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VOLUME VI

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VOLUME VI

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PREFACE

The present volume follows the same general pattern as its successful predecessors and contains some sixty-nine independently tested and checked syntheses arranged in chapters according to the Mendeleef groups. The compounds which may be obtained through these directions are listed not only in the table of contents, but in a subsequent formula index and in a cumulative index for all six volumes. It might be pointed out that this comprehensive index now covers 389 syntheses and a considerably greater number of compounds.

The contributions to this volume cover a wide variety of substances, from active metals to isotopically labeled acids. Among these, the reader will notice a large proportion of coordination compounds and "complexes," in keeping with one of the trends in inorganic research. It is very gratifying to the editors also to point out the great increase in contributions from abroad, which make this a truly international periodical. It has seemed best for this volume to render into English those syntheses which were submitted in other languages (with the permission of the authors, of course).

Contributions for Volume VII are invited, and manuscripts (in triplicate) should be submitted to the editor of that volume, Prof. Jacob Kleinberg, Department of Chemistry, University of Kansas, Lawrence, Kansas. Offers to check syntheses are always heartily welcomed, too, for without this important service this series would come to an abrupt halt.

The governing boards of INORGANIC SYNTHESES are

pleased to announce the appointment of Prof. Frank P. Dwyer of The Australian National University; Dr. Lowell E. Netherton of the Victor Chemical Company; and Prof. S. Young Tyree, Jr., of the University of North Carolina, as new members of the Editorial Board.

In the preparation of this volume the editor is deeply indebted to Drs. Ludwig Maier and Bodo Bartocha for translations from the German, to Mrs. Jeannette Grisé Thomas for her patient help in editing and retyping the contributions, to Mr. Donald H. Levy for adding many finishing touches to the manuscript, and to Miss Janet D. Scott for her truly invaluable expert help in preparing the index and naming the compounds.

Eugene G. Rochow

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CHAPTER IA

1. POTASSIUM DIOXALATOCUPRATE(II) 2-HYDRATE

$$CuSO_4 + 2K_2C_2O_4 \rightarrow K_2[Cu(C_2O_4)_2] + K_2SO_4$$

SUBMITTED BY STANLEY KIRSCHNER*
CHECKED BY JOHN A. MCLEAN, JR.,† AND GERARDINE MEERMAN†

The oxalate anion is capable of acting as a bidentate chelating agent[1] and forms five-membered rings with many metal ions. A simple, rapid preparation resulting in a high yield of the potassium salt of a copper(II) complex containing this chelating anion is presented which is a modification of a method used for the sodium salt.[2] All the chemicals used were of reagent quality.

Procedure

A solution of 12.5 g. (0.05 mol) of copper(II) sulfate 5-hydrate dissolved in 25 ml. of water is heated to 90° and is added rapidly and with vigorous stirring to a solution of 36.8 g. (0.2 mol) of potassium oxalate 1-hydrate in 100 ml. of water which is at 90°. The solution is then cooled to 10° in an ice-water bath and the resulting precipitate is filtered, washed rapidly with 25 ml. of cold water, and dried in an oven at 50° for 12 hours. The yield is 17.1 g. (97%). *Anal.* Calcd. for $K_2[Cu(C_2O_4)_2]\cdot 2H_2O$: C, 13.58; H, 1.14; K, 22.10. Found: C, 13.78; H, 1.05; K, 22.48.

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Properties

The compound is soluble in warm water but begins to decompose slowly into copper(II) oxalate, which precipitates shortly after dissolution of the complex. The decomposition is hastened by the addition of strong acid. The material is only very slightly soluble in the common organic solvents such as acetone, benzene, carbon tetrachloride, chloroform, ethanol, and methanol. The blue crystals lose water rapidly above 150° and the resulting compound decomposes at 260°.

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CHAPTER IB

2. COPPER(I) IODIDE

$$2CuSO_4 + 4KI + 2Na_2S_2O_3 \rightarrow 2CuI + 2K_2SO_4 + Na_2S_4O_6 + 2NaI^*$$

SUBMITTED BY GEORGE B. KAUFFMAN† AND ROBERT P. PINNELL†
CHECKED BY JAMES PETERSON,‡ DAVID WILLIAMS,‡ AND A. L. ALLRED‡

The only stable copper(I) salts are those which are either insoluble in water or largely covalent. In agreement with Fajans's rules the stability of the copper(I) halides increases from the fluoride through the iodide, the iodide ion being the largest and most polarizable of the halide ions. Thus copper(I) fluoride has never been prepared in the pure state, while the chloride and bromide can be prepared by treating solutions containing copper(II) ion and the corresponding halide ion with various reducing agents.[1] However, the copper(II) iodide initially formed by the combination of copper(II) ion and iodide ion in aqueous solution decomposes almost immediately by a redox reaction to yield copper(I) iodide and free iodine,[2] a reaction which is the basis for the well-known iodometric determination of copper. It is extremely difficult, however, to remove the iodine completely from the

* Actually copper(II) iodide and iodine are formed as intermediates, but they are consumed during the course of the reaction:

$$2CuSO_4 + 4KI \rightarrow 2CuI_2 + 2K_2SO_4$$
$$2CuI_2 \rightarrow 2CuI + I_2$$
$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

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‡ Northwestern University, Evanston, Ill.

product, and therefore sodium thiosulfate is used to react with the iodine.[3] Since excess thiosulfate may result in the formation of copper-thiosulfate complexes, while excess iodide may dissolve the product to give soluble copper-iodide complexes, a solution of potassium iodide and sodium thiosulfate mixed in the correct stoichiometric ratio is used to titrate a copper(II) sulfate solution in this synthesis.

Miscellaneous methods such as heating copper with iodine,[4] dissolution of copper in hot concentrated hydriodic acid,[5] treatment of copper(I) cyanide with hydriodic acid,[6] and heating copper with iodoform[7] are of little preparative significance.

Procedure

Twenty-five grams (0.1 mol) of copper(II) sulfate 5-hydrate is placed in a 400-ml. beaker and dissolved in 150 ml. of water.* A second solution is prepared by placing 36.5 g. (0.22 mol) of potassium iodide and 28.0 g. (slightly more than 0.11 mol) of sodium thiosulfate 5-hydrate in a 100-ml. volumetric flask, adding water to the mark, and shaking thoroughly.† The second solution is added to the first from a buret with continuous, rapid stirring until no further precipitation occurs (90.9 ml. is theoretically required).‡

The dense, white precipitate is allowed to settle for ca. 15 minutes and is then collected on a small, sintered-glass funnel (medium porosity), washed with several 20-ml. portions

* Acid should not be added to repress hydrolysis, for when sodium thiosulfate is added, colloidal sulfur may form, contaminating the product.

† Although the amount of water is not critical, quantitative preparation of this solution simplifies the subsequent titration, since the volume required to reach the end point can then be calculated.

‡ In the course of the titration the color of the suspension changes from chocolate through khaki and light tan, becoming pale flesh-colored at the end point. Since the exceedingly fine precipitate settles only slowly, color provides a convenient indication of the end point. A slight excess of the titrant is not harmful, but a large excess may decrease the yield by formation of soluble copper-iodide complexes.

of water, ethanol, and finally ether. The product is powdered and dried *in vacuo* over sulfuric acid for several days.* The yield is quantitative except for manipulative losses.

A 1-g. sample is dissolved in concentrated nitric acid, the resulting iodine removed by filtration through a sintered-glass funnel, washed with water, and the washings added to the yellow filtrate. The latter is diluted with water and the copper determined by electrolytic reduction. *Anal.* Calcd. for CuI: Cu, 33.4. Found: Cu, 33.1.

Properties

Copper(I) iodide is a dense, pure white solid, crystallizing with a zinc-blende structure below 300°. It is less sensitive to light than either the chloride or bromide, although passage of air over the solid at room temperature in daylight for 3 hours results in the liberation of a small amount of iodine. It melts at 588°, boils at 1,293°, and unlike the other copper(I) halides, is not associated in the vapor state. Being extremely insoluble (0.00042 g./l. at 25°), it is not perceptibly decomposed by water. It is insoluble in dilute acids, but dissolves in aqueous solutions of ammonia, potassium iodide, potassium cyanide, and sodium thiosulfate. It is decomposed by concentrated sulfuric and nitric acids.

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* Copper(I) iodide retains moisture tenaciously. The air-dried product contains ca. 4% water,[8] while the drying procedure recommended reduces this to ca. 0.2%.[7,9] The product may be dried overnight in a phosphorus(V) oxide drying pistol at 100°. When heated in air below 200°, oxygen displaces iodine, yielding copper(II) oxide.[9]

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3. DIPYRIDINESILVER(I) PERCHLORATE

$$AgNO_3 + 2C_5H_5N + NaClO_4 \rightarrow [Ag(C_5H_5N)_2]ClO_4 + NaNO_3$$

Submitted by George B. Kauffman* and Robert P. Pinnell*
Checked by Robert D. Stone†

In general, tertiary amines do not readily form coordination compounds, the order of stability of metal-amine complexes being tertiary < secondary < primary < ammonia. However, the heterocyclic, tertiary amine pyridine, a compound of relatively high dipole moment, coordinates readily, and many pyridine complexes have been prepared.

Perchlorates are unusual in that most are either extremely soluble or only sparingly soluble in water. Silver(I) perchlorate is one of the most soluble salts known, while its coordination compound with pyridine is so insoluble that pyridine can be precipitated quantitatively from aqueous solution by treatment with silver(I) perchlorate.[1] Although several complexes of pyridine and silver(I) perchlorate have been described,[1,2] the one in which silver(I) exhibits its common coordination number of two is the most stable. This compound provides a stable, nondeliquescent starting material for synthesizing the perchlorates of the dipyridine complexes of unipositive bromine[3] and iodine.[4]

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† Monsanto Chemical Co., Dayton, Ohio.

