.093 mol; 37% excess) of sodium sulfate 10-hydrate for 20 minutes. The solution is filtered through a Whatman 542 paper, and the product is precipitated by the addition of an equal volume of ethanol at $<20°$.* The substance is filtered under vacuum, washed with ethanol and then acetone and dried as before. The product is purified by dissolution in water and reprecipitation with ethanol; yield, 16.5 g. (63% based on the potassium salt). *Anal.* Calcd. for $Na_4[Co_2(C_2O_4)_4(OH)_2] \cdot 5H_2O$: C, 14.00; H, 1.76. Found: C, 13.89; H, 1.83.

Properties

The sodium salt is decomposed in the solid state by heat and light. It also decomposes slowly in basic or neutral solution and more rapidly in acidic solution. The decomposition in alkaline solution occurs as follows:[4]



$$[(C_2O_4)_2Co(OH)_2Co(C_2O_4)_2]^{4-} \rightarrow$$

$$Co2^{2+} + 2CO_2 + 3C_2O_4^{2-} + 2OH^-$$

In alkaline solution a brown precipitate, probably $Co_2O_3 \cdot xH_2O$, rapidly forms:

$$4Co^{2+} + 8OH^- + O_2 + (2x - 4)H_2O \rightarrow 2[Co_2O_3 \cdot xH_2O]$$

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* The temperature of precipitation is critical. The checkers report that no precipitation of the sodium salt occurs at temperatures above about 20°.

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54. RESOLUTION OF THE TRIOXALATOCOBALTATE(III) ION

Submitted by George B. Kauffman,* Lloyd T. Takahashi,* and Nobuyuki Sugisaka*
Checked by Karl H. Pearson,† Lewis W. Sequin,† and Stanley Kirschner†

Oxalate chelation has long been used as a diagnostic tool in coordination chemistry, and consequently the complex oxalates have been extensively investigated.[1] Since Werner's resolution of $K_3[Cr(C_2O_4)_3]$ with strychnine in 1912,[2] more resolution and racemization studies have been made of oxalato complexes than of any other class of coordination compounds.

The first resolution of trioxalatocobaltates was accomplished in 1916 with strychnine.[3] The method of spontaneous crystallization of antipodes from a racemic mixture of a complex was first demonstrated with $K_3[Co(C_2O_4)_3]$;[4] above 13.2°, the optical antipodes may be crystallized and mechanically separated. In practice, however, the standard technique of fractional crystallization of the strychnine diastereoisomers has been used.[4–7] Partial resolution on optically active quartz has also been reported.[8] Selective decomposition of the antipodes by circularly polarized light

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† Wayne State University, Detroit, Mich.,

was investigated with negative results by Jaeger and Berger,[9] but partial resolution using this method has been claimed by Tsuchida, Nakamura, and Kobayashi.[10]

Diastereoisomer formation with the optically active complex *l*-tris(1,10-phenanthroline)nickel(II) cation has been shown by Dwyer and Sargeson[11] to provide a rapid general resolution method for trioxalato complexes of Co(III), Cr(III), and Rh(III). The method, with modifications, is given below.

Procedure

The water content of the racemate, as well as of the optical antipodes of $K_3[Co(C_2O_4)_3]$, varies with the temperature of crystallization and conditions of drying. For this reason, the yields and optical rotations given are approximate.

Inasmuch as the optical antipodes of $K_3[Co(C_2O_4)_3]$ *racemize rapidly in solution, all operations should be carried out as quickly as possible using ice-cold solutions and ice-cold apparatus.*

A. POTASSIUM *l*-TRIOXALATOCOBALTATE(III) 3-HYDRATE

$$2\{K_3\,dl\text{-}[Co(C_2O_4)_3]\cdot 3H_2O\} + l\text{-}[Ni(C_{12}H_8N_2)_3](ClO_4)_2\cdot 3H_2O \rightarrow K\,l\text{-}[Ni(C_{12}H_8N_2)_3]d\text{-}[Co(C_2O_4)_3]\cdot H_2O + K_3\,l\text{-}[Co(C_2O_4)_3]\cdot 3H_2O + 2KClO_4 + 5H_2O$$

One gram (0.0012 mol) of *l*-tris(1,10-phenanthroline)-nickel(II) perchlorate 3-hydrate[12] (synthesis 59) is dissolved in 18 ml. of a freshly prepared 1:1 by volume acetone-water mixture. The pink solution is cooled in an ice bath to 10° (*not below*) and added to an ice-cold solution of 1.10 g. (0.0023 mol) of potassium *dl*-trioxalatocobaltate(III) 3-hydrate[13,14,]* and 1 g. of potassium acetate in 20 ml. of water. The mixture is allowed to stand in an ice bath for 6 minutes with occasional stirring. Scratching the walls of the beaker may facilitate precipitation. The green diastereoisomer which precipitates is collected on a 5-cm.

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* Inasmuch as this compound is sensitive to both heat and light, it is suggested that freshly prepared or recrystallized material be used.

Büchner funnel and treated as described in Part B. The *l*-antipode is *immediately* precipitated from the filtrate by slow addition, with stirring, of 100 ml. of ice-cold ethanol. The green precipitate is collected on a 5-cm. Büchner funnel, washed with three 10-ml. portions of ice-cold ethanol or methanol, and air-dried. The yield is approximately 0.50 g. (91%). For a 0.032% aqueous solution in a 1-dm. tube, $\alpha_D^5 = -0.62°$, and $[\alpha]_D^5 = -1940°$. The high optical density of even so dilute a solution makes observation of the field difficult. With the Rudolph high-precision polarimeter, the half-shade angle control should be used at its maximum opening.

B. POTASSIUM *d*-TRIOXALATOCOBALTATE(III) 3-HYDRATE

$$\text{K } l\text{-}[\text{Ni}(\text{C}_{12}\text{H}_8\text{N}_2)_3]d\text{-}[\text{Co}(\text{C}_2\text{O}_4)_3]\cdot\text{H}_2\text{O} + 6\text{KI} + 2\text{H}_2\text{O}_2 + 4\text{HC}_2\text{H}_3\text{O}_2 \rightarrow l\text{-}[\text{Ni}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{I}_3)_2 + \text{K}_3\, d\text{-}[\text{Co}(\text{C}_2\text{O}_4)_3]\cdot3\text{H}_2\text{O} + 4\text{KC}_2\text{H}_3\text{O}_2 + 2\text{H}_2\text{O}^*$$

The green diastereoisomer from Part A is washed with 20 ml. of ice-cold ethanol, air-dried, and suspended in 20 ml. of ice water. Two milliliters (0.0018 mol) of 3% hydrogen peroxide, two drops (approximately 0.0018 mol) of glacial acetic acid, and 1 g. (0.006 mol) of potassium iodide are added. The olive-colored mixture is stirred in an ice bath for 4 minutes and is then filtered through a 5-cm. Büchner funnel. If the oxidation continues to occur in the filtrate, it may be necessary to refilter the filtrate once.† The *d*-antipode is precipitated by the addition, with stirring, of 100 ml. of ice-cold ethanol to the filtrate. The product is collected, washed, and dried in the same manner as the *l*-antipode. The yield is approximately 0.27 g. (49%).

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* Hydrogen peroxide oxidizes potassium iodide to free iodine, which in the presence of excess potassium iodide precipitates the *l*-$[\text{Ni}(\text{C}_{12}\text{H}_8\text{N}_2)_3]^{2+}$ ion as the triiodide.

† The insoluble *l*-$[\text{Ni}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{I}_3)_2$ may be converted to the corresponding iodide by treating a cold ethanolic suspension with SO_2 or Na_2SO_3. The iodide may then be used exactly as the perchlorate in the resolution of more $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$.

For a 0.032% aqueous solution in a 1-dm. tube, $\alpha_D^5 = +0.58°$ and $[\alpha]_D^5 = +1810°$ (by checkers, $+1928°$).

Properties

The optical antipodes of potassium trioxalatocobaltate(III) are dark green salts which dissolve readily in water to give deep green solutions. Both are decomposed by light[9,15–18] and heat:[18]

$$2K_3[Co(C_2O_4)_3] \rightarrow 3K_2C_2O_4 + 2CoC_2O_4 + 2CO_2$$

The *d*-antipode is isomorphous with the corresponding rhodium(III) and iridium(III) salts.

Both antipodes racemize rapidly in solution, although less rapidly than the corresponding trioxalatochromates;[3,19] racemization is complete within 24 hours. Racemization is reported to occur even in the solid state.[6] Isotopic exchange studies[20] have shown only limited parallelism between the mechanisms of oxalate exchange and racemization. Optical rotatory dispersion measurements[6,7,21] have been used to determine the absolute configuration of the trioxalatocobaltate(III) ion.

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55. DICHLOROTETRACARBONYLDIRHODIUM

(Rhodium Carbonyl Chloride)

$$2(RhCl_3 \cdot 3H_2O) + 6CO \rightarrow [Rh_2(CO)_4Cl_2] + 6H_2O + 2COCl_2$$

Submitted by J. A. McCleverty* and G. Wilkinson*
Checked by Loren G. Lipson,† Michael L. Maddox,† and Herbert D. Kaesz†

Dichlorotetracarbonyldirhodium has been obtained by the action of carbon monoxide at high temperature and pressure on a mixture of anhydrous rhodium(III) chloride and finely divided copper powder[1] and by reaction of rhodium(III) chloride 3-hydrate with carbon monoxide saturated with methanol at moderate temperatures and atmospheric pressure.[2] The preparation described here is a modification of the latter method, without use of methanol. This procedure is considerably simpler than the recently described preparation which involves adsorption of rhodium chloride on silica gel, chlorination, and subsequent carbonylation.[3]

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† University of California, Los Angeles, Calif.

Procedure

Caution. The reaction must be carried out in a well-ventilated hood.

A tube (20 cm. long and 2 cm. in diameter) with a porous disk (porosity 3 or medium) sealed in at one end and with an ungreased ground joint, is arranged as shown in Fig. 8. Rhodium(III) chloride 3-hydrate* (11.0 g.; 0.042 mol) is pulverized and placed on top of the disk. The apparatus is then flushed with carbon monoxide and lowered into a paraffin-oil bath maintained at 100°. Bath temperatures above 100° should be avoided to prevent the formation of anhydrous rhodium(III) chloride, which is inert to carbon monoxide. Carbon monoxide is passed slowly through the system, a bubbler being attached to the end of the apparatus to indicate the rate of flow. (*Caution. The rate of flow of carbon monoxide through the apparatus must be determined by the capacity of the hood being used. If the flow is too rapid, the escaping noxious gases (carbon monoxide and phosgene) may not be removed entirely from the atmosphere in the hood and may escape into the laboratory.*) At hourly intervals, or more frequently if necessary, the water which condenses near the top of the tube is removed with absorbent cotton. During the reaction, the orange dichlorotetracarbonyldirhodium sublimes about halfway up the reaction tube.

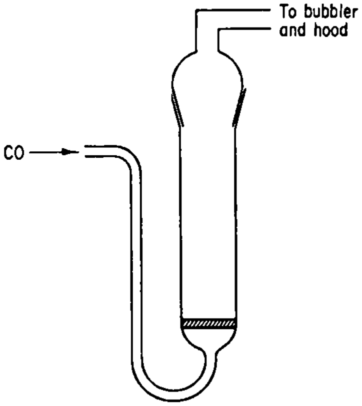

FIG. 8. Apparatus for the preparation of dichlorotetracarbonyldirhodium.

When the reaction is complete (3 to 5 hours), the appa-

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* The commercial salt is often not quite stoichiometric for $RhCl_3 \cdot 3H_2O$.

ratus is withdrawn from the oil bath. When the apparatus has been cooled, the orange-red crystals can be scraped from the reaction vessel and the last traces of compound washed out with dry benzene or hexane. The yield is 8.3 g. (96%). The rhodium carbonyl chloride so obtained is pure enough for most purposes, but it may be recrystallized[4] from hexane or sublimed at 80° at a pressure of 0.1 mm. Hg. The compound is stable in air but should be stored in a desiccator, for it is somewhat sensitive to moisture.

Properties

Dichlorotetracarbonyldirhodium is an orange-red crystalline solid very soluble in most organic solvents (except the aliphatic hydrocarbons) producing orange solutions. The compound has a melting point of 124 to 125°, carbonyl stretching frequencies[5] in petroleum solution (b.p. within the range 40 to 60°) or hexane at 2105 (m), 2089 (s), about 2080 (vw), 2035 (s), and 2003 (w) cm.^{-1}. It is quite volatile, forming a red crystalline sublimate. Although the pure compound is stable in dry air, its solutions in organic solvents decompose to insoluble brown materials when left exposed to air.

Dichlorotetracarbonyldirhodium reacts readily with ligands such as phosphines, arsines, stibines, and phosphites[4,5] to form mononuclear complexes. It reacts with cyclopentadienylsodium to form π-cyclopentadienyldicarbonylrhodium.[7] With hydrochloric acid[8] it produces the anion $[Rh(CO)_2Cl_2]^-$, and with β-diketones in the presence of base forms dicarbonylrhodium β-diketonates.[9]

The complex has an unusual booklike structure[10] with chloride bridges, and there is evidence for a metal-metal bond.