Procedure

Seventeen grams (0.10 mol) of silver nitrate is dissolved in ca. 70 ml. of water contained in a 250-ml. beaker. Fifty milliliters (0.62 mol) of pure pyridine (b.p. 115 to 116°) is added slowly with stirring, whereupon the solution becomes warm.* Then a solution of ca. 18 g.† (ca. 0.15 mol) of sodium perchlorate in 20 ml. of water is added slowly with continuous stirring. After cooling to 10° in an ice bath, the large amount of fine white granular precipitate which results is collected on a large Büchner funnel and washed thoroughly with about six 30-ml. portions of ice water to remove completely any sodium nitrate. It is then air-dried and dried *in vacuo* over sulfuric acid for several days. The yield of crude product is 35.9 g. (98.1%).

This product is purified by dissolving with mechanical stirring in a minimum amount (ca. 150 ml.) of a dry chloroform–dry pyridine mixture (5:1 by volume).‡ To this solution, filtered if necessary through a small Büchner funnel to remove any traces of undissolved residue, anhydrous ethyl ether (ca. 300 ml.) is slowly added with mechanical stirring until the product is completely precipitated as a fine white crystalline powder. This is collected on a large Büchner funnel and washed with six 30-ml. portions of absolute ethanol to remove traces of pyridine and chloroform. It is then washed with anhydrous ethyl ether, air-dried, and dried *in vacuo* for several days over sulfuric acid, care being taken to prevent contact of the product with acid.§ The yield is 28.0 g. (76.7%; m.p. 150 to 151°).¶

* The white, needlelike crystalline precipitate which first forms redissolves upon further addition of pyridine. Use of more than the theoretical amount of pyridine is required.

† This corresponds to ca. 21 g. of the monohydrate.

‡ Once the purification has been started, it should be carried through to completion, since the chloroform-pyridine solution darkens on standing, resulting in an impure product.

§ The potentially explosive properties of silver amine perchlorates should constantly be kept in mind.

¶ Melting point reported by checker.

Caution. Heating, especially to dryness, may result in a violent explosion. For analysis the sample is dissolved in excess 1 *N* nitric acid at room temperature. Then silver is determined gravimetrically as silver chloride by precipitation with hydrochloric acid. *Anal.* Calcd. for $[Ag(C_5H_5N)_2]ClO_4$: Ag, 29.52. Found: Ag, 29.39.*

Properties[1]

Dipyridinesilver(I) perchlorate, as prepared above, is a fine white crystalline powder, which is relatively stable toward air and light at ordinary temperatures and gives practically no odor of pyridine. In a capillary tube it clumps together at 144° and melts sharply at 147°. It is virtually insoluble in cold water, only slightly soluble in hot water, but very soluble in pyridine. The hot-water solution appears to be light-sensitive.

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* The checker suggests a potentiometric analysis: the sample is dissolved in excess 6 *N* nitric acid and acetone added to enhance the end point determination. The solution is then cooled to 5° and titrated potentiometrically with 0.1 *N* hydrochloric acid. *Anal.* Calcd. for $[Ag(C_5H_5N)_2]ClO_4$: Ag, 29.52. Found: 29.06; 28.90.

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CHAPTER IIA

4. ANHYDROUS MAGNESIUM CHLORIDE

$$MgCl_2 \cdot NH_4Cl \cdot 6H_2O \xrightarrow{HCl} MgCl_2 + NH_4Cl + 6H_2O$$

SUBMITTED BY D. BRYCE-SMITH*
CHECKED BY R. M. HUNT†

The preparation of magnesium chloride by the action of chlorine on the metal appears to be impracticable, although reports are conflicting.[1,2] Dry chlorine has been observed not to react with magnesium at the melting point.[3] Magnesium oxide, carbon, and chlorine at 750° have been reported to yield the chloride.[4] The heating of a mixture of magnesium oxide and ammonium chloride has been briefly reported to give magnesium chloride,[5] but this could not be confirmed.[3] It appears to be difficult to dehydrate magnesium chloride 6-hydrate without some loss of hydrogen chloride, although heating in hydrogen chloride,[6] and phosgene[7] have been said to be effective; a failure of the former method has, however, been experienced.[3] The action of heat on magnesium ammonium chloride 6-hydrate gives magnesium chloride, but the product contains a little oxygen.[3] The present method is based on that of Richards and Parker.[8]

Procedure

Magnesium ammonium chloride 6-hydrate can be purchased but is easily prepared by evaporation of an aqueous solution containing equimolar proportions of magnesium

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† Callery Chemical Co., Callery, Pa.

chloride 6-hydrate and ammonium chloride. Twenty grams is placed in a Pyrex boat* contained in a silica tube 50 cm. in length and 2 cm. in diameter. The tube is heated electrically, or better by gas, to 400 to 500° over 5 minutes,† a fast stream of dry hydrogen chloride being passed. When the evolution of water ceases (ca. 30 minutes), the temperature is slowly raised over a period of 1½ hours until the salt just fuses at 712° to a clear liquid.‡ Heating is immediately discontinued, and the product is cooled in a stream of dry hydrogen chloride. The yield is almost quantitative. Analysis based on chlorine content indicates a purity of better than 99%.

Properties

Anhydrous magnesium chloride melts at 712° to a clear, mobile liquid, which attacks fused silica. Pyrex is somewhat more resistant. The salt has been described as butter-yellow in color, but the present method gives a colorless product. The crystals are soft and highly deliquescent in moist air. The compound gives a clear solution in water with the evolution of much heat and forms etherates and alcoholates.

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* A platinum boat may be used if an especially pure product is required. The checker reports doubtful purity of the sample when a nickel boat and stainless-steel thermocouple are used but good results with a Pyrex boat and a Vicor thermocouple well.

† It is noted by the checker that the boat contents are carried away excessively if the rate of heating is too fast.

‡ Any turbidity in the melt indicates the presence of oxygen in the product.

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5. MAGNESIUM CYCLOPENTADIENIDE

$$Mg + 2C_5H_6 \rightarrow Mg(C_5H_5)_2 + H_2$$

SUBMITTED BY W. A. BARBER*
CHECKED BY WILLIAM L. JOLLY†

It has been known for many years[1] that alkali metals react with cyclopentadiene at room temperature, liberating hydrogen and forming the alkali salt MC_5H_5. Until recently, however, apart from these metals, only iron has been reported to react directly with the hydrocarbon, forming the "sandwich-type" compound ferrocene.[2] This reaction takes place at 200 to 300°, but proceeds for only a short time, after which the iron no longer reacts. Magnesium cyclopentadienide, $Mg(C_5H_5)_2$, has been prepared by the thermal decomposition of the cyclopentadienyl Grignard reagent[3,4] and also by the direct reaction of magnesium metal with cyclopentadiene vapor at 500 to 600°.[5,6] The method described below is a detailed procedure for the latter of these two preparations and gives an essentially pure product in good yield.

Procedure A

Commercial dicyclopentadiene (b.p. 170°) is placed in a flask and boiled to crack the dimer to the monomer. A 20-cm. glass-bead column permits taking relatively pure

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monomer (b.p. 42°) overhead. Cyclopentadiene thus produced is mixed with prepurified nitrogen and passed through a Pyrex tube $1\frac{1}{4}$ in. o.d. which is heated electrically to 500

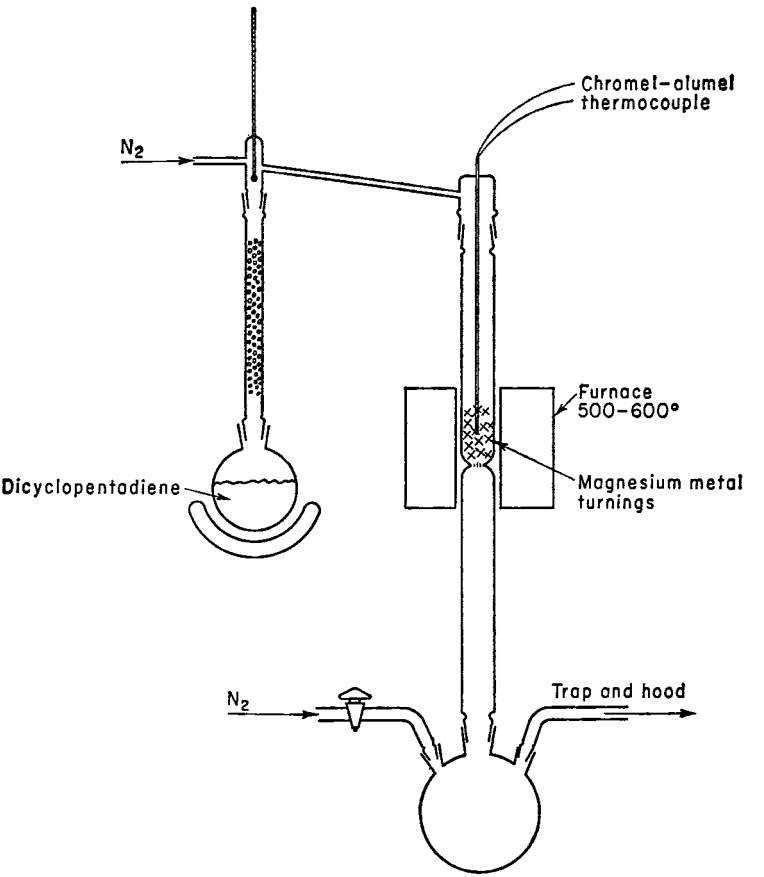

FIG. 1. Apparatus for the preparation of magnesium cyclopentadienide.

to 600°. Magnesium metal turnings are supported in the furnace tube by a circle of nichrome gauze at the tube constriction as shown in Fig. 1. The product, which falls from the furnace as a white solid, can be collected in a three-necked flask as shown. The unreacted cyclopentadiene is collected in a Dry Ice–ethanol trap. Yields of better than

80% based on the cyclopentadiene consumed have been obtained in this manner.

The apparatus should be initially charged and flushed with dry nitrogen. Prepurified nitrogen as commercially available has been found to be adequate. The dicyclopentadiene can be the commercial 95% product used without further purification. No special pretreatment of the magnesium turnings is necessary. When the furnace temperature is above 500°, the dicyclopentadiene can be heated to boiling temperature and will crack to give a steady flow of cyclopentadiene. With the size apparatus described, a nitrogen flow rate of about 275 to 300 ml./min. seems to be optimum. At the start of the run, either crystals which are frequently yellowish are deposited or liquid droplets are formed. Generally, a temporary shortening of the residence time by increasing the nitrogen flow will stop the formation of the liquid contaminant. The product appears as a white snow falling from the furnace and collects in aggregates on the walls of the tube below the furnace, from which it drops into the receiver flask below. If the dicyclopentadiene is kept at a rapid boil, about a gram of material can be collected every 2 minutes. The solid product produced by this method is very light and microcrystalline (30 g. will half fill a 1-l. flask).

It is generally quite pure; however, since purity is directly dependent upon conversion which in turn depends upon flow rate and temperature, initial preparations could result in products contaminated with cyclopentadiene. If this should occur, the magnesium cyclopentadienide could be purified by sublimation *in vacuo* after the contaminant has dimerized.

If it is desirable to collect a larger quantity of the solid product during a single experiment, the cyclopentadiene flow should be stopped and the receiver flask rapidly changed. With some practice this can be accomplished with a minimum of decomposition.

If the magnesium cyclopentadienide is collected as a solid,

it can later be dissolved for use in further reactions. A suitable solvent can be rapidly added to the solid in the receiver flask. The transfer of the product in solution is much simpler and far safer than handling the finely divided solid. An aliquot of the solution can be decomposed in water and titrated with acid to determine the concentration of the product in solution.

The magnesium cyclopentadienide will rapidly accumulate on the wall of the furnace tube below the furnace, and to prevent complete clogging of the tube this must be removed. We have used for this purpose a magnetically operated scraper, but the product can be sublimed or melted down with heating tape, infrared lamp, or cautiously with a flame.

A variation of this procedure is to place a solvent in the receiver flask and collect the product as a solution in which it is more easily handled. Xylene is quite good for this purpose.

Procedure B

A less pure compound in quantities of the order of 5 to 10 g. can be produced in a horizontal furna ceusing a Pyrex tube and a porcelain boat to contain a sample of magnesium powder. The cyclopentadiene is generated as in Procedure A and is passed with a nitrogen carrier gas through the furnace and over the magnesium metal in the boat at a temperature of 500 to 600°. In this case the product deposits as a white to yellow solid on the cooler portions of the exit tube from the furnace and can be resublimed further along the tube for purification. This method is limited by the tendency of the product to fill completely the diameter of the tube and block further passage of vapor.

Properties

Magnesium cyclopentadienide is a white crystalline solid of melting point 176° which sublimes readily under atmos-

pheric pressure at 100°. It is extremely reactive to air and moisture and to carbon dioxide and carbon disulfide, but is soluble without decomposition in purified anhydrous ether, tetrahydrofuran, benzene, or xylene. It readily reacts with transition metal halides to form other cyclopentadienyl compounds. For example, it reacts with anhydrous iron-(III) chloride to give ferrocene, and with aldehydes and ketones to form fulvenes. Some crystal-structure work shows it to have the same configuration as ferrocene, with similar cell dimensions. Its high reactivity and ease of preparation make it an attractive intermediate.

Caution should be observed when handling solid magnesium cyclopentadienide. The solid can catch fire if exposed to air and must be kept under an inert atmosphere; however, in the absence of air and moisture it can be kept for indefinite periods of time without evidence of decomposition.

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6. CRYSTALLINE BASIC CALCIUM ORTHOPHOSPHATE (Hydroxyapatite)

$$10CaHPO_4 + 2H_2O \xrightarrow{300^\circ} Ca_{10}(PO_4)_6(OH)_2 + 4H^+ + 4H_2PO_4^-$$

or

$$14CaHPO_4 + 2H_2O \xrightarrow{300^\circ} Ca_{10}(PO_4)_6(OH)_2 + 4Ca^{++} + 8H_2PO_4^-$$

SUBMITTED BY A. PERLOFF* AND A. S. POSNER†
CHECKED BY NORMAN E. MILLER‡

Methods for the synthesis of calcium hydroxyapatite have been reported in the past,[1,2] but all of them produced either poorly crystallized or somewhat impure products. The following procedure[3] produces a very well-crystallized compound which has a high degree of purity. The reaction is simply the hydrolysis of calcium monohydrogen phosphate to hydroxyapatite in a closed system. The major disadvantage is the small amount of material obtained from each hydrolysis because of the small capacity of the bombs used. Larger reaction vessels would minimize this objection.

Procedure

An orthophosphoric acid solution, 1 volume of reagent-grade 85% phosphoric acid to 5 volumes of distilled water, is saturated with reagent-grade calcium phosphate. After allowing the excess calcium phosphate to settle, the clear, saturated solution is decanted into a beaker. This solution is heated to its boiling point and well-crystallized calcium

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monohydrogen phosphate precipitates out. The calcium monohydrogen phosphate is filtered from the hot solution, washed thoroughly with distilled water, rinsed with absolute alcohol, and finally dried at 105°. About 3.8 to 3.9 g. of calcium monohydrogen phosphate may be obtained from 68 to 75 ml.* of saturated solution. This product is then ground to a fine powder and used as the starting material in the apatite preparation.

Pure, well-crystallized hydroxyapatite is obtained by reacting 0.1 g. of calcium monohydrogen phosphate with 10 to 12 ml. of distilled water in a platinum-lined, Morey-Ingerson type, hydrothermal bomb[4] at 300°.† To facilitate the removal of the apatite from the bomb it is convenient to place the calcium monohydrogen phosphate in a small platinum cup or basket which is then inserted in the bomb with the aid of tweezers. The bulk of the material remains in the cup when the reaction is completed. With the cup of calcium monohydrogen phosphate inside the bomb, the water is then added, a platinum disk which serves as a gasket is laid over the bomb well, and the bomb is sealed and placed in a furnace to be heated to 300°. Better crystal growth seems to be obtained if the bomb is held at 300° for several days, but the reaction is complete for a bomb held overnight at 300°. When the bomb is opened, the cup is lifted out with tweezers and the apatite is washed and scraped from the cup into a sintered-glass filter. It is then washed with water, rinsed with alcohol, and dried at 105°.

The presence of certain cation impurities can strongly influence the final product. During some preparations the platinum lining developed cracks, and iron and chromium ions from the steel bomb were introduced into the water. When this happened, the final product contained a large proportion of well-crystallized whitlockite [β-$Ca_3(PO_4)_2$].

* This yield is reported by the checker.

† The checker reports good results using the technique of Swoboda, Tolle, and Vaughan:[5] $\frac{1}{2}$ in. of platinum tubing (0.010 in. wall) was sealed on one end by welding, loaded, and then sealed on the other end by welding.

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Properties

With the recommended procedure well-developed, clear hexagonal dipyramidal crystals of hydroxyapatite, ranging up to 0.3 mm. in length, have been obtained. The crystals are uniaxial negative with index of refraction $\epsilon = 1.643 \pm 0.002$ and $\omega = 1.649 \pm 0.002$. Atomic parameters and unit cell dimensions as measured by x-ray diffraction are published elsewhere.[6]

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7. CALCIUM METAL POWDER

SUBMITTED BY T. P. WHALEY*
CHECKED BY W. J. MCCREARY†

Calcium halides and sodium metal react at elevated temperatures to form an equilibrium mixture[1–5] of metals and halides:

$$CaCl_2 + 2Na \rightleftharpoons Ca + 2NaCl$$

At these temperatures the salts are miscible in all proportions and consequently form a single phase. The metals, on the other hand, are miscible only to the extent dictated by the temperature and relative concentrations of the

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metals,[6–8] forming two distinct phases (calcium in sodium and sodium in calcium) over a rather wide range. By using an excess of sodium, however, one can retain the metals as a single, homogeneous phase and thus freeze the equilibrium as a two-phase mixture.

When the equilibrium mixture is permitted to cool rapidly, the heavier salt phase settles and solidifies, thus leaving the lighter metal phase on top as a liquid. Inasmuch as calcium metal starts to precipitate and settle before the solidification point of the salt phase is reached, some of the calcium is trapped in the salt phase and, together with the calcium which is dissolved by the molten salt, is not recovered in the following synthesis. Once the sodium chloride–calcium chloride layer has solidified, however, the precipitating calcium remains trapped in the metal layer. When the metal layer freezes, its composition consists of calcium crystals embedded in a sodium matrix which may be removed by preferential reaction with a lower alcohol.[9]

Procedure

The apparatus employed (Fig. 2) consists of a 500-ml. stainless-steel beaker *C* used in conjunction with an atmosphere chamber *D* equipped with gas outlets and a lid. The chamber may be constructed of 4½-in.-o.d. mild-steel pipe or from a 1500-ml. stainless-steel beaker.* The gas inlet is connected to an argon (or helium) supply by means of a length of ¼-in. copper tubing, coiled as shown so as to permit flexibility in handling. The best heat source is a vertical crucible furnace with 5-in. diameter chamber. (A Hoskins crucible furnace was found to be quite satisfactory.) A length of ¼-in. stainless-steel tubing, sealed at one end, serves as a combination thermocouple well and stirrer.