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56. CHLOROCARBONYLBIS(TRIPHENYLPHOSPHINE)RHODIUM AND CHLOROCARBONYLBIS(TRIPHENYLARSINE)-RHODIUM

$$[Rh_2(CO)_4Cl_2] + 4(C_6H_5)_3M \rightarrow 2[\{(C_6H_5)_3M\}_2Rh(CO)Cl] + 2CO$$

$$(M = P, As)$$

Submitted by J. A. McCleverty* and G. Wilkinson*
Checked by Loren G. Lipson,† Michael L. Maddox,† and Herbert D. Kaesz†

Dichlorotetracarbonyldirhodium reacts readily with phosphines and arsines to form the four-coordinate phosphine or arsine carbonyl chlorides.[1,2] The complexes may also be prepared by refluxing rhodium(III) chloride 3-hydrate with a large excess of triphenylphosphine or triphenylarsine in 2-methoxyethanol.[3]

Procedure

Caution. The reaction is carried out in a well-ventilated hood.

Dichlorotetracarbonyldirhodium (synthesis 55) (1.30 g.; 0.0034 mol) is dissolved in 25 ml. of benzene. On addition of 25 ml. of benzene containing either triphenylphosphine (3.49 g.; 0.0133 mol) or triphenylarsine (4.08 g.; 0.0133 mol) a vigorous reaction takes place and the color of the solution

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changes from orange to yellow. After 5 minutes, the solution is evaporated to about one-half its original volume on a steam bath, and 20 ml. of ethanol is added. The yellow crystals that precipitate upon the addition of the alcohol are filtered from the solution, washed with 30 ml. of anhydrous ether, and dried in the air. The yield of the phosphine complex is 4.04 g. (88%), and of the arsine complex, 4.52 g. (87%). The compounds obtained in this way are pure, as is shown by elemental analysis, including direct oxygen microanalysis.

Analysis

Direct Microdetermination of Oxygen in Phosphorus-containing Compounds (by J. Cuckney and G. Wilkinson).* Although the direct method for the microdetermination of oxygen by the standard procedure has been stated not to give satisfactory results for phosphorus-containing compounds,[5] a minor modification allows good results to be obtained. Compounds containing fluorine do not give satisfactory results, however.

The modification of the standard procedure involves the use of a disposable sample boat. A piece of copper foil approximately 1½ × ½ in. in size is shaped manually into boat form. It is flamed in a Bunsen burner and dipped into methanol. After this cleaning operation, the boat is placed in a glass tube and heated briefly with a Bunsen flame while being swept with a stream of hydrogen (*caution!*); it is then ready for use in the procedure described by Oliver.[5] Some typical results are given in Table I. *Anal.* Calcd. for $C_{37}H_{30}ClOP_2Rh$: O, 2.32. Found: O, 2.30, 2.34. By checkers: Calcd: C, 64.32; H, 4.38; mol. wt., 691. Found: C, 64.49; H, 4.61; mol. wt., 688 ± 4. Calcd. for $C_{37}H_{30}ClOAs_2Rh$: O, 2.05. Found: O, 1.95, 2.10. By checkers: Calcd: C, 57.06; H, 3.88:, mol. wt., 778. Found: C, 57.65; H, 4.43; mol. wt., 790 ± 13.

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* Microanalytical Laboratory, Imperial College of Science and Technology, London, England.

TABLE I. EXAMPLES OF DIRECT OXYGEN ANALYSES ON PHOSPHORUS-CONTAINING COMPLEXES*

Compound†	% Oxygen‡	
	Calcd.	Found
$Mo(CO)_3(PClPh_2)_3$	5.7	5.9
$ReOCl_3(PPh_3)_2$	1.9	1.9
$ReOCl_2(OEt)(PPh_3)_2$	3.8	3.7
$ReOCl_2(PPh_3)$acac	7.6	7.4
$ReCl_2(PPh_3)_2$acac	3.6	4.0
$[HPPh_3][ReOCl_4(PPh_3)]$	1.8	2.1
$[\pi\text{-}C_5H_5Fe(CO)_2PPh_3]Cl\cdot 3H_2O$	15.1	15.0
$Rh(CO)Cl(PPh_3)_2$	2.3	2.3
$[Rh(C_2H_5COO)_2PPh_3]_2$	12.5	12.3

* Microanalyses by the Microanalytical Laboratory, Imperial College of Science and Technology, London, England.

† acac = acetylacetone.

‡ The weight of the analytical sample is adjusted to correspond to a final titration of the liberated iodine with about 3 ml. of 0.02 *N* sodium thiosulfate. The errors on all values are ±0.3.

Properties

Chlorocarbonylbis(triphenylphosphine)rhodium and chlorocarbonylbis(triphenylarsine)rhodium form bright yellow crystalline solids which are readily soluble in chloroform and dichloromethane, moderately soluble in benzene and carbon tetrachloride, and sparingly soluble in ether and aliphatic hydrocarbons. The phosphine complex (m.p. 195 to 197°) and the arsine complex (m.p. 242 to 244°) are reported[2] to have carbonyl stretching frequencies (using KBr disks) at 1960 and 1963 cm.$^{-1}$, respectively.*

Both compounds react with chlorine or iodine by adding a molecule of the halogen to give $[(C_6H_5)_3M]_2Rh(CO)X_2Cl$ (X = Cl or I).[4]

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* With Nujol mulls, using the Perkin-Elmer Model 21 spectrophotometer with calcium fluoride optics, the authors found single broad bands at approximately 1970 cm.$^{-1}$. With chloroform solutions, using the Perkin-Elmer Model 421 grating spectrophotometer, the checkers found single broad bands at 1977 and 1972 ± 3 cm.$^{-1}$ for the phosphine and arsine complexes, respectively.

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57. SODIUM HEXACHLORORHODATE(III) 2-HYDRATE AND POTASSIUM HEXACHLORORHODATE(III) 1-HYDRATE

$$2Rh + 6NaCl + 3Cl_2 + 4H_2O \rightarrow 2\{Na_3[RhCl_6]\cdot 2H_2O\}$$
$$Na_3[RhCl_6]\cdot 2H_2O + 3HCl \rightarrow H_3[RhCl_6]\cdot aq.^* + 3NaCl$$
$$H_3[RhCl_6]\cdot aq. + 3NaCl \rightarrow Na_3[RhCl_6]\cdot 2H_2O + 3HCl$$
$$H_3[RhCl_6]\cdot aq. + 3KCl \rightarrow K_3[RhCl_6]\cdot H_2O + 3HCl$$

Submitted by George B. Kauffman† and James Hwa-san Tsai†
Checked by James P. Collman,‡ William L. Young, III,‡ and David A. Buckingham‡

Although compounds of the platinum metals are commercially available, many workers, for reasons of economy, prefer to prepare them from the elements. Rhodium, one of the rarest and most expensive of the platinum metals, is not attacked by acids (even aqua regia), and its dissolution in alkaline fusion mixtures (e.g., fused sodium carbonate and potassium nitrate mixtures) or in molten salts (e.g., molten potassium hydrogen sulfate) is inefficient and tedious. Chlorination during heating yields a mixture of water-insoluble chlorides, but in the presence of sodium

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[*] The exact composition of the principal species in aqueous solutions of hexachlororhodate(III) which have been acidified with hydrochloric acid is not known. For simplicity, the designation $H_3RhCl_6\cdot aq.$ is used here.

[†] California State College at Fresno, Fresno, Calif. Acknowledgment is made to the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

[‡] University of North Carolina, Chapel Hill, N.C.

chloride, sodium hexachlororhodate(III), which is a convenient water-soluble intermediate, is obtained.[1,2]

Although sodium hexachlororhodate(III) is reported to decompose at 600[3] or 650°[4] in air, it can be heated in a stream of chlorine up to 980° without change.[5] By employing high temperatures, excess sodium chloride, and mechanical agitation of the reaction mixture, an almost quantitative conversion can be accomplished in one chlorination step. The compound may also be obtained from a solution containing the theoretical ratios of rhodium(III) chloride and sodium chloride.[2,6] It may be conveniently stored *in vacuo* over sulfuric acid as the stable 2-hydrate rather than as efflorescent higher hydrates or the deliquescent anhydrous salt.[7]

Potassium hexachlororhodate(III) 1-hydrate may be obtained by chlorination of a mixture of powdered rhodium and potassium chloride, followed by crystallization from the reaction mixture solution in the presence of excess potassium chloride.[4] It may also be prepared by reaction of sodium hexachlororhodate(III) solution with concentrated potassium chloride solution, followed by evaporation to incipient crystallization.[8] Both of these methods are reported to yield potassium pentachloroaquorhodate(III) if potassium chloride is not present in excess.[2,8] Anhydrous potassium hexachlororhodate(III) is obtained by heating potassium hexachlororhodate(III) 1-hydrate at 100 to 120°.[8]

Procedure

NOTE. The procedures include modifications suggested by the checkers and checked independently by the authors.

A Vycor combustion boat (15 × $1\frac{1}{2}$ × 1 cm.)* containing an intimate mixture of 1.03 g. (0.010 mol) of finely divided

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* The yield varies with the exposed surface area of the reaction mixture and hence is dependent upon the amount of material and the dimensions of the boat. When the sodium chloride melts, the denser rhodium tends to settle to the bottom of the reaction mixture and is no longer exposed to the chlorine. If the mixture is spread out in the manner shown in Fig. 9, the maximum yield is obtained.

rhodium metal (powder) and 3.50 g. (0.060 mol) of powdered sodium chloride is placed in a Vycor combustion tube. The tube is then inserted in a preheated (900°) tube furnace which is supported in a level position (Fig. 9). When the tube and contents have attained a temperature of 900°, a slow stream of gaseous chlorine[*] is passed through the tube (*hood!*). After several minutes, the entire furnace and tube are tilted to an angle of about 20° by adjusting the jacks (angles greater than 20° may cause some of the molten reaction mixture to flow out of the boat; angles less than 20° may leave some rhodium unexposed to chlorine). After approximately $1\frac{1}{2}$ minutes in this position, the furnace and tube are tilted about 20° in the opposite direction, and this alternate tilting is continued at $1\frac{1}{2}$-minute intervals for 30 minutes, after which the tube and contents are allowed to cool in a stream of chlorine.[†]

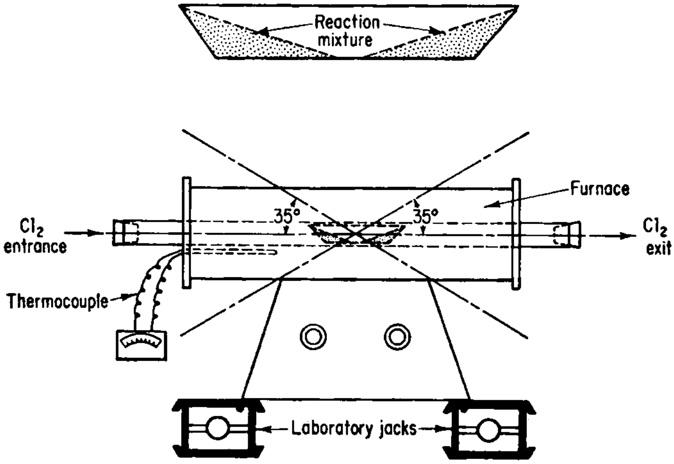

Fig. 9. Apparatus for the preparation of sodium hexachlororhodate(III).

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[*] The excess chlorine should be absorbed in a trap containing a basic solution, e.g., sodium hydroxide. A flow rate giving 60 to 100 bubbles/minute is satisfactory. Tygon tubing and rubber stoppers are sufficiently chlorine-resistant to be used for connections.

[†] Exposure of sodium hexachlororhodate(III) to air at temperatures above 600 to 650° results in decomposition.[3,4]

The deep red mixture is transferred to a 50-ml. beaker, using a minimum volume (15 to 20 ml.) of hot 1 *N* hydrochloric acid* to rinse the last traces from the boat and tube. After being gently heated and stirred until all soluble material has dissolved, the hot burgundy-colored mixture is quantitatively transferred through a *double thickness* of Whatman no. 42 filter paper† into a 100-ml. beaker with the aid of a minimum volume (about 10 ml. in 2-ml. portions) of hot 1 *N* hydrochloric acid.

The solution is concentrated to 20 ml. on a steam bath and then cooled to about 0 to 5°. Hydrogen chloride gas (e.g., from a HCl/H_2SO_4 generator)[9] is slowly bubbled for 30 minutes through the concentrated burgundy-colored solution in an ice bath. The solution turns a dark burgundy-purple and contains hexachlororhodic(III) acid. The precipitated sodium chloride is removed by filtration with a coarse sintered-glass funnel and washed with cold concentrated (12 *N*) hydrochloric acid (5 to 8 ml.). An almost quantitative recovery (3.45 to 3.50 g.) of sodium chloride is obtained. At this stage, either the sodium salt (Procedure A) or the potassium salt (Procedure B) of the hexachlororhodate(III) anion may be isolated from the filtrate.

A. SODIUM HEXACHLORORHODATE(III) 2-HYDRATE

The filtrate is evaporated almost to dryness on a steam bath; a 1.5-g. (0.026 mol) quantity of sodium chloride in 10 ml. of warm water is added; and the burgundy-colored solution is evaporated to dryness. The residue is powdered

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* The hydrochloric acid solution retards formation of the pentachloroaquorhodate(III) anion.

† About 95 to 97% of the rhodium has been converted into a soluble product. Rhodium metal is not attacked by ordinary reagents. Hence, because of difficulties in cleaning the funnel, use of a sintered-glass funnel to remove insoluble material is not recommended. A small amount of unreacted rhodium metal (0.05 to 0.08 g.) may be recovered from the wet filter paper by dispersing the paper in warm concentrated (15 *N*) nitric acid and washing away the paper by decantation with distilled water.

and returned to the original beaker, and 10 ml. of cold water is added. One milliliter of ethanol is then added, followed by gradual addition of 50 ml. of acetone with stirring. The dark red crystals which form are collected on a filter and washed with approximately 30 ml. of fresh acetone. One further recrystallization is performed. The red crystalline product is collected on a sintered-glass funnel, washed with approximately 50 ml. of acetone, and air-dried. On powdering and drying to constant weight (about 3 days) *in vacuo* over sulfuric acid, 3.6 to 3.8 g. of pink sodium hexachlororhodate(III) 2-hydrate is obtained (86 to 90% yield).* *Anal.* Calcd. for $Na_3[RhCl_6]\cdot 2H_2O$: Rh, 24.46; Cl, 50.57. Found: Rh, 24.41, 24.48; Cl, 49.71, 49.76. By checkers: Cl, 50.18.

B. POTASSIUM HEXACHLORORHODATE(III) 1-HYDRATE†

Ten milliliters of water is added to the filtrate (p. 220), followed by slow addition, with stirring, of 18 ml. of 25% potassium chloride solution. On cooling for 30 minutes in an ice bath, dark burgundy-colored crystals form. These crystals are collected on a fritted-glass filter and washed with 60% ethanol (about 75 ml.) until free of chloride ion.‡ The product is washed further with 25 ml. of 95% ethanol and then with two 50-ml. portions of diethyl ether. Upon air drying, 4.10 to 4.30 g. of potassium hexachlororhodate(III) 1-hydrate is obtained (91 to 95% yield). *Anal.* Calcd.

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* Large reddish black crystals may be obtained by dissolving the product in a minimum quantity of hot water and allowing the solution to evaporate at room temperature for several days. The weight loss on drying the efflorescent crystals *in vacuo* over sulfuric acid shows them to correspond closely to the 12-hydrate.

† The potassium salt may also be prepared directly by the substitution of potassium chloride (6.0 g.) for sodium chloride in the fusion step (page 219). The regular procedure is then followed except that larger volumes of solution are needed because of the lower solubility of the potassium salt (76 to 85% yields).

‡ Potassium chloride is relatively soluble in 60% ethanol, whereas $K_3[RhCl_6]\cdot H_2O$ is relatively insoluble.

for $K_3[RhCl_6]\cdot H_2O$: Cl, 47.18. Found (by checkers): Cl, 47.20.

On drying at 100° or by vacuum, anhydrous potassium hexachlororhodate(III) is obtained. *Anal.* Calcd. for $K_3[RhCl_6]$: Cl, 49.13. Found (by checkers): Cl, 49.52.

Properties

In aqueous solution, hexachlororhodates(III) and hexachloroiridates(III) exist in equilibrium with the corresponding pentachloroaquo compounds[8] (e.g., $M_3[RhCl_6] + H_2O \rightleftarrows MCl + M_2[Rh(H_2O)Cl_5]$). Anhydrous sodium hexachlororhodate(III), a deliquescent rose-colored powder, is reportedly obtained from the various hydrates by heating to 150°;[10] according to another report,[3] heating at 120° is sufficient for complete dehydration. At temperatures above 600°[3,4] dehydration should be carried out in a stream of chlorine[11] to prevent decomposition: $2Na_3[RhCl_6] \rightarrow 2Rh + 6NaCl + 3Cl_2$. Under these conditions, the melting point, which is greatly lowered by traces of sodium chloride, is 902°.[4] The fact that the anhydrous compound is insoluble in a 1:1 acetone-ether solution whereas sodium hexachloroiridate(IV) is soluble has been suggested as the basis for a quantitative separation of rhodium from iridium.[5]

Sodium hexachlororhodate(III) and its hydrates are freely soluble in water, forming dark burgundy-colored solutions which become brown on heating or standing.[1,11] Aqueous solutions are quantitatively reduced to metallic rhodium by hydrogen under pressure,[12] zinc,[13] or magnesium.[3] Alkali metal hydroxides cause precipitation of the yellow hydrated oxide,[1,14] whereas aqueous ammonia causes precipitation of $[Rh(NH_3)_5Cl]Cl_2$,[1,11,15] and treatment with hydrogen sulfide results in precipitation of rhodium(III) sulfide.[1,16]

The chemical and physical properties of the potassium salt are very similar to those of the sodium salt.

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Edited by Henry F. Holtzclaw, Jr.

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58. AMMONIUM HEXACHLOROIRIDATE(IV)

$$Ir + 2NaCl + 2Cl_2 \rightarrow Na_2[IrCl_6]$$
$$Na_2[IrCl_6] + 2NH_4Cl \rightarrow (NH_4)_2[IrCl_6] + 2NaCl$$

Submitted by George B. Kauffman* and Larry A. Teter*
Checked by J. W. Hogarth† and F. P. Dwyer†‡

Iridium is an extremely inert metal which is not attacked by acids, aqua regia, or fused alkalies. It reacts readily with chlorine, however, especially in the presence of alkali

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‡ Deceased.

metal chlorides, to yield hexachloroiridates(IV), the most important derivatives of tetrapositive iridium. The ammonium salt is a particularly useful compound inasmuch as it can be readily precipitated in a pure state and is not hygroscopic. These properties, as well as the fact that on ignition it yields a residue of pure metallic iridium, have led to its extensive use in the past for determining the atomic weight of iridium.[1,2]

Ammonium hexachloroiridate(IV) can be prepared by the metathesis of sodium hexachloroiridate(IV) with ammonium chloride or by the addition of ammonium chloride to either a solution of iridium(IV) hydroxide in hydrochloric acid or of iridium(IV) chloride.[3,4] Although many workers have prepared sodium hexachloroiridate(IV) by chlorinating mixtures of sodium chloride and iridium,[5–9] few exact data are available concerning optimum temperatures, reaction times, and yields.

Among the hexachloroiridates, the compounds of tripositive iridium are more stable than those of the tetrapositive metal. Wöhler and Balz[10] report that in a stream of chlorine, sodium hexachloroiridate(IV) begins to decompose into hexachloroiridate(III) at 570°. At 750° the product is primarily sodium hexachloroiridate(III), which in turn decomposes into metallic iridium above 900°. The chlorine content of the residue was found to be dependent upon the temperature. That the reaction proceeds stepwise has been shown in a more recent study by Puche.[11] Typical results of chlorination studies of mixtures of sodium chloride (4.00 g.) and iridium (2.00 g.) are as follows:[12]

Product	Yield, %, for furnace temp., °C. ± 15°/reaction time hours			
	450/7	625/$\frac{1}{4}$	700/$\frac{1}{4}$	800/$\frac{1}{4}$
Soluble product	42.3	98.9	84.8	63.4
$(NH_4)_2[IrCl_6]$ after oxidation and precipitation	37.3	95.0	80.0	56.6

Temperatures of 450 to 560°, i.e., below the dissociation temperature of sodium hexachloroiridate(IV), were found to be unsatisfactory because of the slow rate of conversion. A temperature of about 625° seems optimum. The product in this case consists mainly of sodium hexachloroiridate(IV) as well as hexachloroiridate(III), unchanged sodium chloride, and unchanged iridium. Sodium hexachloroiridate(III) can be readily oxidized to sodium hexachloroiridate(IV) by chlorine water or aqua regia:

$$2Na_3[IrCl_6] + Cl_2 \rightarrow 2Na_2[IrCl_6] + 2NaCl$$

Procedure

An intimate mixture of 2.00 g. (0.0104 mol) of finely divided iridium and 4.00 g. (0.0685 mol) of sodium chloride is spread out in the center of a Pyrex or Vycor* combustion tube.† The tube is heated in a tube furnace to about 625°. A stream of chlorine is slowly passed through the tube (*hood*!) until the mixture sinters to a molten black mass (15 to 30 minutes). A slight positive pressure of gas should be maintained at the exit tube. Tygon tubing and rubber stoppers are sufficiently chlorine-resistant to be used for connections. The cooled melt is transferred to a 100-ml. beaker, using about 20 ml. of boiling water to rinse the last traces from the tube. After being gently heated and stirred until all soluble material has dissolved, the hot dark brown mixture is quantitatively transferred through filter paper‡ into another 100-ml. beaker with the aid of a minimum volume of hot water (about 10 ml.). The filtrate is boiled gently for about 10 minutes with 10 ml. of aqua regia

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[*] Pyrex may soften slightly at the temperature to be employed.

[†] A porcelain combustion boat fastened to a length of rigid wire is convenient for inserting the sample and dumping it into the tube without loss.

[‡] Iridium is not attacked by ordinary reagents. Use of a sintered-glass funnel to remove insoluble material is not recommended because of difficulty in cleaning.

(1 HNO_3:4HCl).* To the hot solution is added 2 g. of ammonium chloride in 5 ml. of boiling water. The beaker is first allowed to cool to room temperature and is then further cooled in an ice bath for about 30 minutes. The opaque black crystals are separated by suction filtration,† washed in order with two 10-ml. portions of 20% ammonium chloride solution, successive 10-ml. portions of 95% ethanol until the washings are free from chloride ion, and two 10-ml. portions of diethyl ether. The yield of air-dried product is 4.13 to 4.36 g. (90 to 95%). *Anal.* Calcd. for $(NH_4)_2[IrCl_6]$: Ir, 43.58; N, 6.35; H, 1.81. Found: Ir, 43.59; 43.60. By checkers: Ir, 43.40; N, 6.55; H, 1.84. (Ignition should be carried out in a stream of hydrogen in order to decompose any IrO_2 to metallic iridium.)

Properties[13]

Ammonium hexachloroiridate(IV) forms strongly refracting octahedra which vary from red-black to almost black depending on crystal size. Above 200° it decomposes to metallic iridium, nitrogen, ammonium chloride, and hydrogen chloride.

Although it is only sparingly soluble in water (1.09 g./100 g. at 25°; 4.38 g./100 g. at 80°), the solutions are intensely red-brown; one part of the salt can be detected visually in 40,000 parts of water. Solubility is decreased by addition of ammonium chloride. In dilute solution, hydrolysis proceeds to a small extent but can be repressed by addition of hydrochloric acid. Above 80° the solution apparently decomposes.

Aqueous solutions of ammonium hexachloroiridate(IV) are readily reduced to hexachloroiridate(III) by a variety

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* A more easily filtered product is obtained by using aqua regia than by using chlorine water. For the same reason the product is allowed to precipitate slowly from a hot solution. Thorough removal of aqua regia by boiling prevents oxidation of ammonium ion in the next step.

† The deep red color of the filtrate is deceptive; the solution actually contains little product (see Properties).

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of reducing agents such as potassium iodide, sulfur dioxide, and sodium oxalate. The reaction with potassium iodide can be used for the quantitative determination of iridium.[3,14]

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59. RESOLUTION OF THE TRIS(1,10-PHENANTHROLINE)NICKEL(II) ION

Submitted by George B. Kauffman* and Lloyd T. Takahashi*
Checked by Karl H. Pearson,† Lewis W. Sequin,† and Stanley Kirschner†

The aromatic heterocyclic base 1,10-phenanthroline (*o*-phenanthroline) forms chelate complexes of varying

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* California State College at Fresno, Fresno, Calif. The authors express appreciation for helpful discussions with the late Dr. Francis P. Dwyer, Australian National University, and for a generous supply of 1,10-phenanthroline from the G. Frederic Smith Co., Columbus, Ohio.

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stabilities with a number of transition metal ions.[1] Of the three types of bivalent nickel compounds,[2,3] $[Ni(H_2O)_4(o\text{-phen})]X_2$,* $[Ni(H_2O)_2(o\text{-phen})_2]X_2$, and $[Ni(o\text{-phen})_3]X_2$, the tris complexes are by far the most stable. Thus, $[Ni(o\text{-phen})_3](ClO_4)_2$ precipitates on addition of sodium perchlorate to a solution of the bis complex in accord with the equilibrium:

$$3[Ni(H_2O)_2(o\text{-phen})_2]^{2+} \leftrightarrows 2[Ni(o\text{-phen})_3]^{2+} + [Ni(H_2O)_6]^{2+}$$

However, the less stable mono complexes have been recently isolated.[4,5]

The tris complex has been extensively studied. Measurements have been made of magnetic susceptibility,[6] spectra,[7] reaction rates,[8,9] racemization,[10] and biological activity.[11] Although of outer-orbital (sp^3d^2) configuration, the octahedral tris complex may be conveniently resolved in a single precipitation by use of potassium antimony *dextro*-tartrate because of the large difference in solubility of the diastereoisomers.[12] The antipodes are then obtained as the sparingly soluble perchlorates.

Procedure

$$NiCl_2 \cdot 6H_2O + 3(o\text{-phen} \cdot H_2O) \rightarrow dl\text{-}[Ni(o\text{-phen})_3]Cl_2 + 9H_2O$$

Caution. Tris(o-phenanthroline) complexes should be handled with care because of potential high toxicity.

A solution of *dl*-tris(1,10-phenanthroline)nickel(II) chloride is prepared by adding 3.0 g. (0.015 mol) of 1,10-phenanthroline 1-hydrate to a solution of 1.2 g. (0.005 mol) of nickel(II) chloride 6-hydrate in 40 ml. of water. As the mixture is stirred, the white crystals slowly dissolve and the green solution changes to a deep burgundy color.

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* "*o*-phen" represents 1,10-phenanthroline ($C_{12}H_8N_2$).