To the stainless-steel beaker is added 46 g. of freshly cut

* The checker reports that contamination of the calcium by iron is prevented by using type 347 stainless steel for the reaction vessel.

sodium metal and 55 g. of anhydrous* calcium chloride. The filled beaker is placed inside the atmosphere chamber which is then covered with the lid, and the entire assembly is placed in the crucible furnace. An argon (or helium)

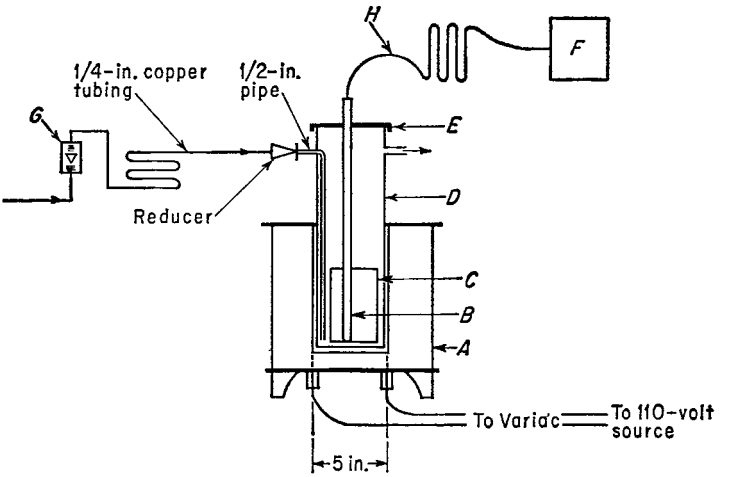

FIG. 2. Apparatus for the preparation of calcium. *A*, vertical crucible furnace; *B*, stainless-steel thermocouple well; *C*, stainless-steel reactor (500-ml. beaker); *D*, atmosphere chamber; *E*, lid for atmosphere chamber; *F*, potentiometer; *G*, rotameter (flowmeter); *H*, chromel-alumel thermocouple.

flush of about 5 l./min. is started and continued throughout the entire heating and cooling cycle. The furnace is placed on an asbestos pad, and the heating conducted in or near a fume hood in order to exhaust the sodium oxide smoke.

The reaction mixture is heated to about 850° and maintained at that temperature for approximately 5 minutes. Above about 750° sodium vapor swept out by the argon stream burns on exposure to air and shows up as a flame issuing from the reaction vessel. The white smoke is sodium oxide. Mild agitation with the stainless-steel thermocouple well assists in reaching equilibrium at this

* See INORGANIC SYNTHESES, **4**, 104 (1953) for the preparation of anhydrous metal halides. Sufficiently anhydrous calcium chloride for this synthesis may be prepared by heating the "commercial anhydrous" calcium chloride from a fresh, unopened bottle for about 2 hours at 400 to 500° in a stream of dry argon.

temperature. The heat is turned off, the thermocouple well is removed so that it will not be trapped when the salt layer solidifies, and the furnace, together with its contents, is permitted to cool to room temperature. The reaction vessel is removed and about 50 ml. of mineral oil is added; this layer of oil protects the sodium-calcium mixture during the next step.

The oil-covered reaction mixture is heated* on a hot plate to about 110°, and the now fluid metal layer is poured into 200 ml. of mineral oil in a 1-l. beaker. It may be necessary to "spoon" the melted metal mixture from the reactor if it will not pour readily. The solidified melt, which consists of sodium embedded with 10 to 20% of finely divided calcium, is cut into pieces small enough to fit through a 24/40 standard taper opening.† A pair of tin snips or large scissors makes a convenient tool for cutting sodium.

Calcium separation. *Caution.* This operation should be conducted in a hood. The calcium isolation equipment consists of a 2-l. three-necked flask equipped with an air-cooled condenser, mechanical stirrer, and nitrogen inlet. To the flask is added 1 l. of methanol and 16 ml. of water,‡ and a slow nitrogen purge is started. The pieces of calcium-embedded sodium are drained free of mineral oil, washed with kerosine, and added to the methanol at such a rate that only two or three pieces are present in the reaction vessel at one time; i.e., the sodium in all but two pieces is permitted to react with the methanol before addition of the next piece of the calcium-embedded sodium. The finely divided calcium is liberated and falls to the bottom as shiny platelets as the sodium matrix reacts with the hydrous

* Heating above 120° should be avoided; sodium tends to ignite when exposed to moist air above this temperature.

† Mechanical separation of the sodium-calcium phase from the salt cake is favored by using a reaction vessel of small diameter to minimize the interface area.

‡ Electron diffraction studies indicate that the water reacts to coat the surface of the calcium particles with a thin oxide layer. This coating presumably is the barrier which delays the reaction of calcium with methanol.

methanol. The sodium methoxide which is formed in the reaction dissolves in the excess methanol.

When all the sodium-calcium mixture has been added to the water-methanol solution and has reacted (this requires about 30 minutes), the methanolic solution of sodium methoxide is permitted to cool and is then decanted carefully from the calcium. The calcium is washed by adding about 100 ml. of methanol (containing 2% water) to the calcium, swirling to ensure contact, and then decanting. This is repeated twice with 100 ml. of ethanol, and finally the calcium is treated with two successive washes with a low-boiling hydrocarbon such as hexane, petroleum ether, etc. The residual hydrocarbon is permitted to evaporate from the calcium in a stream of nitrogen directed into the reaction flask, and the dried calcium powder is then added to a tared, wide-mouthed bottle. The calcium-filled bottle is purged of air with a slow stream of nitrogen before an air-tight lid is applied. The yield is approximately 3 g. of calcium metal.*

All equipment used in the preparation is decontaminated as soon after use as possible. The atmosphere chamber and thermocouple well contain condensed sodium vapor which is destroyed by soaking in a 10% solution of isopropyl alcohol in kerosine. The solidified salt layer is chipped from the beaker and the residual sodium killed with alcohol. The liberated calcium is killed with water. Finally, the beaker is decontaminated with a 10% solution of isopropyl alcohol in kerosine.

Properties

Calcium is a silvery-white metal that tarnishes slowly in humid air with the formation of a thin oxide coating. The

* The equilibrium under feasible conditions is such as to preclude the possibility of really good yields based on one reactant without utilizing very large excesses of the other reactant. However, yields can be improved by rapid quenching of the red-hot, sodium-filled container in a large drum of lubricating oil in order to freeze out the mixture with a higher calcium conversion.

pure metal melts at 850°, boils at 1440°, and has a density at 20° of 1.55. The high heat of formation of calcium oxide makes calcium metal the preferred reducing metal for winning refractory metals from their oxides. For this reason, it is used in winning thorium,[10] uranium,[11] titanium,[12] and zirconium[13] from their respective oxides and in winning thorium[14] and many of the rare earth metals[15] from their halides. It is also used in the preparation of many alloys, such as lead-calcium, aluminum-calcium, calcium-silicon, etc. It is an excellent getter for oxygen and/or nitrogen in the purification of rare gases and finds widespread use in the preparation of calcium hydride.

Calcium crystallizes from sodium solution in flat platelets that have a beautiful, although irregular, dendritic structure. The particle size depends on the rate of cooling, but under ordinary circumstances varies between about 0.01 and 2.0 mm. The apparent density of the isolated powder is about 0.5. Its finely divided nature enhances its reactivity in most of the reactions wherein it is used.

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8. FINELY DIVIDED CALCIUM METAL

SUBMITTED BY R. H. MARSHALL* AND T. P. WHALEY*
CHECKED BY W. J. MCCREARY†

Finely divided calcium for laboratory purposes can also be prepared by recrystallizing bulk calcium from a sodium solution. The bulk calcium dissolves in sodium at elevated temperatures and, upon cooling, crystallizes out in small dendritic platelets that become trapped in a sodium matrix when the sodium solidifies. As in the previous synthesis, the sodium matrix may be removed by preferential reaction with a hydrous lower alcohol.

Procedure

The apparatus and technique employed are identical with those described in the previous synthesis.

Using the same apparatus as described above, 40 g. of freshly cut sodium and 8 g. of clean calcium turnings (or bulk calcium) are heated to approximately 850° under an argon atmosphere. After mild agitation at this temperature with the stainless-steel thermocouple well, the sodium-calcium solution is permitted to cool to room temperature. (The thermocouple well is removed before the sodium solidifies; i.e., at about 100°.) Fifty milliliters of mineral oil is added to the solidified melt, and the metal mixture is then reheated to 110° and poured into 200 ml. of cold mineral oil in a 1-l. beaker. The melt may be too viscous to pour cleanly; if so, the product may be removed with a spoon or spatula. The solidified product is then cut into pieces small enough to pass through a 24/40 standard taper joint and the calcium is separated by the procedure[1] described in the previous synthesis.

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The yield is approximately 7 g. of finely divided calcium. The principal difference between the products of the two syntheses lies in the nitrogen content. Commercial undistilled calcium has a relatively high nitride content which is not removed in the recrystallization from sodium and subsequent isolation. The calcium produced from calcium chloride in the previous synthesis, on the other hand, should have a low nitride content if low-nitrogen argon or helium is used as the atmosphere.*

Reference

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* Properties of calcium are given in the previous synthesis.

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CHAPTER IIB

9. MERCURY(II) CHLORIDE THIOUREA COMPLEXES

SUBMITTED BY I. AUCKEN*
CHECKED BY RUSSELL S. DRAGO†

Four different thiourea complexes of mercury(II) are easily prepared from aqueous solutions of mercury(II) chloride and thiourea. The proportions of reagents are not as critical as the temperature, elevation of which results in precipitation of black mercury(II) sulfide. Electrical conductivities and freezing points provide evidence for the constitution of the complexes.