A. *d*-TRIS(1,10-PHENANTHROLINE)NICKEL(II) PERCHLORATE 3-HYDRATE

$$2\{dl\text{-}[\mathrm{Ni}(o\text{-phen})_3]\mathrm{Cl}_2\} + 2(d\text{-}\mathrm{KSbC_4H_4O_7}\cdot\tfrac{1}{2}\mathrm{H_2O}) + 6\mathrm{H_2O} \rightarrow d\text{-}[\mathrm{Ni}(o\text{-phen})_3]d\text{-}(\mathrm{SbC_4H_4O_7})_2\cdot 7\mathrm{H_2O} + 2\mathrm{KCl} + l\text{-}[\mathrm{Ni}(o\text{-phen})_3]\mathrm{Cl}_2$$

$$d\text{-}[\mathrm{Ni}(o\text{-phen})_3]d\text{-}(\mathrm{SbC_4H_4O_7})_2\cdot 7\mathrm{H_2O} + 2\mathrm{NaOH} \rightarrow d\text{-}[\mathrm{Ni}(o\text{-phen})_3](\mathrm{OH})_2 + 2(d\text{-}\mathrm{NaSbC_4H_4O_7}) + 7\mathrm{H_2O}$$

$$d\text{-}[\mathrm{Ni}(o\text{-phen})_3](\mathrm{OH})_2 + 2\mathrm{NaClO_4} + 3\mathrm{H_2O} \rightarrow d\text{-}[\mathrm{Ni}(o\text{-phen})_3](\mathrm{ClO_4})_2\cdot 3\mathrm{H_2O} + 2\mathrm{NaOH}$$

To the burgundy-colored solution which has been cooled to about 15° is added *slowly with stirring* a similarly cooled solution of 5.0 g. (0.015 mol) of potassium antimony *d*-tartrate $\frac{1}{2}$-hydrate in 100 ml. of water, whereupon the pink crystalline diastereoisomer precipitates.* The mixture is cooled rapidly in an ice bath to about 5° and is filtered through a 5-cm. Büchner funnel. The *l*-antipode is *immediately* precipitated from the filtrate (*A*) with sodium perchlorate as described in Part B. The diastereoisomer (approximately 3.0 g.) is washed with two 10-ml. portions of ice water and purified by dissolving in 30 ml. of 1.0 *M* sodium hydroxide, filtering to remove undissolved material, and reprecipitating by dropwise addition of glacial acetic acid (approximately 1 ml.) until the solution is slightly acidic (pH about 6). The purified diastereoisomer is washed with three 10-ml. portions of ice water and air-dried. The yield is approximately 2.9 g. (89%). For a 0.440% solution in 0.10 *M* sodium hydroxide in a 2-dm. tube: $\alpha_{\mathrm{D}}^{28.5} = +7.50°$, $[\alpha]_{\mathrm{D}}^{28.5} = +915°$, and $[\alpha]_{\mathrm{D}}^{15} = +950°$.[12]

The diastereoisomer is dissolved in a minimum volume (about 75 ml.) of 0.05 *M* sodium hydroxide by stirring, and undissolved material is removed by filtration. Five milliliters of 1.0 *M* sodium perchlorate (7.02 g. $\mathrm{NaClO_4\cdot H_2O}$/50 ml. of solution) is added *dropwise*, and the resulting pink precipitate is collected on a 5-cm. Büchner funnel and

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* If commercial-grade tartar emetic is used, the precipitate may be tan. Scratching the beaker walls may facilitate precipitation.

washed with three 10-ml. portions of ice water. The crystals are dissolved in a minimum volume (about 90 ml.) of warm (55 to 60°) 30% by volume acetone-water mixture;* the solution is cooled to about 25° in an ice bath; and the perchlorate is fractionally precipitated by dropwise addition of 1.0 *M* sodium perchlorate (1.0 ml. for the first fraction,† 9.0 ml. for the second fraction). The *d*-perchlorate is washed with three 10-ml. portions of ice water and is purified by dissolving in a minimum volume (about 75 ml.) of warm (55 to 60°) 30% by volume acetone-water mixture,* cooling the solution to about 25° in an ice bath, and reprecipitating by dropwise addition of 4.0 ml. of 1.0 *M* sodium perchlorate. The pink crystals of *d*-perchlorate 3-hydrate are washed with three 10-ml. portions of ice water and air-dried. The yield is 0.87 g. (40%). For a 0.4084% solution in 50% by volume acetone-water mixture in a 2-dm. tube: $\alpha_D^{25} = +12.06°$, $[\alpha]_D^{25} = +1476°$, and $[\alpha]_D^{15} = +1463°$.[12]

Analysis

Nickel is determined by heating the sample with sulfuric acid until all fuming has ceased, dissolving the residue in sulfuric acid, diluting, making the solution ammoniacal, and electrolyzing. Calcd. for $[Ni(C_{12}H_8N_2)_3](ClO_4)_2 \cdot 3H_2O$: Ni, 6.89. Found: Ni, 6.89.

B. *l*-TRIS(1,10-PHENANTHROLINE)NICKEL(II) PERCHLORATE 3-HYDRATE

$$l\text{-}[Ni(o\text{-phen})_3]Cl_2 + 2NaClO_4 + 3H_2O \rightarrow l\text{-}[Ni(o\text{-phen})_3](ClO_4)_2 \cdot 3H_2O + 2NaCl$$

Five milliliters of 1.0 *M* sodium perchlorate‡ is added dropwise to the pink filtrate (*A*) from Part A, and the pink

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* The acetone-water mixtures should be freshly prepared, inasmuch as the concentration of the mixture may change even over a 24-hour period.

† The first fraction, which may contain some of the less soluble *dl*-perchlorate, is discarded.

‡ Excess sodium perchlorate may precipitate potassium perchlorate.

crystalline precipitate is collected on a 5-cm. Büchner funnel, washed with 10 ml. of ice water, and dissolved in a minimum volume (approximately 100 ml.) of warm (55 to 60°) freshly prepared 30% by volume acetone-water mixture. The solution is cooled to about 25° in an ice bath, and the *l*-antipode is reprecipitated by dropwise addition of 15.0 ml. of 1.0 *M* sodium perchlorate. The pink crystals of the *l*-perchlorate 3-hydrate are washed with four 10-ml. portions of ice water and air-dried. The yield is 1.15 g. (53.4%). For a 0.3960% solution in 50% by volume acetone-water mixture in a 2-dm. tube: $\alpha_D^{25} = -11.74°$, $[\alpha]_D^{25} = -1482°$, and $[\alpha]_D^{15} = -1463°$.[12] *Anal.* Calcd. for $[Ni(C_{12}H_8N_2)_3](ClO_4)_2 \cdot 3H_2O$: Ni, 6.89. Found: Ni, 6.87.

Properties[12]

The optical antipodes of tris(1,10-phenanthroline)nickel(II) perchlorate are more stable than those of the corresponding tris(2,2′-bipyridine)[tris(2,2′-dipyridyl)] compound.[13] In 18 hours, solutions of the 1,10-phenanthroline complexes lose only 50% of their activity. When examined at 589.0 and 546.1 mμ, the antipodes show a large abnormal rotatory dispersion. The precipitation of $[Ni(o\text{-phen})_3][Co(CO)_4]_2$ is the basis for a method of determining cobalt tetracarbonyl hydride.[14]

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60. BIS(4-IMINO-2-PENTANONATO)NICKEL(II)*
[Nickel(II) Acetylacetone Imide]

$$2C_5H_9NO + Ni(NO_3)_2 + 2NH_4OH \rightarrow [(C_5H_8NO)_2Ni] + 2NH_4NO_3 + 2H_2O$$

Submitted by A. W. Struss† and Dean F. Martin†
Checked by Norman E. Griswold‡

This reaction is analogous to the preparation of bis(4-imino-2-pentanonato)copper(II) [bis(4-amino-3-penten-2-onato)copper(II)] described by Holtzclaw, Collman, and Alire,[1] and it consists in mixing an ethanolic solution of the β-keto imine (β-imino ketone) with an ammoniacal metal salt solution. Advantages of this technique are the simplicity of preparation and the fact that acetylacetone imide (4-imino-2-pentanone) can be purchased.§ The product is useful as a starting material in ligand-exchange reactions.

Procedure

To a solution of 12.0 g. (0.12 mol) of acetylacetone imide (4-imino-2-pentanone) in 100 ml. of 95% ethanol is added a

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* Following submission of this synthesis, a similar synthesis for the compound was reported independently by Dr. R. D. Archer.[2]

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‡ University of Nebraska, Lincoln, Neb.

§ Aldrich Chemical Company, Milwaukee, Wis.

solution of 20.4 g. (0.07 mol) of nickel(II) nitrate 6-hydrate in 300 ml. of water containing 25 ml. of 15 *M* aqueous ammonia.* The reaction mixture is shaken vigorously until a light orange precipitate forms. This mixture is allowed to stand at room temperature overnight (approximately 10 hours). After filtration, the 12.0 g. of crude product is recrystallized from 900 ml. of a 1:1 mixture of benzene and petroleum ether (b.p. 90 to 110°). The first crop of crystals weighs at least 8.0 g. After reducing the volume of the filtrate to 50 ml., a second crop of 0.60 g. may be obtained. The total yield after recrystallization is at least 8.6 g. (56.2%) (m.p. 249 to 251°). *Anal.* Calcd. for $(C_5H_8NO)_2$-Ni: C, 47.1; H, 6.28; N, 11.0. Found: C, 46.80; H, 6.36; N, 11.11. By checker: C, 46.95; H, 6.33; N, 11.07.

Properties

Bis(4-imino-2-pentanonato)nickel(II) crystallizes from a benzene–petroleum ether mixture as dark red needles or as fine red-orange needles. The two forms have identical melting points. The compound is very soluble in chloroform, but less soluble in benzene, pyridine, and carbon tetrachloride, and very insoluble in water. The compound crystallizes from pyridine without adduct formation.[4] The compound is diamagnetic and apparently has the trans configuration.[2] Partial resolution in optically active fractions has been achieved by means of a chromatographic technique.[3] Molecular weight determinations indicate that the compound is monomeric in chloroform and benzene solution.[3] The visible absorption spectrum of this compound in chloroform is characterized by a band centered at 552 mμ (ϵ = 43).[2] The ultraviolet absorption maxima for solutions in 1:1 benzene–petroleum ether occur at 298, 348, and 364 mμ (ϵ = 4150, 4760, and 4460, respectively).[3]

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* A large excess of ammonia will reduce the yield. The yield is 27.8% when 50 ml. of 15 *M* aqueous ammonia is used.

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Edited by Henry F. Holtzclaw, Jr.

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61. TETRAAMMINEPALLADIUM(II) TETRACHLOROPALLADATE(II) AND *trans*-DICHLORODIAMMINEPALLADIUM(II)

$$Pd + 2HNO_3 + 4HCl \rightarrow H_2[PdCl_4] + 2H_2O + 2NO_2\uparrow$$
$$H_2[PdCl_4] + 2NaCl \rightarrow Na_2[PdCl_4] + 2HCl\uparrow$$
$$Na_2[PdCl_4] + 4NH_3 \rightarrow [Pd(NH_3)_4]Cl_2 + 2NaCl$$
$$[Pd(NH_3)_4]Cl_2 + 2HCl \rightarrow \textit{trans}\text{-}[Pd(NH_3)_2Cl_2]\downarrow + 2NH_4Cl$$
$$[Pd(NH_3)_4]Cl_2 + Na_2[PdCl_4] \rightarrow [Pd(NH_3)_4][PdCl_4]\downarrow + 2NaCl$$

Submitted by George B. Kauffman* and James Hwa-san Tsai*
Checked by Lowell P. Eddy,† Leonard Johannes,† and David Parker†

Tetraamminepalladium(II) tetrachloropalladate(II), the palladium analog of Magnus' green salt, $[Pt(NH_3)_4][PtCl_4]$, may be prepared by treatment of aqueous ammonium tetrachloropalladate(II) with aqueous ammonia,[1,2] by addition of aqueous ammonia to a palladium(II) chloride solution,[2–5] by treatment of aqueous tetraamminepalladium(II) chloride with palladium(II) chloride solution,[6] and by precipitation on mixing a freshly prepared solution of a tetraamminepalladium(II) salt with cold aqueous potassium tet-

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* California State College at Fresno, Fresno, Calif. For support of this research, acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society.
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rachloropalladate(II).[7] Modification of this last method, given below, which uses metallic palladium as a starting material, gives a pure product in almost quantitative yield. Evaporation of the tetraamminepalladium(II) chloride solution and addition of hydrochloric acid precipitates *trans*-dichlorodiamminepalladium(II), which is a compound used in the separation of palladium from other platinum metals, the determination of the atomic weight of palladium, and the preparation of dipositive palladium complexes. Tetraamminepalladium(II) tetrachloropalladate(II), Vauquelin's red salt, is a "polymerization isomer" of *trans*-dichlorodiamminepalladium(II).[8]

Procedure

Caution. This synthesis should be performed in a hood.

A 2.134-g. (0.0202-mol) quantity of palladium metal is dissolved in aqua regia (3 ml. of 15 *N* HNO_3 + 12 ml. of 12 *N* HCl) which has been allowed to stand for about 30 minutes. If powdered palladium is used, no heat is required to effect solution; for other forms of palladium metal, some heating is usually required. The solution is evaporated on a steam bath to a brown-black syrup, which is then covered with 5 ml. of 12 *N* hydrochloric acid and evaporated to moist salts. This treatment with hydrochloric acid is repeated twice more to remove nitric acid and to destroy nitrosyl complexes.[9] The resulting tetrachloropalladic(II) acid is dissolved, with stirring and heating, in a minimum volume of water (approximately 100 ml.), and 4.0 g. (0.068 mol) of sodium chloride is added. The dark brown solution is concentrated to one-half its volume on a hot plate and is then evaporated to dryness on a steam bath. This evaporation removes excess hydrochloric acid, which if allowed to remain leads to contamination of the tetraamminepalladium(II) tetrachloropalladate(II) with the isomeric *trans*-dichlorodiamminepalladium(II). Removal of hydrochloric acid also prevents loss of product owing to the solubility of the red salt in acid solution. Use of a steam bath, rather than a hot plate, for the final stage of the evaporation prevents thermal decomposition of sodium tetrachloropalladate(II), which may decompose at higher temperatures.