Procedure

A. MERCURY(II) CHLORIDE MONOTHIOUREA[1,4]

$[Hg(SCN_2H_4)Cl]Cl$

Equimolar proportions of mercury(II) chloride (27.15 g.) and thiourea (7.61 g.) in aqueous solution are heated together on a water bath for a short time. The cooled white precipitate of needle-shaped crystals may be washed with small quantities of cold water and dried on filter paper, or with alcohol followed by drying *in vacuo*.‡

A. Rosenheim and V. J. Meyer assigned the formula $Hg(CSN_2H_4)Cl_2 \cdot 1/2H_2O$ to the water-washed crystals of melting point 234° (with decomposition) and gave the fol-

* East Ham Technical College, London, England.
† University of Illinois, Urbana, Ill.
‡ The yield obtained by the checker was 98%.

lowing analysis. *Anal.* Calcd. for $Hg(CSN_2H_4)Cl_2 \cdot 1/2H_2O$: C, 3.37; H, 1.40; N, 7.87; Hg, 56.18. Found: C, 3.39; H, 1.27; N, 7.97; Hg, 56.60, 56.72. P. C. Rây assigned the formula $CH_4N_2Cl_2SHg$ to the crystals dried *in vacuo* and gave the following analysis. *Anal.* Calcd. for $CH_4N_2Cl_2SHg$: C, 3.46; H, 1.18; N, 8.07; Hg, 57.64; Cl, 20.46; S, 9.22. Found: C, 3.82; H, 1.63; N, 8.14; Hg, 56.62; Cl, 20.45; S, 10.03.

B. MERCURY(II) CHLORIDE DITHIOUREA[1,2,3]

$[Hg(SCN_2H_4)_2]Cl_2$

When any aqueous solution of mercury(II) chloride is gradually added to an aqueous solution of thiourea at room temperature, each addition produces a turbidity which disappears on shaking; however, when the reactants are in the proportion of 1 mol of mercury(II) chloride to 2 mols of thiourea, the turbidity thickens to a snow-white microcrystalline precipitate of star-shaped clusters and sheaves of needles. Vigorous stirring during the actual precipitation and use of exact quantities [2.715 g. $HgCl_2$; 1.522 g. $CS(NH_2)_2$] is necessary for a near 100% yield, since excess thiourea would dissolve some of the precipitate, and excess mercury(II) chloride would form a little of the monocomplex which is difficultly soluble and would need to be washed out. However, a fairly good yield is obtainable even without weighing. The precipitated dithiourea derivative may be filtered at the pump, washed thoroughly with cold water in which it is almost insoluble, and dried in a desiccator. It melts at 250° with blackening.* *Anal.* Calcd. for $HgCl_2 \cdot 2CSN_2H_4$: Hg, 47.28; S, 15.1; Cl, 16.7; N, 13.26. Found: Hg, 46.80.† Found: Hg, 47.8; S, 14.8; Cl, 16.67.‡ Found: Hg, 49.52, 49.06, 48.67; N, 13.19.§

* The yield obtained by the checker was 92%.

† This analysis was given by R. Maly.

‡ This analysis was given by A. Claus.

§ This analysis was given by A. Rosenheim and V. J. Meyer.

C. MERCURY(II) CHLORIDE TRITHIOUREA[5]

$[Hg(SCN_2H_4)_3]Cl_2$

This can be prepared simply by stirring a cold, practically saturated aqueous solution of mercury(II) chloride into a cold, practically saturated aqueous solution of thiourea until the white precipitate (of the di-derivative) almost entirely redissolves. Large, colorless crystals separate out when the solution is filtered and allowed to evaporate at ordinary temperature, say, in a vacuum desiccator. The crystals may be dissolved in hot water, whereupon little decomposition takes place, and square microscopic platelets crystallize out of the filtered solution on cooling. The dried crystals sinter at about 174° and begin to decompose at about 179°. The yield is only moderately good.* *Anal.* Calcd. for $HgCl_2 \cdot 3CSN_2H_4$: N, 16.80. Found: N, 16.76, 16.89.

D. MERCURY(II) CHLORIDE TETRATHIOUREA[1,3]

$[Hg(SCN_2H_4)_4]Cl_2$

Fairly concentrated aqueous solutions containing 1 mol of mercury(II) chloride to 4 mols (or more) of thiourea are mixed, the white precipitate (of the di-derivative) redissolving in the excess of thiourea. The clear solution is evaporated down to, say, half bulk and filtered hot. Large, colorless, well-formed, prismatic crystals of the tetra-derivative slowly grow out of the cooling solution. These crystals are more richly faceted than those of the tri-derivative. They may be quickly washed two or three times with small quantities of cold water, redissolved in hot water, and recrystallized quickly by shaking and cooling the hot concentrated solution, whereupon microscopic hexagons crystallize out and may be washed as before and dried. They sinter at 140° and decompose at 182°.† *Anal.* Calcd. for

* The yield obtained by the checker was 17%.

† The yield obtained by the checker was 23%.

$HgCl_2 \cdot 4CSN_2H_4$: Hg, 34.78; N, 19.50. Found: Hg, 34.70; N, 19.83.*

Properties

The tetra-derivative, which is described in Beilstein[6] as easily soluble in water, in fact gives barely a 1% solution at 0°. At room temperature the solubility is higher but only about one-fourth that of mercury(II) chloride and one-sixth that of thiourea. The tri-derivative is still less soluble in water, giving a 0.2% solution at 0°, and the mono-derivative even less so. The least soluble is the di-derivative which is precipitated on mixing 0.1% solutions of mercury(II) chloride and thiourea.[2] It is also virtually insoluble in brine and alcohol[2] and only sparingly soluble in hydrochloric acid.[1]

TABLE I

Temperature	Constitutional formula of mercury derivative	Molar conductivity Ω ohm^{-1} at 64 l.	128 l.	250 l.	256 l.	512 l.	1024 l.
25°	$[HgCl_2]$	23.1	3.55		5.66[7]		
21.5°	$[Hg(SCN_2H_4)Cl]Cl$	cf. 18° Ω NaCl			99[4] / 104[9]		
	$[Hg(SCN_2H_4)_2]Cl_2$			169[5]			
17°	$[Hg(SCN_2H_4)_3]Cl_2$			171[5]			
17°	$[Hg(SCN_2H_4)_4]Cl_2$	164	181	200 216 cf. 25° Ω $CaCl_2$			244[1]

It was formulated as $[Hg(SCN_2H_4)_2Cl_2]$[1,8] after A. Werner, before P. C. Rây's work on the mono-derivative.[4] Although this wholly covalent formulation is not impossible, especially in view of the production of mercury(II) sulfide (not oxide) by addition of soda solution,[2] it does not fit in with the tables of electrical conductivities and freezing-point depressions (Tables I and II).

* This analysis was given by A. Rosenheim and V. J. Meyer.

TABLE II

Mercury derivative	g./100 g. aq.	Δ	M (obs.)	M (calcd.)	i[5]
$[Hg(SCN_2H_4)_3]Cl_2$	0.197	0.022°	166(±5%)	500	3
$[Hg(SCN_2H_4)_4]Cl_2$	0.430	0.052°	153(±4%)	576	4
$[Hg(SCN_2H_4)_4]Cl_2$	0.619	0.079°	145(±2%)	576	4

Thus the mono-derivative ionizes as a binary electrolyte and the tri-derivative as a ternary electrolyte in aqueous solution. The tetra-derivative does not exist at those dilutions, having completely dissociated, even at 0°, into the comparatively stable tri-derivative and free thiourea.

The di-derivative persists as the enigma of a family of complexes, which affords an excellent example of coordinative electronegativity decline (diminution of the electronegativity of a central atom as a result of coordination to it). Here a fairly electronegative, and therefore covalent, mercury atom is converted by coordination into a weakly electronegative, and consequently electrovalent, atom reminiscent of sodium or calcium rather than mercury.

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CHAPTER III

10. GALLIUM(III) BROMIDE

$$2Ga + 3Br_2 \rightarrow Ga_2Br_6$$

SUBMITTED BY N. N. GREENWOOD* AND I. J. WORRALL*
CHECKED BY T. C. ICHNIOWSKI,† A. MARTIN,† AND ALAN F. CLIFFORD†

Gallium(III) bromide (Ga_2Br_6) can be prepared by the direct reaction of metallic gallium with liquid bromine at low temperatures,[1] but the reaction is violent and therefore easier to control if the halogen, suitably diluted with an inert carrier gas, is passed over heated gallium.[2,3] The compound can also be prepared from gallium and hydrogen bromide, as reported by C. R. Smoot and H. C. Brown,[4] in high purity; however, the bromine method is valued because dry bromine is more readily obtained than dry hydrogen bromide and is easily handled.

Procedure

AnalaR bromine, which has been dried over phosphorus(V) oxide, is placed in flask *A* (see Fig. 3) and pellets of gallium (10 g.) are dropped into tube *B* which is then sealed at point 1. The apparatus, previously dried by flaming it under vacuum, is swept out with dry nitrogen and the gas is then passed through a sintered-glass bubbler under the bromine at a rate which is adjusted to give rapid reaction in tube *B*, though the flow rate should not be so fast that

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the tribromide is entrained as a fog and swept through the apparatus. (The U-tube *F* is incorporated to prevent undue losses should this temporarily occur.) It is necessary to heat the gallium in *B* gently with a Bunsen flame during the reaction. Some dibromide is formed as an intermediate but is completely converted to the tribromide as the products are distilled in the stream of bromine vapor into tube *C*.

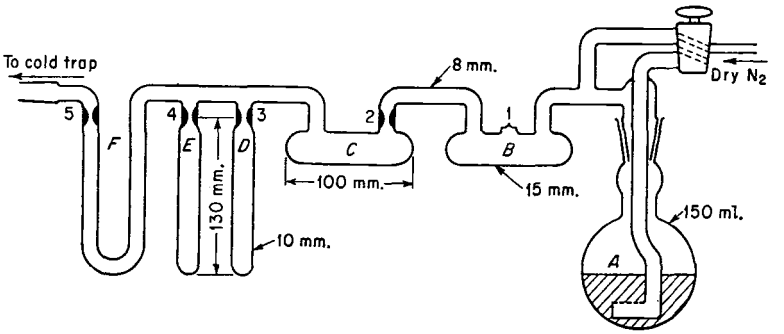

FIG. 3. Apparatus for the preparation of gallium(III) bromide.