From this point on, either of two alternative procedures may be followed, depending upon the product desired. If the synthesis is to lead to tetraamminepalladium(II) tetrachloropalladate(II), Procedure 1 should be followed; if dichlorodiamminepalladium(II) is the desired compound, Procedure 2 should be used.

1. Tetraamminepalladium(II) tetrachloropalladate(II). The dark red-brown residue from the above evaporation is dissolved in 200 ml. of water, and the solution is divided into two equal portions, *A* and *B*. Portion *A* is diluted to 300 ml. and is heated to vigorous boiling. To the vigorously boiling solution, approximately 10 ml. of 5 *N* aqueous ammonia is slowly added dropwise and with stirring until the solution has become a light straw-yellow. During the addition of the ammonia, the yellow precipitate of *trans*-dichlorodiamminepalladium(II), which forms as an intermediate following the addition of each drop, is allowed to dissolve before the next drop of ammonia is added. Occasionally, a fine black precipitate forms and does not dissolve despite vigorous boiling. Undissolved precipitate will lower the yield of desired compound but does not seem to have any other effect on the course of the reaction. If such a precipitate forms and will not redissolve with vigorous boiling, it may be filtered from the solution after the reaction mixture has cooled to room temperature. After the addition of the ammonia is completed, the solution is allowed to cool to room temperature and is carefully brought to a pH of 8 with pHydrion paper by the dropwise addition, with stirring, of several milliliters of 5 *N* hydrochloric acid.

To the solution is next added slowly and with stirring

90 ml. of solution *B*, whereupon a copious rose-red precipitate of tetraamminepalladium(II) tetrachloropalladate(II) forms. The acidity of the suspension is readjusted to about pH 8 with pHydrion paper by the addition of several drops of 5 *N* ammonia, and the remainder of solution *B* is added slowly with stirring. The product is collected immediately on a 5-cm. Büchner funnel and washed with successive 10-ml. portions of water until the washings no longer give a positive test for chloride ion; it is then washed twice with 10-ml. portions of acetone and is air-dried. Immediate isolation of the product from the solution is necessary to prevent hydrolysis, which produces a brown precipitate and a yellow solution. The yield of tetraamminepalladium(II) tetrachloropalladate(II) is 3.99 g. (93.4%). *Anal.* Calcd. for $[Pd(NH_3)_4][PdCl_4]$: Pd, 50.34; N, 13.25. Found: Pd, 50.20. By checker: Pd, 50.61; N, 13.36.

2. *trans*-Dichlorodiamminepalladium(II). The dark red-brown residue from the evaporation step of the general procedure given above is diluted to 600 ml., and, after bringing the solution to a vigorous boil, 20 ml. of 5 *N* aqueous ammonia is added dropwise with stirring. If a precipitate forms and will not redissolve despite vigorous boiling, it may be filtered from the solution after the reaction mixture has cooled. After the ammonia has been added, the solution is evaporated to 200 ml. on a hot plate and then to 100 ml. on a steam bath. The solution is allowed to cool to room temperature, 10 ml. of 6 *N* hydrochloric acid is added, and the mixture is cooled in an ice bath for 15 minutes. The yellow crystalline product is collected on a 5-cm. Büchner funnel, washed twice with 10-ml. portions of 3 *N* hydrochloric acid and then with several 10-ml. portions of ice water until the washings are neutral to pHydrion paper. The yield of air-dried *trans*-dichlorodiamminepalladium(II) is 4.10 g. (96.0%). *Anal.* Calcd. for $[Pd(NH_3)_2Cl_2]$: Pd, 50.34. Found: Pd, 50.20. By checkers: Pd, 50.35.

Properties

Tetraamminepalladium(II) tetrachloropalladate(II) is a rose-red powder which is stable up to 180° but which isomerizes at higher temperatures to *trans*-dichlorodiamminepalladium(II).[2,3] The reaction is not reversible. Although tetraamminepalladium(II) tetrachloropalladate(II) is insoluble in cold water,[2,3] it reacts with boiling water to produce a brown residue.[3,4] When the aqueous solution is cooled, *trans*-dichlorodiamminepalladium(II) precipitates.[4] Tetraamminepalladium(II) tetrachloropalladate(II) dissolves in aqueous ammonia on long heating to give a solution which contains tetraamminepalladium(II) chloride.[2] Acidification or evaporation of this solution produces *trans*-dichlorodiamminepalladium(II),[2–4] a yellow water-insoluble nonelectrolyte which is stable below 210° but which decomposes into palladium, ammonium chloride, and hydrogen chloride above this temperature.[10] Similarly to tetraamminepalladium(II) tetrachloropalladate(II), the *trans*-dichlorodiamminepalladium(II) dissolves in aqueous ammonia to form tetraamminepalladium(II) chloride.[2,3,7]

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62. TRIS(ETHYLENEDIAMINE)PLATINUM(IV) CHLORIDE

$$Pt + 6HCl + 4HNO_3 \rightarrow H_2PtCl_6 \cdot xH_2O + 4NO_2 + (4 - x)H_2O$$

$$H_2PtCl_6 \cdot xH_2O + 5C_2H_4(NH_2)_2 \rightarrow [Pt(en)_3]Cl_4 + 2[C_2H_4(NH_2)_2 \cdot HCl] + xH_2O$$

Submitted by D. C. Giedt* and C. J. Nyman*
Checked by John Young† and R. Kent Murmann†

Tris(ethylenediamine)platinum(IV) chloride was first reported by A. Werner[1] in 1917. Several variations of his method have been used,[2] but basically the preparation from platinum involves three steps: (1) the preparation of the hexachloroplatinic(IV) acid, (2) the preparation of the crude tris(ethylenediamine)platinum(IV) chloride, and (3) purification. The following procedure is a modification of Werner's method.

Procedure

Preparation of Hexachloroplatinic(IV) Acid.‡ Three and eight-tenths grams (0.02 mol) of platinum metal is dissolved in 80 ml. of hot aqua regia (three volumes of concentrated hydrochloric acid to one volume of concentrated nitric acid). Nitric acid is removed from the reaction mixture by five successive evaporations with concentrated (12 *N*) hydrochloric acid. The solution should be evaporated almost to dryness each time. An electric hot plate is best for this process inasmuch as overheating causes the

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‡ Alternatively, hexachloroplatinic(IV) acid may be purchased commercially for use in the following parts of the procedure.

hexachloroplatinic(IV) acid to be reduced to platinum metal. After the excess hydrochloric acid is driven off, the solution becomes a deep orange viscous liquid. At this point it is removed from the hot plate and the pure orange hexachloroplatinic(IV) acid crystallizes. If the acid does not crystallize immediately on cooling, the solution should be reheated to remove any traces of excess hydrochloric acid that may still be present.

Preparation of Crude Tris(ethylenediamine)platinum(IV) Chloride. Ten and one-tenths grams (0.019 mol, assuming the 6-hydrate) of hexachloroplatinic(IV) acid is dissolved in 80 ml. of absolute ethanol. After cooling this solution in an ice bath, 6.6 ml. of 98% ethylenediamine [5 mols of ethylenediamine per mol of hexachloroplatinic(IV) acid] is slowly added with constant stirring. A pale yellow precipitate forms immediately. The mixture is heated to 65° and is maintained at 65 ± 1° in a water bath for 2 hours. Care must be exercised not to heat the reaction mixture above 70° inasmuch as a brown gum occasionally forms at higher temperatures. The mixture is stirred constantly during the digestion period. Absolute ethanol is added as required to keep the volume of the reaction mixture constant. The mixture is allowed to cool to room temperature, and the tris(ethylenediamine)platinum(IV) chloride is separated from the ethanol solution by suction filtration. The crude yellow product is washed twice with absolute ethanol. The yield of the crude wet product is about 17 g.

Purification. Seventeen grams of the crude product is recrystallized as follows. The product is dissolved in 20 ml. of boiling water. Twenty milliliters of concentrated (12 *N*) hydrochloric acid is added; a white precipitate forms immediately. Gentle heating is continued until the solution is again at the boiling point, and then the minimum quantity of boiling water (about 80 ml.) necessary to dissolve all of the solid at the boiling point of the solution is added in small portions. The solution is allowed to cool slowly and stand for several hours at room temperature so that slow crystallization occurs. The tris(ethylenediamine)platinum(IV) chloride, which crystallizes as long white needles, is collected on a coarse Hirsch funnel and dried by sucking air through it. The entire recrystallization procedure is then repeated twice, using amounts of water and hydrochloric acid in the same proportion to the weight of solute as indicated above. After the third recrystallization, the wet crystals are rapidly washed twice with 10-ml. portions of 6 *N* hydrochloric acid and water at 0° and once with a minimum amount (10 ml. or less) of water at 0°. The product is dried for 3 hours at 105°. The final yield of tris(ethylenediamine)platinum(IV) chloride is 6.7 g. (66%, based on platinum metal). *Anal.* Calcd. for $[Pt(en)_3]Cl_4$: Pt, 37.71; Cl, 27.42. Found: Pt, 37.69, Cl, 27.51.

Properties

Tris(ethylenediamine)platinum(IV) chloride is a white crystalline solid which is readily soluble in water and stable toward decomposition in both acidic and basic solution. Resolution of the complex cation into its optical isomers has been achieved by fractional precipitation of l-$[Pt(en)_3]Cl_2(d\text{-}C_4H_4O_6)$ on addition of ammonium *d*-tartrate to the racemic mixture.[3] Racemization of the cation occurs only under extreme conditions and is accompanied by little exchange of bound ethylenediamine. A solution of the complex is quantitatively reduced to platinum metal by magnesium and hydrochloric acid. The solid complex is quantitatively reduced to platinum metal upon ignition.

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63. *cis*-DICHLORO(ETHYLENEDIAMINE)-PLATINUM(II)

$$K_2[PtCl_4] + H_2NCH_2CH_2NH_2{\cdot}2HCl + 2NaOH \rightarrow [Pt(en)Cl_2] + 2NaCl + 2KCl + 2H_2O$$

Submitted by Gordon L. Johnson*
Checked by Theodore A. Michelfeld†

An early preparation of *cis*-dichloro(ethylenediamine)-platinum(II), $[Pt(en)Cl_2]$, was reported by Jörgensen,[1] who obtained the compound by the slow addition of a dilute solution of ethylenediamine to a cold aqueous solution of potassium tetrachloroplatinate(II), $K_2[PtCl_4]$. More recently this same compound has been synthesized by Drew,[2] by Basolo, Bailar, and Tarr,[3] and by Heneghan and Bailar[4] using procedures based upon the method of Jörgensen. Watt and McCarley[5] synthesized the compound from *cis*-dibromo(ethylenediamine)platinum(II), which was prepared by the Jörgensen method. All of these procedures are time-consuming and sometimes produce a product in low yield and in a rather impure state. The following method for the preparation of *cis*-dichloro(ethylenediamine)platinum(II) overcomes these difficulties.

Procedure

To a solution containing 4.15 g. (0.010 mol) of potassium tetrachloroplatinate(II)‡ in 50 ml. of water is added 1.33 g.

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‡ The preparation of potassium tetrachloroplatinate(II) has been described by R. N. Keller, Inorganic Syntheses, **2**, 247 (1946). The author used this general method in preparing the compound, but used hydrazinium(2+) chloride instead of sulfur dioxide as the reducing agent for the platinum(IV) compound. A procedure using hydrazinium(2+) chloride as the reducing agent for hexachloroplatinic(IV) acid 6-hydrate has been described by W. E. Cooley and D. H. Busch, Inorganic Syntheses, **5**, 208 (1957).

(0.010 mol) of ethylenediamine 2-hydrochloride. The resulting solution is heated to boiling and is kept boiling gently for 30 minutes during the dropwise addition of a solution containing 0.90 g. (0.022 mol) of sodium hydroxide dissolved in 30 ml. of water. The addition of sodium hydroxide is continued until the acidity of the solution remains constant at pH 6.* It will be found that upon each addition of sodium hydroxide to the pale yellow solution the pH rises rapidly as free ethylenediamine is liberated from its hydrochloride and then decreases slowly as the ligand reacts with the tetrachloroplatinate(II) ion. If at any time the solution becomes more alkaline than pH 6, platinum black forms. If this occurs, the solution should be cooled immediately and filtered to remove the metallic platinum before the reaction is continued. (Mechanical stirring of the solution will help to prevent local rises in pH and consequent precipitation of platinum during the addition of the base.)

cis-Dichloro(ethylenediamine)platinum(II) and the chief by-product of the reaction, bis(ethylenediamine)platinum(II) tetrachloroplatinate(II), $[Pt(en)_2][PtCl_4]$, start to precipitate from the solution before all of the ethylenediamine 2-hydrochloride has been neutralized by the base. When the reaction is complete, the mixture is evaporated to dryness on the steam bath and the residue is transferred to a sintered-glass funnel with the aid of five 3-ml. portions of 0.001 *N* hydrochloric acid solution. Air is drawn through the funnel until the product is thoroughly dry.

The crude *cis*-dichloro(ethylenediamine)platinum(II) is purified by dissolving it in approximately 250 ml. of liquid ammonia[5] and separating it by filtration from the insoluble violet-colored bis(ethylenediamine)platinum(II) tetrachloroplatinate(II). The liquid-ammonia filtrate is allowed to evaporate, and the residue is washed into a sintered-glass

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* Accutint Indicator Paper (wide range B) made by Anachemia Chemicals Ltd., Montreal, Canada, and Champlain, N.Y., is suitable for checking the pH of the solution during the course of the reaction.

funnel with several 2-ml. portions of acidified wash water; it is then washed with ethanol and with ether and allowed to dry in the air. The yield is 2.22 g. (68.1% based on K_2PtCl_4). *Anal.* Calcd. for $[Pt(en)Cl_2]$: Pt, 59.83; C, 7.36; H, 2.47; N, 8.59; Cl, 21.75. Found: Pt, 60.00; C, 7.35; H, 2.57; N, 8.60; Cl, 21.88.

Properties

The *cis*-dichloro(ethylenediamine)platinum(II) prepared by this method is a yellow powder which is practically insoluble in cold water and in cold dilute hydrochloric acid; it is moderately soluble in liquid ammonia and in boiling water. The compound forms yellow needles when recrystallized from water acidified with hydrochloric acid.[4] Recrystallization from *N*,*N*-dimethylformamide is effected by the addition of water and then cooling. Darkening of the dry compound occurs at approximately 230°. The compound is soluble, without reaction, in hot 12 *M* hydrochloric acid. It is stable for several hours in contact with a cold saturated sodium hydroxide solution; however, the compound dissolves rapidly, by reaction, upon treatment with a hot 1 *M* sodium hydroxide solution. The reactions of $[Pt(en)Cl_2]$ with water and 0.008 and 0.016 *M* potassium hydroxide solutions have been studied.[6] The six most intense x-ray diffraction lines have been reported.[5]

The product is a useful starting material for the preparation of several platinum(IV) compounds such as dichlorodihydroxo(ethylenediamine)platinum(IV), $[Pt(en)(OH)_2Cl_2]$, and tetrachloro(ethylenediamine)platinum(IV), $[Pt(en)Cl_4]$.[3,4]

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64. *cis-* AND *trans-*TETRACHLOROBIS(DIETHYL SULFIDE)PLATINUM(IV)

$$cis\text{- or } trans\text{-}[\mathrm{Pt}\{(\mathrm{C_2H_5})_2\mathrm{S}\}_2\mathrm{Cl_2}] + \mathrm{Cl_2} \rightarrow cis\text{- or } trans\text{-}[\mathrm{Pt}\{(\mathrm{C_2H_5})_2\mathrm{S}\}_2\mathrm{Cl_4}]$$

Submitted by George B. Kauffman,* James Hwa-san Tsai,* and Lloyd T. Takahashi*
Checked by J. W. Hogarth† and F. P. Dwyer†‡

The complexes of platinum(IV), less well known than those of platinum(II), can be prepared by oxidation of the latter. Such a conversion often proceeds with retention of configuration. Early workers[1,2] reported that halogenation of either *cis-* or *trans-*dihalobis(dialkyl sulfide)platinum(II) resulted in only one product. The compound obtained by Loir[3] and Rây and Bose-Rây[4] by treating diethyl sulfide with aqueous or alcoholic $H_2[Pt(OH)_2Cl_4]$ was probably mainly the trans isomer. The preparation given here, based on the work of Angell, Drew, and Wardlaw,[5] involves the chlorination of *cis-* and *trans-*dichlorobis(diethyl sulfide)platinum(II) in cold benzene solution. In this nonpolar solvent, isomerization is minimized.

Procedure

A. *cis-*TETRACHLOROBIS(DIETHYL SULFIDE)PLATINUM(IV)

A slow stream of chlorine (60 to 100 bubbles/minute)§ is bubbled for 8 to 10 minutes through a pale yellow solution of

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† Australian National University, Canberra, A.C.T., Australia.

‡ Deceased.

§ The bore of the delivery tube must be sufficiently large to avoid clogging with product, which begins to precipitate immediately on chlorination.

1.20 g. (0.0027 mol) of *cis*-dichlorobis(diethyl sulfide)platinum(II)[6] in approximately 40 ml. of benzene which has been cooled to but not below 5° in an ice bath. The bright yellow precipitate of *cis*-tetrachlorobis(diethyl sulfide)platinum(IV) is separated from the cold bright yellow solution by suction filtration, washed with two 10-ml. portions of diethyl ether, and air-dried (oven-drying causes isomerization to the trans isomer). The yield of crude product is 1.19 g. (86%). The product melts at 129 to 130°, solidifies, and then remelts at 195°.*

The product may be recrystallized with a recovery of about 90% by dissolving it in a minimum amount of chloroform (approximately 5 ml./g. of isomer), adding diethyl ether (approximately 7 ml./g. of isomer), cooling for 15 minutes in an ice bath, separating the small bright yellow crystals by suction filtration, washing them with two 10-ml. portions of diethyl ether, and air-drying. The yield of purified product is about 1.10 g. (79% yield, based on $[Pt\{(C_2H_5)_2S\}_2Cl_4]$). The product melts at 131°, solidifies, and then remelts at 197°.* *Anal.* Calcd. for $PtC_8H_{20}S_2Cl_4$: Pt, 37.73; C, 18.56; H, 3.86. Found: Pt, 37.38. By checkers: Pt, 37.90; C, 18.61; H, 3.96.

B. *trans*-TETRACHLOROBIS(DIETHYL SULFIDE)PLATINUM(IV)

The chlorination procedure is the same as that for the cis isomer except that only 7.5 ml. of benzene (an excess may result in an oily product) is used to dissolve the 1.85-g. (0.0042-mol) sample of *trans*-dichlorobis(diethyl sulfide)platinum(II) and the impure product is recovered quantitatively by evaporation of the benzene solution with a stream of air. The orange-yellow residue is dissolved in a minimum amount (45 to 55 ml.) of boiling ethanol, and the solution is allowed to cool first to room temperature† and then in an ice bath for 15 minutes. The fine, lemon-yellow

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* For method of measuring melting points, see Properties.

† Preliminary slow cooling yields purer crystals.

crystals are separated by suction filtration, washed with two 10-ml. portions of 30% cold aqueous ethanol,* and air-dried. The yield is 1.25 g. (58%). The product sinters at about 188° and melts at 201°. *Anal.* Calcd. for $PtC_8H_{20}S_2Cl_4$: Pt, 37.73; C, 18.56; H, 3.86. Found: Pt, 37.90. By checkers: Pt, 37.31; C, 18.51; H, 3.82.

Properties[5]

As prepared above, *cis*-tetrachlorobis(diethyl sulfide)-platinum(IV) is bright yellow, whereas the trans isomer is lemon-yellow. If the cis isomer is heated on a melting-point block well below its melting point, it isomerizes and does not melt until the temperature reaches 195 to 198°. However, if the substance is placed on a melting-point block which has been preheated to 133°, it melts, solidifies almost immediately, and remelts at 201°, the melting point of the trans isomer. The trans isomer also sinters at about 10° below its melting point.

Both isomers are less soluble in benzene than are the corresponding platinum(II) isomers. The trans compound is much more soluble than the cis compound; both may be recrystallized from this solvent, but in low yield. Each isomer is soluble in methanol, ethanol, or acetone, but virtually insoluble in diethyl ether or cold water.

Isomerization of the cis isomer occurs in polar solvents, especially at elevated temperatures. The cis isomer can be converted to the trans isomer by boiling for several minutes n methanol or ethanol, but recrystallization from these solvents is possible if accomplished quickly.

The cis isomer is decomposed by warm concentrated nitric acid, whereas the trans isomer is not attacked.

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Edited by Henry F. Holtzclaw, Jr.

NOBLE GASES (RARE GASES, INERT GASES)

65. INTRODUCTION TO THE CHEMISTRY OF COMPOUNDS OF THE NOBLE GASES*

SUBMITTED BY H. H. HYMAN† AND C. L. CHERNICK†

As early as 1785, Cavendish recognized and demonstrated that atmospheric nitrogen contains a constituent that "cannot be reduced to nitrous acid." Ramsey and Rayleigh, in 1894, concluded a series of investigations on the differences between chemical and atmospheric nitrogen and announced the discovery of the gas "argon." This work was quickly followed by the isolation, mainly by Ramsey, of the remaining members of the noble gas family. For this group, which occupies the position in the periodic table between the halogens and the alkali metals, the most characteristic chemical property was taken to be the absence of chemical reaction.

Concepts of valence and the construction of the periodic table have always been associated with one another. As the idea of electronic distribution in orbitals developed, the role of the noble gases and the concept of filled shells were stressed in many theoretical developments. It must be emphasized that most theoreticians never thought in terms of an absolute prohibition of reactions for the noble gases. Indeed, for awhile the possibilities of compound formation for xenon and even for krypton were suggested. It was only after a number of claims for the synthesis of compounds were discredited and the best investigations of such

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* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

† Argonne National Laboratory, Argonne, Ill.

reactions led to negative results that the lack of reaction of these gases came to be regarded as more or less established. Inasmuch as the absence of reaction for these gases comprised a convenient pedagogic tool, teachers of inorganic chemistry and valence theory have overemphasized the absolute nature of this prohibition.

In 1962, N. Bartlett, having made O_2PtF_6 from oxygen and platinum hexafluoride, reasoned that the comparable ionization energy of xenon might lead to a similar reaction. When he mixed xenon and platinum hexafluoride, these were found to undergo reaction at room temperature in a simple glass system. Bartlett suggested $Xe^+PtF_6^-$ as the most likely formula for the resulting yellow powder, but the exact nature of this reaction has not yet been firmly established. At Argonne National Laboratory, the reaction between xenon and platinum hexafluoride was duplicated; in addition, xenon was shown to undergo reaction at room temperature with ruthenium hexafluoride, but not with uranium hexafluoride or neptunium hexafluoride. When the reaction of xenon with ruthenium hexafluoride was studied quantitatively, approximately twice as much hexafluoride was consumed as with platinum hexafluoride. This suggested the role of the hexafluoride as a fluorine carrier and led to the studies of reactions of xenon with fluorine.

Shortly after publication of the observations on the synthesis of xenon tetrafluoride, research was initiated with the noble gases in a number of laboratories. Xenon difluoride, xenon hexafluoride, xenon oxide tetrafluoride, and xenon trioxide were synthesized and reasonably well characterized within a rather short time. A number of other compounds have since been isolated, including xenon tetraoxide, a family of perxenates, and a variety of complex fluorides such as $XeF_2 \cdot 2SbF_5$, $XeF_6 \cdot BF_3$, and Cs_2XeF_8.

The syntheses of fluorides of krypton and radon have also been demonstrated. Krypton fluorides are harder to make and probably are less stable than the corresponding xenon fluorides. Fluorides of radon would be expected to be more stable than those of xenon. However, the high radioactivity associated with the radon makes predictions of stability rather tenuous.

Very shortly after the synthesis of the xenon compounds, the techniques of infrared absorption, Raman, and nuclear magnetic resonance spectroscopy were brought to bear on the structure of individual molecules, while x-ray and neutron diffraction studies were used to reveal the structure of solid phases. The difluoride of xenon is a linear molecule, and the tetrafluoride exhibits a square-planar arrangement. The highly reactive nature of the hexafluoride has made it difficult to obtain the necessary experimental data to establish its structure, and a conflict has developed over whether or not it shares the octahedral symmetry characteristic of other hexafluorides studied to date. The infrared and Raman spectra of the hexafluoride appear to be too complex to indicate octahedral symmetry. In $XeOF_4$ the oxygen occupies a position above the xenon, whereas the fluorine atoms retain the square-planar array. The XeO_3 molecule appears to be best interpreted in terms of a symmetrical distribution of the three oxygen atoms around the xenon as a trigonal pyramid. Preliminary spectral results indicate that xenon tetraoxide has a tetrahedral structure.

Xenon difluoride dissolves in water, yielding a solution which contains undissociated XeF_2 molecules which have a half-life of about 7 hours at 0°. It eventually hydrolyzes to yield the expected products, xenon, hydrogen fluoride, and oxygen. The hydrolysis reactions of the tetrafluoride and hexafluoride are somewhat more complicated. The addition of the stoichiometric amount of water to the hexafluoride results in the formation of xenon oxide tetrafluoride. Hydrolysis of either fluoride with an excess of water or acid yields in solution a stable xenon(VI) species, which has been shown to be hydrated xenon trioxide. Removal of the excess water leaves xenon trioxide as a solid residue. Inasmuch as this solid is an extremely sensitive explosive, such solutions must be handled with care.

Hydrolysis of xenon hexafluoride or tetrafluoride with a sodium hydroxide solution results in the precipitation of a stable xenon(VIII) salt, sodium perxenate, Na_4XeO_6, which on heating does not decompose until around 300°. Similar hydrolysis with potassium hydroxide can yield a yellow precipitate which is a mixed potassium perxenate–xenon trioxide salt, and is explosive even when damp. With more concentrated base, the much more stable hydrated perxenate may be isolated.

Studies of the nonaqueous chemistry of xenon fluorides have also been initiated. Whereas xenon tetrafluoride is only sparingly soluble in hydrogen fluoride, xenon difluoride and xenon hexafluoride are very soluble indeed. Electrical conductivity, absorption and Raman spectroscopy, and nuclear magnetic resonance measurements have been employed in studying these solutions. The observations have been interpreted in terms of dissolution without appreciable dissociation for xenon difluoride and xenon tetrafluoride, and dissolution with extensive ionization for xenon hexafluoride. The extensive solubility and ionization of xenon hexafluoride contrast strikingly with the behavior of other hexafluorides (e.g., uranium hexafluoride).