When all the gallium has reacted and the tribromide has been transferred to *C*,* the bromine bubbler is by-passed and the product melted under a slow stream of nitrogen to remove any dissolved bromine. Throughout all these stages the exit gases are passed through a cold trap (CO_2 or liquid nitrogen) to collect excess bromine and prevent the ingress of moisture. The apparatus is sealed at point 2, the cold trap removed, and the system evacuated on a diffusion pump, a hard vacuum being essential at this stage to facilitate the sublimation (at 120°) of the solid tribromide from *C* to the areas round the mouths of tubes *D* and *E*. The sublimation train is sealed at point 5 and the product (m.p. 122.5 ± 0.05°) is melted into tubes *D* and *E* which are sealed at points 3 and 4. The yield is nearly quantitative based on the weight of gallium metal used.

* The bulb *C* is heated in an oil bath held just below the melting point of the tribromide.

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Properties

Gallium(III) bromide is a hygroscopic, white solid which sublimes readily and melts at 122.5° to a covalent, dimeric liquid. The solid is ionic and its electrical conductivity at the melting point is twenty-three times that of the liquid.[5] The vapor pressure of the liquid at T°K is given by the equation $\log p(\text{mm.}) = 8.554 - 3129/T$ and the heat of dissociation of the dimer in the gas phase is 18.5 kcal./mol.[3] At 125° the liquid has the following properties:[5,6] density, 3.1076; dynamic viscosity, 2.780 c.p.; surface tension, 34.8 dynes/cm.; and specific conductivity, 7.2×10^{-7} ohm^{-1} cm.^{-1} Gallium(III) bromide readily hydrolyzes in water and forms addition compounds with ligands such as ammonia, pyridine, and phosphorus oxychloride.

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11. GALLIUM(I) TETRABROMOGALLATE(III)

$$2Ga_2Br_6 + 2Ga \rightarrow 3Ga^+GaBr_4^-$$

Submitted by N. N. Greenwood* and I. J. Worrall*
Checked by T. C. Ichniowski,† A. Martin,† and Alan F. Clifford†

Gallium(II) bromide ($Ga^+GaBr_4^-$) is prepared by reducing the more volatile tribromide with slightly less than the

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† Purdue University, West Lafayette, Ind.

stoichiometric amount of gallium and then distilling off the trace of unreacted tribromide.[1] It is essential to avoid an excess of gallium metal, as this dissolves in the dibromide and cannot be removed without distilling (and partly decomposing) the product.

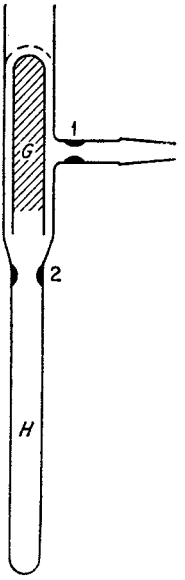


FIG. 4. Apparatus for preparation of gallium(I) tetrabromogallate-(III).

Procedure

About 20 g. of gallium(III) bromide (preceding prep.) is weighed accurately and transferred to reaction vessel *H* (Fig. 4) by the following technique: the sample of tribromide in tube *D* (p. 32) is sublimed to one end, the clear glass marked with a sharp file, and the tube weighed. The tube is broken open and sealed into a wider tube (Fig. 5) which is evacuated and sealed at point 1. The tribromide is melted and transferred quantitatively into section *G* which is sealed at 2, the weight transferred being determined by reweighing the empty pieces of tube *D*. Slightly less than the theoretical amount of gallium [say, 2.24 g. instead of the required 2.253 g./20.00 g. of gallium(III) bromide] is placed in the reaction vessel *H* (Fig. 4).* Tube *G* is opened, sealed in as indicated, and the apparatus evacuated and sealed

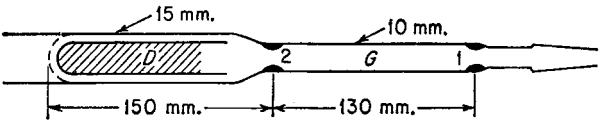


FIG. 5. Apparatus for transferring gallium(III) bromide.

at point 1. The tribromide is quantitatively transferred to *H* which is then sealed at point 2 and heated at 180°

* The checkers note that liquid gallium has a tendency to stick to glass and polyethylene, which makes its quantitative transfer difficult.

until all the gallium has reacted (about 24 hours). The excess of tribromide is then distilled from the clear liquid by raising one end of the tube out of the furnace or oil bath and cooling it with a blast of cold air (hair dryer) for a further 24 hours. The product at this stage is sufficiently

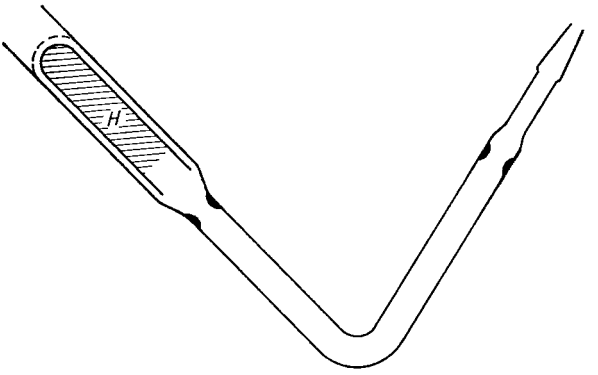


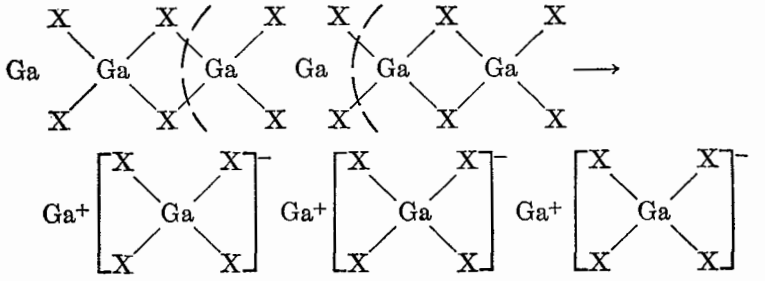
FIG. 6. Apparatus for fractionally freezing gallium(I) tetrabromogallate(III).

pure for most chemical purposes. Highly purified gallium(I) tetrabromogallate(III), melting point 166.7°, is obtained by fractionally freezing the product in an evacuated apparatus (Fig. 6), about one-fifth of the sample being rejected at each cycle.

Properties[1,2]

Gallium(I) tetrabromogallate(III) is a white, diamagnetic solid which reacts with water, liberating hydrogen and forming a brown precipitate. It melts at 166.7° to a colorless, highly conducting liquid with a dynamic viscosity of 6.596 c.p. and a specific conductivity of 0.1546 ohm^{-1} $cm.^{-1}$ at 170°. The density is given by the equation $d_4^t = 3.4656 - 0.00169(t - 170)$. Its properties are very similar to those of the corresponding chloride ($Ga^+GaCl_4^-$, m.p. 172.4°) which is also a molten salt. It is noteworthy that for both compounds reduction of the trihalide to dihalide occurs without change in volume.[2] Thus, referring to

the equation for the reduction, the volume of 2 gram moles of gallium(III) bromide (398 ml.) is very similar to the volume of the 3 gram moles of dibromide formed (397 ml.), despite the addition of 2 gram atoms of gallium (23 ml.):



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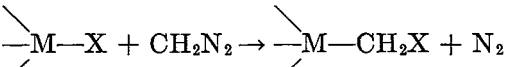
CHAPTER IVA

12. HALOMETHYL DERIVATIVES OF SILICON, GERMANIUM, AND TIN BY THE DIAZOMETHANE METHOD



SUBMITTED BY DIETMAR SEYFERTH* AND EUGENE G. ROCHOW†
CHECKED BY JULIAN B. HONEYCUTT, JR.,‡ AND ROBERT C. BRYAN‡

The reaction of the appropriate halides with diazomethane is an elegant laboratory-scale method for the synthesis of halomethyl derivatives of silicon, germanium, tin, and lead.[1–4] However, good yields are obtained only with the following types:

$HSiX_3$	GeX_4	SnX_4
SiX_4	$RGeX_3$	$RSnX_3$
XCH_2SiX_3		R_2SnX_2
		$(XCH_2)_3SnX$

Low yields are obtained with halides of the following types, and a copper catalyst is necessary:

$RSiX_3$	R_2PbX_2
$(XCH_2)_2SiX_2$	R_3PbX

No reaction occurs between diazomethane and halides of

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† Harvard University, Cambridge, Mass.
‡ Ethyl Corporation, Baton Rouge, La.

the following types:

R_2SiX_2 R_2GeX_2 R_3SnX
R_3SiX

(X = halogen: Cl, Br, I; and R = unsubstituted alkyl group.)

The synthesis of chloromethyldichlorosilane, chloromethylgermanium trichloride, and chloromethyldimethyltin chloride are described below as examples of the general procedure. Copper was included in the silicon and germanium runs to further improve the reaction, but it is not necessary with the halides employed herein.

Extremely vigorous stirring is necessary to obtain good yields, and anhydrous conditions must be employed. As both the reactants and products are subject to atmospheric hydrolysis, precautions must be taken throughout the entire operation. The authors used a drying tube filled with Drierite to protect the system, while the checkers employed an atmosphere of dry nitrogen.

With appropriate modifications for handling the starting material the method may be used under similar conditions for any of the preparations indicated above.