Almost before the news of the preparations had been published, theoreticians had begun to explore the nature of the bonding between the noble gases and fluorine. Many saw a relationship to the bonding in the halogen fluorides, such as chlorine trifluoride and bromine pentafluoride. However, scientists who agreed upon the similarity between the noble gas fluorides and the halogen fluorides did not necessarily agree on the nature of the bonding in either case. Early attempts at predicting the shapes and sizes of the noble gas fluoride molecules were not especially successful. There now seems to be general agreement between the known shapes of a number of noble gas fluorides and oxides and the theoretical models. However, the shape of the hexafluoride has resulted in a controversy between the molecular-orbital model and the localized electron-pair bond model. According to the former, xenon hexafluoride should exhibit octahedral symmetry, while the latter suggests a structure distorted from such symmetry. The evidence from infrared and Raman spectroscopy, as already indicated, would seem to favor an unsymmetric molecule. However, alternative explanations for these spectra have been suggested, involving perhaps low-lying excited electronic states for the hexafluoride.

Although the compounds formed by the noble gases will undoubtedly be explained and described by the same general theories that prove successful in correlating the properties of other compounds, the noble gas compounds seem to pose a rather formidable challenge. It is to be hoped that the rapidly accumulating body of information will stimulate theoreticians to meet this challenge and inevitably increase our understanding of chemical bond formation. The synthesis of xenon compounds is relatively simple, and many laboratories should be able to contribute to this accumulation of information.

Syntheses of xenon tetrafluoride (synthesis 66), xenon hexafluoride (synthesis 67), and xenon difluoride (synthesis 68) appear in this volume.

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Edited by Henry F. Holtzclaw, Jr.

66. XENON TETRAFLUORIDE

$$Xe + 2F_2 \rightarrow XeF_4$$

Submitted by J. G. Malm* and C. L. Chernick*
Checked by Stanley M. Williamson†

Xenon tetrafluoride has been prepared by a number of methods. Irradiation of a mixture of xenon and fluorine with ultraviolet light produces xenon difluoride if the reaction product is immediately condensed from the gas phase.[1] However, if the difluoride is allowed to remain in the reaction zone, the tetrafluoride is produced.[2] Passage of an electric discharge through a mixture of xenon and fluorine also produces xenon tetrafluoride.[3] Perhaps the best method is the one in which xenon and fluorine are heated together either in a closed system[4] or in a flow system.[5] The method which uses a closed system allows a somewhat better control of purity and is described below.

Procedure

Caution. Among the materials that may be inadvertently produced while manipulating the xenon fluorides is xenon trioxide. This may be formed by hydrolysis of xenon tetrafluoride and subsequent drying of the hydrolysis product. Xenon trioxide is a potentially dangerous explosive. Milligram quantities can cause extensive damage. If the procedure described below is followed exactly and moisture is rigorously excluded, no formation of explosive materials should occur. Occasionally, however, in glass traps protecting diffusion pumps, materials have collected which on warming have

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* Argonne National Laboratory, Argonne, Ill. Work performed under the auspices of the U.S. Atomic Energy Commission.

† University of California, Berkeley, Calif.

exploded or reacted with the glass to produce materials which have subsequently exploded.

The reactor should be designed to handle 30 atmospheres pressure (approximately 4 times the expected pressure), and adequate shielding should be used. Because of the use of fluorine, the procedure should be performed in a good hood.

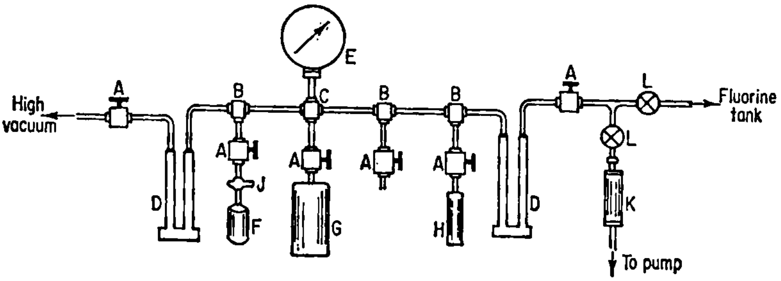

FIG. 10. Apparatus for preparation and purification of xenon tetrafluoride.

**A*. 30,000-p.s.i. valve, Monel body, Teflon packing.
B. 30,000-p.s.i. Monel tee.
C. 30,000-p.s.i. Monel cross.
D. Welded nickel U-tube.
E. Welded Monel Bourdon gage (0 to 1000 mm.).
**F*. 130-ml. welded nickel reactor vessel ($1\frac{7}{8}$ in. o.d. × $\frac{1}{32}$ in. wall × 3 in. long).
**G*. 1500-ml. welded nickel storage and measuring vessel (4 in. o.d. × $\frac{1}{8}$ in. wall × $9\frac{1}{4}$ in. long).
**H*. 85-ml. welded nickel storage and measuring vessel ($1\frac{1}{8}$ in. o.d. × $\frac{1}{16}$ in. wall × $6\frac{1}{4}$ in. long).
J. Brass valve: Hoke type A431.
K. Soda-lime trap.
L. Monel valve: Hoke type 413.

* The dimensions of these vessels are approximate. The lengths are those of the main volume, and do not include the length of the connecting nipples.

The apparatus used for the preparation and purification of xenon tetrafluoride is shown in Fig. 10. The total volume of the manifold including the U-tubes, but excluding all reaction and storage vessels, is about 105 ml. All parts are fabricated of nickel* or Monel and are pretreated by

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* Details concerned with the welding of nickel may be obtained from the Huntington Alloy Products Division, International Nickel Company, Inc., Huntington, W.Va.

heating to dull red heat, first with hydrogen in the system and then with fluorine. The pretreatment produces a protective fluoride coating on the inside of the system and prevents attack by the xenon tetrafluoride on the nickel. After removal of the fluorine, the system is evacuated to 5×10^{-5} mm. Hg, or less. The volume of reaction vessel *F* should be determined before beginning the procedure.

One part of xenon* (0.361 g; 0.00275 mol) is condensed into the reaction vessel *F* by means of liquid nitrogen. The quantity of xenon is best measured by the pressure, according to gas law calculations based on the known volume of the vessel *F*.

The valve *J* is closed and approximately five parts of fluorine (0.524 g.; 0.0138 mol), by pressure, is measured out and condensed into the vessel *F*, which is still immersed in liquid nitrogen. The fluorine is measured out in a manner similar to that used for the xenon. The large vessel *G* is used in order to have a sufficiently large volume. Fluorine is allowed to flow into the manifold and the vessel *G* until the pressure is about 300 mm. greater than the calculated required pressure. (The vapor pressure of fluorine at liquid-nitrogen temperature is about 300 mm.) The valve to the fluorine tank is closed, the valve *J* is then opened, and the fluorine is introduced into the vessel *F* until the change in pressure is equivalent to the calculated amount needed. When the required quantity has been introduced, valve *J* is closed, the liquid-nitrogen bath is replaced with an electric furnace, and the vessel *F* is heated to 400° for one hour. Under these conditions, the pressure is about 7.0 atmospheres or slightly less. Larger pressures favor the formation of xenon hexafluoride. Considerably lower pressures favor the formation of xenon difluoride.

After cooling to room temperature, the reaction vessel is

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* Xenon can be purchased from Air Product and Chemicals, Inc., Allentown, Pa., or from Air Reduction Company, 150 E. 42nd St., New York, N.Y.

immersed in a Dry Ice–trichloroethylene bath (−78°) and the excess fluorine is pumped away. Essentially pure xenon tetrafluoride remains in the reaction vessel, although in some cases small amounts of the more volatile hexafluoride are also produced. The hexafluoride will preferentially expand into the vacuum manifold if the reaction vessel is allowed to warm to room temperature. The resultant material in the manifold can be separated or discarded. This procedure is repeated until the pressure obtained on opening the reaction vessel at room temperature is not greater than 3 mm. Further purification can be achieved by distilling the reaction product into a nickel U-tube cooled to −78° while pumping to 10^{-5} mm. Hg, thus removing any hydrogen fluoride, xenon, or fluorine trapped in the crystals. The final purity may be checked by examination of the infrared spectrum of the product in the 500- to 650-cm.^{-1} range. Xenon tetrafluoride has a fundamental in this region which is a doublet with peaks at 581 and 591 cm.^{-1} The most likely impurities are xenon hexafluoride and xenon difluoride. The hexafluoride exhibits a strong peak at 612 cm.^{-1} and a slightly weaker one at 520 cm.^{-1} The difluoride produces peaks at 550 and 565 cm.^{-1} As little as 1% of either of these may easily be detected. Yields of at least 0.51 g. (90%), based on original amounts of xenon, may be obtained.

Properties

At 25°, xenon tetrafluoride is a colorless crystalline solid with a vapor pressure of 2.5 mm. It can be stored unchanged in nickel or glass vessels, although the latter must be thoroughly dried. It readily hydrolyzes in moist air or water to form xenon, oxygen, hydrogen fluoride, and a stable xenon species in solution.[6] Hydrogen at 300° reduces the tetrafluoride quantitatively to xenon and hydrogen fluoride. Xenon tetrafluoride dissolves readily in anhydrous hydrogen fluoride and may be recovered quantitatively on evaporation.

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67. XENON HEXAFLUORIDE

$$Xe + 3F_2 \rightarrow XeF_6$$

Submitted by C. L. Chernick* and J. G. Malm*
Checked by Stanley M. Williamson†

Xenon hexafluoride may be prepared in essentially the same way as xenon tetrafluoride (synthesis 66), except for increasing the fluorine-to-xenon ratio and the final pressure at reaction temperature.[1–4] Variations of temperature, pressure, mol ratio, and time make possible the formation of xenon difluoride, xenon tetrafluoride, or xenon hexafluoride. The conditions described below have been found to give good yields and purity for xenon hexafluoride.

Procedure

Caution. Among the materials that may be inadvertently produced while manipulating xenon fluorides is xenon trioxide. Xenon trioxide is a potentially dangerous explosive. Milli-

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[*] Argonne National Laboratory, Argonne, Ill. Work performed under the auspices of the U.S. Atomic Energy Commission.

[†] University of California, Berkeley, Calif.

gram quantities can cause extensive damage. If the procedure described below is followed exactly and moisture is rigorously excluded, no formation of explosive materials should occur. Occasionally, however, in glass traps protecting diffusion pumps, materials have collected which on warming have exploded or reacted with the glass to produce materials which have subsequently exploded.

The reactor should be designed to handle 400 atmospheres pressure at room temperature, and adequate shielding should be used. Because of the use of fluorine, the procedure should be performed in a good hood.

The apparatus and experimental procedures are similar to those used for the tetrafluoride (synthesis 66), except for the use of the heavier-walled vessel *H* instead of the vessel *F*. In order to add the required amount of fluorine, it will be necessary either to use a larger vessel *G* or to repeat the measuring and condensing procedures.* The xenon-to-fluorine mol ratios used are about 1:20 [0.689 g. (0.00525 mol) of xenon and 4.18 g. (0.110 mol) of fluorine]. The gas mixture is heated to 300° for 16 hours. The hexafluoride is purified by distillation, the less volatile fraction of lower fluorides being discarded. The purity may be checked by examination of the infrared spectrum, noting the presence of bands at 520 and 612 cm.^{-1} and the absence of peaks for the difluoride and the tetrafluoride. The spectrum should also be studied in the 900- to 1000-cm.^{-1} region, where oxyfluorides have fundamentals, for example, $XeOF_4$ at 928 cm.^{-1}.

Properties

Xenon hexafluoride is a colorless solid with a vapor pressure of about 30 mm. at 25°. In a poly(chlorotrifluoro-

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* The checker points out that the necessity of taking several portions of fluorine can be eliminated if nitrogen that has previously been chilled to its triple point by pumping on the Dewar flask is used as a coolant. The reactor should first be cooled with regular liquid nitrogen. Then the use of the solid-liquid nitrogen mixture will reduce the vapor pressure of fluorine from 300 to about 20 mm.

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ethylene) (Kel-F) tube it was observed to turn yellow at 42° and to melt at 46°. After solidifying, it was again colorless. The vapor is greenish-yellow.

The compound is stable at room temperature and may be stored unchanged in thoroughly dried nickel vessels. Samples sealed in quartz react slowly to produce a colorless liquid which has been identified as $XeOF_4$.

Xenon hexafluoride hydrolyzes in excess dilute acid or water to produce XeO_3 [Xe(VI)] in solution. Hydrolysis with strong base results in the precipitation of a perxenate salt [Xe(VIII)]. Xenon hexafluoride is a fairly strong fluorinating agent, and it forms addition compounds with other fluorides such as BF_3, AsF_5, SbF_5, and alkali metal fluorides.

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68. XENON DIFLUORIDE

$$Xe + F_2 \rightarrow XeF_2$$

Submitted by James L. Weeks* and Max S. Matheson*
Checked by DeForest F. Smith† and W. G. Schwab†

Xenon and fluorine react to form xenon difluoride, a crystalline solid, when irradiated with ultraviolet light in the fluorine absorption band (2300 to 3500 A.). If the

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* Argonne National Laboratory, Argonne, Ill. Work performed under the auspices of the U.S. Atomic Energy Commission.

† Union Carbide Nuclear Company, Oak Ridge, Tenn.

product is continuously trapped at −78°, essentially pure xenon difluoride is produced.[1] Xenon difluoride and fluorine will photolyze further at room temperature, with no trapping, to produce at least 80% yields of xenon tetrafluoride.[2] Xenon difluoride has also been prepared by the reaction of xenon with fluorine in a circulating system at 400°,[3] by the reaction of xenon with carbon tetrafluoride in a high-voltage discharge,[4] and by the reaction of xenon and fluorine at high pressures.[5]

Procedure

Caution. Although the method described below yields pure xenon difluoride, some xenon tetrafluoride will be produced if any xenon difluoride remains in the reaction zone. Because of this possibility, the care suggested in handling xenon tetrafluoride (synthesis 66) should also be exercised in dealing with xenon difluoride, so as not to produce any xenon trioxide. If the procedure is followed exactly and moisture is rigorously excluded, no formation of explosive materials should occur. Occasionally, however, in glass traps protecting diffusion pumps, materials have collected which on warming have exploded or reacted with the glass to produce materials which have subsequently exploded.

Because of the use of fluorine, the procedure should be performed in an efficient hood.

The reaction vessel and other experimental equipment are shown in Fig. 11. The cell is constructed of nickel* and Monel in a closed-loop design. *A* is a cylindrical reaction chamber about 100 ml. in volume and 9 cm. long. Vacuum-tight sapphire windows *B*,† 3 mm. thick, allow the light to

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* Cells constructed of fused silica are readily attacked by fluorine to produce silicon tetrafluoride, which complicates the purification of the xenon difluoride.

† Sapphire-to-metal seals can be obtained from any of the following: Advanced Vacuum Products, Inc., Stamford, Conn.; Reuter-Stokes Electronic Components, Cleveland, Ohio; Ceramaseal, Inc., New Lebanon Center, N.Y.

enter the cell and intensities to be measured behind the cell. Nickel tubing forming the loop for convection circulation of the gases is about 8 mm. i.d. Heating tape may be wrapped on the rear "leg" of the loop and operated at temperatures up to 100° to help effect adequate gas circulation. The bottom U-bend *C* is placed in a bath at −78° contained in a Dewar. *D* is a cylindrical ballast container with a volume of about 400 ml.; it is added to allow more product to be formed. *E* is a Bourdon-type pressure gage of Monel (0 to 1000 mm. Hg),* which is useful in following the rate

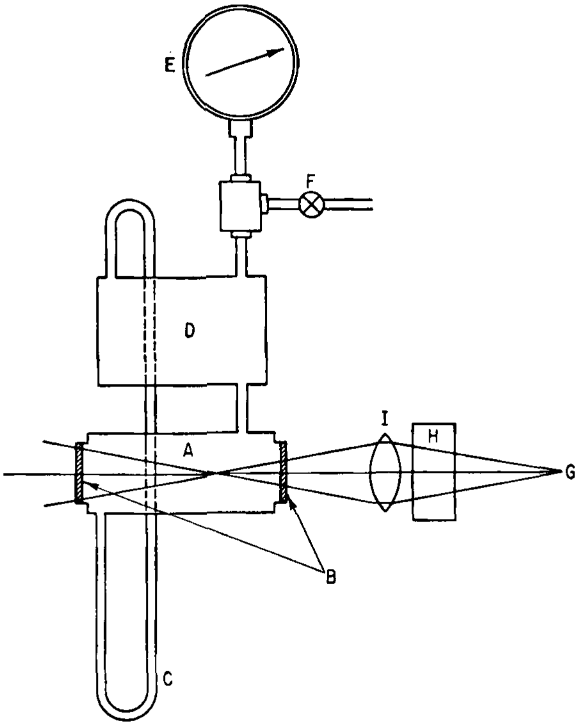

FIG. 11. Apparatus for the photochemical preparation of xenon difluoride.

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* Available from several commercial sources, including the Helicoid Gage Division of the American Chain and Cable Company, Inc., Bridgeport, Conn. A gage free from oil should be specified (often designated "Oxygen—Use no oil.").

of reaction. *F* is a Monel valve for connection to a nickel and Monel vacuum system (synthesis 66) for filling and emptying the cell. The light source *G* is a 1000-watt high-pressure mercury arc, such as General Electric AH-6. (Other light sources can be used if they have reasonably high intensities in the region of fluorine absorption.) *H* is an optional filter or monochromator for allowing only the wavelengths absorbed by fluorine to enter the cell.* *I* is a fused-silica lens to concentrate the light in a narrow intense beam inside the reaction chamber.

Xenon is introduced into the cell until a pressure of 500 mm. Hg is obtained, as measured by the pressure gage on the cell. The xenon is frozen by means of liquid nitrogen. Then the calculated amount of fluorine is bled into the cell, from the vacuum system manifold, so that on warming to room temperature an amount of fluorine equal to about 500 mm. pressure has been introduced. The cell is then closed off at *F* and, if one desires to follow the rate of reaction, the liquid nitrogen is removed to allow the cell to come to room temperature for a reading of initial total pressure.

When the bath at −78° is in place and the current is turned on for the heating tape, the irradiation is begun. Decreases in total pressure of about 20 mm./hour are common. The rate of pressure drop decreases as the fluorine is consumed, and less light is absorbed by fluorine. The irradiation is continued until the rate of production of xenon difluoride, as indicated by the rate of pressure drop, is negligible. The cell is then reattached to the nickel vacuum system. The xenon difluoride is held at −78° in the U-bend as the unreacted xenon and fluorine, if any, are pumped away. The xenon difluoride can then be purified by distillation at room temperature into a trap at −78° while the pumping is continued.

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* A 2.0-cm. fused-silica cell containing an aqueous solution of cobalt(II) and nickel(II) sulfates (45.0 g./l. $CoSO_4 \cdot 7H_2O$ and 500 g./l. $NiSO_4 \cdot 6H_2O$). This solution transmits 75% of the light near 2900 A., where the maximum absorption of fluorine occurs.

With the conditions and apparatus described above, after an irradiation of one to two days, the yield is approximately 2 g. of xenon difluoride. By increasing the initial total pressure and/or the cell volume, larger quantities of the difluoride can be prepared.

The purity of the xenon difluoride can be checked by measuring the absorption in the infrared (synthesis 66). Samples prepared as described above, with continuous trapping, contain less than 1% xenon tetrafluoride, even if the initial fluorine-to-xenon ratio is varied from 0.1 to over 6.

Properties

Xenon difluoride forms solid, water-white crystals which have a vapor pressure of approximately 3 to 4 mm. at room temperature and a penetrating, nauseating odor, but which have a negligible vapor pressure at −78°. The compound has a melting point about 140°, sublimes easily, and can be grown into crystals of millimeter dimensions. It reacts quantitatively with hydrogen at 300° to give xenon and hydrogen fluoride. Xenon difluoride can be stored indefinitely in predried nickel or glass vessels. It dissolves in water, giving undissociated XeF_2 in solution, with a half-life of 7 hours at 0°. Eventually, it decomposes completely to xenon and hydrogen fluoride.

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SUBJECT INDEX

Names used in the cumulative subject index for Volumes I through VIII are based for the most part upon those adopted in Volume II (Appendix, page 257; see also the heading *Nomenclature* in this index), with a few changes that have been standardized and approved since publication of Volume II. No major changes seemed to be required for general conformity with the "Definitive Rules for Nomenclature of Inorganic Chemistry," 1957 Report of the Commission on the Nomenclature of Inorganic Chemistry of the International Union of Pure and Applied Chemistry (*J. Am. Chem. Soc.*, **82**, 5523-5544 (1960).

With a view to keeping the index within reasonable limits, a few changes in policy have been made, some of them more in line with *Chemical Abstracts* practice. Thus more names than silanes, germanes, phosphines, and the like, including names of organic compounds, are now entered in inverted form. For example, as the only entries for metal alkyls, aryls, 1,3-diketone and certain other derivatives: *Sodium, cyclopentadienyl-; Manganese, bis(2,4-pentanedionato)-* instead of *Manganese(II) acetylacetonate.* In this way many entries beginning with numerical prefixes are avoided. Numerical and some other prefixes are also avoided by restricting entries to group headings where possible: *Cobalt carbonyls* as the only entry for $[Co(CO)_3]_4$, with the formula given there; *Silicon chlorides; Sodium periodates* for the meta- and para-(ortho-); *Sodium sulfites* including $NaHSO_3$.

Another change is the use of **boldface type** to indicate individual preparations described in detail, whether for numbered syntheses or for intermediate products (in the latter case, usually without stating the purpose of the preparation). Group headings, as *Calcium orthophosphates*, are in lightface type unless all the formulas under them are boldfaced. Under a few general headings such as *Ammonium compounds, substituted*, reference is made to a table of such compounds instead of listing all of the specific compounds that could be entered under the heading. However, **each specific compound is entered in the Formula Index.**

Under other general headings, such as *Chromium(III) complex compounds* and *Ammines*, used for grouping coordination compounds of similar types with names not suitable for individual entries, formulas are no longer given. Hence it is **imperative to consult the Formula Index for entries for specific complexes.** The decision as to names of acids (and their salts and other derivatives) suitable for index entries has been based largely on the *Chemical Abstracts* list of anions ("The Naming and Indexing of Chemical Compounds from Chemical Abstracts," 1962, Appendix III, page 73N). Thus halo, cyano, oxalato, and some other complexes are entered only under their specific names: *Potassium hexachlororhenate(IV); Potassium tetraoxalatouranate(IV)*. One important exception is the handling of phosphorus acid derivatives (thio, halo, amido, etc.), for which names like *Sodium thiophosphate* have been preferred, with sometimes duplicate entries for the "new" organic phosphorus names (*CA*, *ibid.*, §407), as *Sodium phosphorothioate*.

As in previous indexes, two entries are made for compounds having two cations. Unsatisfactory names that have been retained for want of better ones are placed in quotation marks.

Headings are alphabetized straight through, letter by letter, as in *Chemical Abstracts* indexes, not word by word. Roman numerals in Stock names are ignored in alphabetizing unless two or more are otherwise the same. Footnotes are indicated by *n.* following the page number.

Inorganic Syntheses, Volume VIII
Edited by Henry F. Holtzclaw, Jr.

FORMULA INDEX

The chief aim of this formula index, like that of other formula indexes, is to help in locating specific compounds, or even groups of compounds, that might not be easily found in the Subject Index, or in the case of compounds in tables or of many complex coordination compounds, not to be found at all in the Subject Index. *All* specific compounds with definite formulas (or even a few less definite) are entered in this index, whether entered specifically in the Subject Index or not. As in the latter index, **boldface type** is used for formulas of compounds whose preparations are described in detail, in at least one of the references cited.

Wherever it seemed best, formulas have been entered in their usual form (*i.e.*, as used in the text) for easy recognition: PbO_2, $EuSO_4$, Si_2Cl_6, $ThOBr_2$. However, for compounds containing the more uncommon elements and groupings and also for complexes, the significant or central atom has been placed first in the formula in order to throw together as many related compounds as possible. This procedure usually involves placing the cation last (often of relatively minor interest, especially in the case of alkali and alkaline earth metals): $[PtCl_4]K_2$; $[Al(C_2O_4)_3]K_3 \cdot 3H_2O$; $[Co(enta)]_2Ba$. The guiding principle in these decisions has been the chapter in the text in which the preparation of the compound in question is described. Where there is likely to be almost equal interest in two or more parts of a formula, two or more entries have been made: $AgClO_3$ and ClO_3Ag: Al_2Se_3 and Se_3Al_2; SF_6 and F_6S halides other than fluorides are entered only under the other elements or groups in most cases); $NaNH_2$ and NH_2Na; NH_2SO_3H and $(SO_3H)NH_2$.

Formulas for organic compounds are structural or semistructural so far as feasible: $CH_3COCH_2COCH_3$. Consideration has been given to probable interest for inorganic chemists, *i.e.*, any element other than carbon, hydrogen, or oxygen in an organic molecule is given priority in the formula if only one entry is made, or equal rating if more than one entry: $Zr(C_5H_7O_2)_4$, but $NaC{\equiv}CH$ and $CH{\equiv}CNa$. Names are given only where the formula for an organic compound, ligand, or radical may not be self-evident, but not for frequently occurring relatively simple ones like C_5H_5N (pyridine), $C_5H_7O_2$ (2,4-pentanedione), C_5H_5 (cyclopentadienyl).

The formulas are listed alphabetically by atoms or by groups (considered as units) and then according to the number of each in turn in the formula rather than by total number of atoms of each element; formulas with special isotopes follow the usual ones. This system results in arrangements such as the following:

$NH_2SO_3NH_4$
$(NH_2)_2C_2H_4$ (instead of $N_2H_4C_2H_4$, $N_2H_8C_2$, or $C_2H_8N_2$)

$Si(CH_3)Cl_3$ FH
$Si(CH_3)_3Cl$ $F^{18}H$
$Si(CH{=}CH_2)Cl_3$ FNa
$Si(C_2H_4Cl)Cl_3$ $F^{18}Na$

$Cr(CN)_6K_3$ (instead of $CrC_6N_6K_3$)
$Cr(C_2H_3O_2)_2$ (instead of $CrC_4H_6O_4$)
$[Cr(C_2O_4)_3]K_3 \cdot 3H_2O$ (instead of $CrC_6O_{12}K_3 \cdot H_6O_3$ or $CrC_6O_{15}K_3H_6$)
$[Cr(en)_2Cl_2]Cl \cdot H_2O$ ("en" is retained for simplicity and is alphabetized as such rather than as $C_2H_4(NH_2)_2$ or $(NH_2)_2C_2H_4$. Similarly, "dien" stands for diethylenetriamine, "enta" for $[-CH_2N(CH_2CO_2)_2]_2^{4-}$, "*o*-phen" for *o*(or 1,10)-phenanthroline, and "pn" for propylenediamine.)

Footnotes are indicated by *n.* following the page number.