Procedure

Diazomethane is prepared from nitrosomethylurea[5] by the method of Bachmann and Struve.[6] The yield of diazomethane is determined by treatment of a 10-ml. aliquot of its ethereal solution with a solution of an excess of benzoic acid in ether, followed by titration of the excess acid with a standard alcoholic solution of potassium hydroxide. Then the diazomethane solutions are dried over pellets of potassium hydroxide at −50°.

It should be noted that diazomethane is a very toxic material and that it has been known to undergo explosions. Great caution is advised. The preparations should be carried out in a very well-ventilated hood behind a safety

shield, and only small amounts (0.5 mol maximum) should be prepared and used at a time.

A. (CHLOROMETHYL)DICHLOROSILANE

A solution of 40 g. (0.296 mol) of trichlorosilane in 100 ml. of anhydrous ethyl ether in a 1-l., three-necked flask equipped with a mechanical stirrer, a Y-joint holding a pentane thermometer and a drying tube filled with Drierite, and a dropping funnel is cooled to −60° and about 0.5 g. of copper powder is added.* A cold solution of less than one equivalent of diazomethane in ether (0.194 mol of CH_2N_2 in 350 ml. of ether was used in this run) is then added slowly with vigorous stirring. Nitrogen evolution begins immediately. After the addition is complete, the reaction mixture is stirred for 2 hours at −60 to −65° under an atmosphere of dry nitrogen and then allowed to warm to room temperature. Stirring is continued at room temperature for 2 hours. The ether is removed through an 18-in. vacuum-jacketed column (1 in. in diameter) filled with glass helixes.† Another preparation (0.17 mol of diazomethane and 0.296 mol of trichlorosilane) was carried out, and the residues from these two preparations were combined and fractionally distilled to yield 40 g. of chloromethyldichlorosilane, Cl_2HSiCH_2Cl (b.p. 97 to 97.4° at 773 mm.), a yield of 73.3% based on the diazomethane. *Anal.* Calcd. for Cl_2HSiCH_2Cl: C, 8.03; H, 2.02; Cl, 71.17. Found: C, 8.14; H, 2.14; Cl, 71.51.

B. (CHLOROMETHYL)TRICHLOROGERMANE

A solution of 28.0 g. (0.12 mol) of germanium tetrachloride in 130 ml. of anhydrous ether in a 1-l., three-necked flask equipped with a mechanical stirrer, a Y-joint holding a pentane thermometer and a drying tube filled with Dri-

* The reaction flask was most conveniently charged by the checkers in an inert-atmosphere box.

† The checkers used a 10-plate Oldershaw column for all distillations.

erite, and a 500-ml. dropping funnel is cooled to −60° and about 0.5 g. of copper powder is added. A cold solution of diazomethane in ether (0.128 mol of CH_2N_2 in 250 ml.) is poured into the dropping funnel (in about 50-ml. portions at a time) and is added slowly to the germanium tetrachloride solution with vigorous stirring. Nitrogen evolution begins immediately. After the addition is complete, the reaction mixture is stirred for 2 hours at −60 to −70° under an atmosphere of dry nitrogen and subsequently allowed to warm slowly to room temperature. Stirring is continued at room temperature for another 2 hours. Then the ether is distilled through a 12-in. Vigreux column, and the residue is transferred to a small distillation unit equipped with a 6-in. vacuum-jacketed column packed with glass helixes. Fractionation yielded 7.2 g. of unreacted germanium tetrachloride and 20.8 g. of chloromethylgermanium trichloride (b.p. 60 to 65° at 35 mm.), a yield of 93.7% based on the unrecovered germanium tetrachloride. *Anal.* Calcd. for $ClCH_2GeCl_3$: C, 5.26; H, 0.88; Cl, 62.08. Found: C, 5.58; H, 1.03; Cl, 62.10. The higher-boiling residues of this and two other preparations of similar size were combined and fractionated to yield 5.5 g. of bis(chloromethyl)dichlorogermane (b.p. 90° at 21 mm.). *Anal.* Calcd. for $(ClCH_2)_2GeCl_2$: C, 9.91; H, 1.66; Cl, 58.49. Found: C, 10.16; H, 1.56; Cl, 58.26.

C. CHLOROMETHYLDIMETHYLTIN CHLORIDE

A solution of 50 g. (0.228 mol) of dimethyltin dichloride in 750 ml. of anhydrous ether in a 3-l., three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a 1-l. dropping funnel is cooled to −50°. A solution of diazomethane in ether (0.35 mol of CH_2N_2 in 500 ml.) at −5° is added slowly with vigorous stirring. The diazomethane solution is decolorized immediately on contact with the dimethyltin dichloride solution, and evolution of nitrogen is observed. After the addition is complete, the

reaction mixture is light yellow in color. Stirring is continued and the reaction mixture is allowed to warm to room temperature. The now colorless reaction mixture smells strongly of a trialkyltin compound.

The ether is removed by distillation at atmospheric pressure. The residue is then transferred to a 100-ml., round-bottomed flask and fractionation is continued using a 12-in. Vigreux column equipped with a reflux head. A yield of 72.8% of chloromethyldimethyltin chloride (38.7 g.) was obtained as a single fraction boiling at 76 to 79° at 10.5 mm. In similar runs yields ranging from 65 to 80% were obtained. *Anal.* Calcd. for $(CH_3)_2(CH_2Cl)SnCl$: C, 15.42; H, 3.45. Found: C, 14.97; H, 3.35.

Properties

Chloromethyldichlorosilane is a heavy, colorless liquid that fumes on exposure to moist air. Chloromethylgermanium trichloride is a heavy, colorless liquid that is readily hydrolyzed by moisture. Chloromethyldimethyltin chloride, a heavy, colorless liquid, is a potent lachrymator and a vesicant. Caution should be used in handling the last compound. See Table I for data.

TABLE I

Compound	B.p.		n_D^{25}	d_4^{25}
	°C	mm.		
Cl_2HSiCH_2Cl	97–97.5	773		
Cl_3GeCH_2Cl	60–65	35	1.4989	1.833
$Cl_2Ge(CH_2Cl)_2$	90	21	1.5176	
$(CH_3)_2(CH_2Cl)SnCl$	76–79	11	1.5263	

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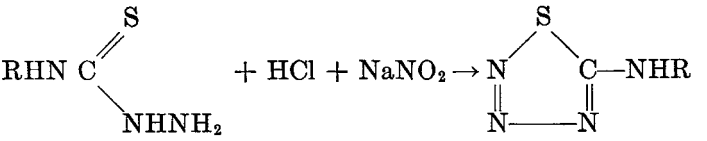
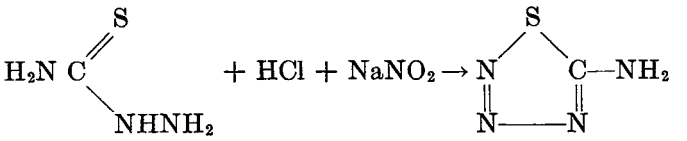
13. THE DIAZOTIZATION OF THIOSEMICARBAZIDE AND 4-ALKYL AND 4-ARYL THIOSEMICARBAZIDES



Submitted by Eugene Lieber,* C. N. Pillai,* Edwin Oftedahl,* and Ralph D. Hites*
Checked by J. A. Chandler†

A. 5-AMINO-1,2,3,4-THIATRIAZOLE



The procedure described is a modification of that first presented by Freund[1,2] involving the diazotization of thiosemicarbazide with emphasis on the removal of product so as to prevent its subsequent decomposition by the nitrous acid. The 1,2,3,4-thiatriazole ring is number 51 in the ring

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† University of Illinois, Urbana, Ill.

index,[3] the sulfur atom being position "1," while the carbon atom is the fifth position.

Procedure

A solution of 91 g. (1 mol) of thiosemicarbazide[4]* in 350 ml. of 3 *N* HCl (1 mol) is prepared. A clear solution is obtained at 30°. The solution is placed in a 1-l., three-necked flask equipped with a mechanical stirrer, thermometer, and dropping funnel and cooled in an ice-salt bath to 10°. A portion of the dissolved thiosemicarbazide precipitates at this stage. A solution of sodium nitrite, 69 g. (1 mol) in 150 ml. of water, is placed in the dropping funnel. The total volume of the solution is 180 ml. The sodium nitrite solution is added dropwise to the stirred mixture, while the temperature is maintained at 10°. When about 130 ml. of the solution has been added (45 minutes), the addition is stopped and the fine white crystalline precipitate filtered off. The filtrate, which is pale blue in color, is put back into the reaction flask and the addition of the sodium nitrite solution continued. The temperature of the reaction mixture should be maintained at 10 to 15° throughout the addition of the sodium nitrite. When about 40 ml. more of the sodium nitrite solution has been added (15 minutes), the reaction mixture tends to assume a very pale yellow color. Addition of the sodium nitrite is stopped at this stage and the rest of the precipitate filtered off. The addition of even a few drops of the sodium nitrite solution to the filtrate causes an intense yellow color. The filtrate is discarded at this stage. The combined precipitates of 5-amino-1,2,3,4-thiatriazole is washed three times with small amounts of ice-cold distilled water and dried under vacuum over sulfuric acid. The yield is 81.5 g. or 80% of theory.†

* The commercially available thiosemicarbazide, Eastman Organic Chemical number 1275, can be used without modification.

† Because of its instability to excess nitrous acid the yield of product may vary. The checker reported an average yield of 74% for three preparations.

Properties

The initial diazotization product of thiosemicarbazide is essentially pure 5-amino-1,2,3,4-thiatriazole.* It consists of fine white needles which decompose with a slight explosion at 136° in a capillary tube; on a hot plate the decomposition point is 128 to 130°, which corresponds to that reported[1,2] in the literature. 5-Amino-1,2,3,4-thiatriazole is markedly unstable in aqueous solution;[5] when prepared and kept at room temperature the solution very soon develops a faint white opalescent cloud of colloidal sulfur. It is also inherently thermally unstable, the temperature and time of decomposition depending on the rate of heating.[2] It is impossible to heat a solution of 5-amino-1,2,3,4-thiatriazole without causing decomposition. A recrystallization can be effected by making a saturated solution in ethanol at room temperature and allowing it to cool at 0°. The recovery on recrystallizing in this manner is about 50% without any increase in purity. Hence, recrystallization is not recommended.

B. 5-(SUBSTITUTED)AMINO-1,2,3,4-THIATRIAZOLES

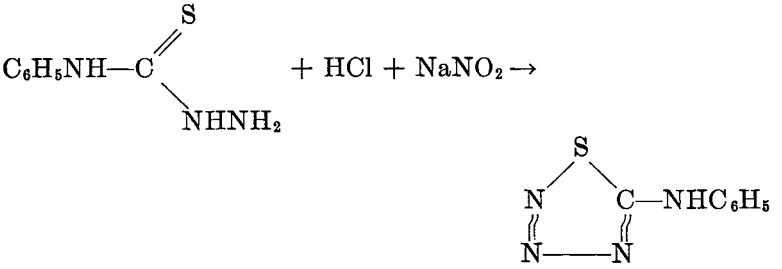
The procedure is essentially similar to that described for the preparation of 5-amino-1,2,3,4-thiatriazole. Freund and Hempel[6,7] have reported observing that the initial diazotization products of 4-aryl-substituted thiosemicarbazides lead to the formation of tetrazoles, while the corresponding 4-alkyl-substituted thiosemicarbazides were considered by Freund and Schwarz[8] to be thiatriazoles. However, Oliveri-Mandala,[9] on the basis of his study of the reaction of alkyl and aryl isothiocyanates with hydrazoic acid, concluded that the initial diazotization product of either 4-aryl or 4-alkyl thiosemicarbazides were open-chain thiocarbamyl azides, $RNHC(:S)N_3$. Lieber, Pillai, and Hites[10] have recently clarified this situation and have shown

* *Anal.* Calcd. for CH_2N_4S: C, 11.75; H, 1.97; N, 54.87; S, 31.4. Found: C, 11.96; H, 1.72; N, 55.2; S, 31.0.

that the reaction of nitrous acid with 4-alkyl or 4-aryl thiosemicarbazides, as well as the reaction of alkyl or aryl isothiocyanates with hydrazoic acid, all lead to identical 5-(substituted)amino-1,2,3,4-thiatriazoles. The procedure described is taken from this latter reference.

Procedure

5-Anilino-1,2,3,4-thiatriazole



The procedure described for 5-anilino-1,2,3,4-thiatriazole is typical. To a stirred and cooled mixture of 16.7 g. (0.10 mol) of 4-phenylthiosemicarbazide (Eastman-Kodak number 5426) and 76 ml. of 15% hydrochloric acid was added 6.9 g. (0.1 mol) of sodium nitrite in 50 ml. of water. The mode of addition of the sodium nitrite used for the preparation of 5-amino-1,2,3,4-thiatriazole was followed. The white powdery material was recovered by filtration. The yield* was 16 g. or 89% of theory. Recrystallization from methanol yields the pure product.

Properties

The diazotization product of 4-phenylthiosemicarbazide is 5-anilino-1,2,3,4-thiatriazole and consists of colorless nee-

* The yields may be expected to vary considerably due to the inherent instability of the thiatriazole ring and will also depend upon the recrystallization technique and its efficiency. The checkers reported an average yield of 73% based on three preparations.

dles,* when recrystallized from methanol, melting with vigorous decomposition at 142 to 143°. On warming in alkaline solution it is converted, accompanied by partial decomposition, to 1-phenyl-tetrazole-5-thiol.[10] The melting points of a series of 5-(substituted)amino-1,2,3,4-thiatriazoles are as follows (the data given in order are the name of the substituent followed by the melting point): methyl, 93 to 96°; ethyl, 66 to 67°; *n*-butyl, 40 to 41°; *n*-heptyl, 75 to 75.5°; *p*-tolyl, 140 to 144°; *o*-tolyl, 114 to 115°; *p*-methoxyphenyl, 136 to 137°; benzyl, 80.5 to 81°; *p*-chlorophenyl, 147 to 148°; allyl, 53 to 53.5°; *o*-methoxyphenyl, 89 to 90°; the 5-dimethylamino-1,2,3,4-thiatriazole melts at 49 to 51°. Methanol is the solvent of choice for recrystallizations except for the 5-allylamino-1,2,3,4-thiatriazole which must be purified from a mixture of ether and petroleum ether. The aryl derivatives exhibit phototropism, turning a pinkish color when exposed to light.

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* *Anal.* Calcd. for $C_7H_6N_4S$: C, 47.15; H, 3.40; N, 31.45; S, 18.00. Found: C, 47.10; H, 3.51; N, 31.60; S, 17.60. Microanalyses were by Dr. C. Weiler and Dr. F. B. Strauss, Oxford, England.

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CHAPTER IVB

14. REFRACTORY METAL POWDERS

SUBMITTED BY T. P. WHALEY*
CHECKED BY W. J. MCCREARY†

Refractory metals such as titanium and zirconium can be won from their oxides by reduction with metals which have oxides with a high heat of formation. Of these, only calcium (or calcium hydride) is capable of producing refractory metals in purities approaching those required for metallurgical uses.

An efficient way of reducing refractory metal oxides[1,2] with calcium is to take advantage of the equilibrium described in the synthesis of calcium metal, wherein calcium chloride and sodium metal interact at high temperatures to produce calcium metal and sodium chloride. Addition of a metal oxide which reacts with calcium but not with sodium removes the calcium as it is formed, thereby permitting the reaction to go to completion.‡ Thus, incorporating a metal oxide such as titanium(IV) oxide into the equilibrium described in the synthesis of calcium metal permits the following reaction to proceed in good yields:

$$TiO_2 + 2CaCl_2 + 4Na \rightarrow 2CaO + 4NaCl + Ti$$

By using an excess of both sodium and calcium chloride[3] completion is assured in accordance with the law of mobile equilibrium.

* Ethyl Corporation, Baton Rouge, La.
† University of California, Los Alamos, N.Mex.

‡ Another equilibrium which is favored at very high temperatures, $Ti + 2CaO \leftrightharpoons TiO_2 + 2Ca$, tends to prevent complete removal of oxygen.

All the by-products of the reaction, and the excess reactants, are soluble in water or dilute acid; thus, if the refractory metal is unreactive toward water, aqueous leaching provides a good method for isolating the product. If appreciable sodium remains, however, it should be "killed" with alcohol before attempting the aqueous leaching.

Procedure

Caution. Finely divided titanium, zirconium, and other refractory metals are often pyrophoric and should be handled with a minimum exposure to air. Weighings should be made in a closed container.

The apparatus employed is identical to that described in the synthesis of calcium metal, as is the procedure for filling the reaction vessel with the reactants. To the stainless-steel beaker is added 55 g. of freshly cut sodium metal and an intimate mixture of 111 g. of anhydrous calcium chloride* and 20 g. of titanium(IV) oxide. (The $CaCl_2$-TiO_2 mixture may be dehydrated by heating at 400 to 500° for an hour in a stream of argon.) The filled beaker is placed inside the atmosphere chamber, which is then covered with a lid, and the entire assembly is placed in the crucible furnace. The furnace should be placed on an asbestos pad and the heating conducted in or near a fume hood in order to exhaust the sodium oxide smoke. An argon flush of about 5 l./min. is started and continued throughout the entire heating and cooling cycle.

The reaction mixture is heated to about 880° and maintained at that temperature until the sodium flame diminishes. (Above about 750°, sodium vapor swept out by the argon stream burns on exposure to air and shows up as a pointed flame issuing from the reaction vessel.) The white smoke is sodium oxide. Mild agitation with the stainless-

* The entire contents of a $\frac{1}{4}$-lb. bottle of reagent-grade calcium chloride can be used. Thus exposure to atmospheric moisture or carbon dioxide during weighing operations is eliminated, inasmuch as $\frac{1}{4}$ lb. of calcium chloride is approximately 1 gram mole.

steel thermocouple tube assists in reaching equilibrium at this temperature. When the sodium flame stops, indicating that the excess unreacted sodium has distilled from the reaction mixture, the stirrer is lifted a few inches so that it will not be trapped when the molten salts solidify, and the system is permitted to cool to room temperature. The argon flush is continued during cooling.

When the reaction vessel has cooled, the beaker containing the reaction mixture is removed from the atmosphere chamber and filled with a solution of 5% methanol in isopropyl alcohol. Any residual sodium will react with this mixture and permit safe aqueous leaching. When all the sodium has been consumed by reaction with alcohol, water is added to the alcohol until an evolution of hydrogen indicates that the excess calcium metal is reacting with the water. When the hydrogen evolution stops after all the calcium metal has been consumed, the contents of the reaction vessel are transferred to a 4-l. stainless-steel beaker. (Some of the reaction mass will adhere to the wall of the reaction vessel; this should be removed by continued washing with water or dilute acid.) The beaker is filled with water and dilute hydrochloric acid is added until the pH is approximately 4. The solids are permitted to settle, and the supernatant liquid is decanted. This procedure is repeated several times until a neutral or acidic pH which persists for at least 30 minutes indicates that all the calcium oxide has been removed; sodium chloride will have been completely removed by this time. The titanium powder is then washed with successive washes of alcohol and ether, dried under argon, and stored in an airtight, argon-filled container. The yield is approximately 10 g. of titanium metal powder.*

* Spectrographic analysis indicated the following major impurities, in parts per million: Na, 300; Ca, 3000; Fe, 2000; and Cu, 1000. The results of an x-ray analysis showed the main constitutent to be an α-Ti solid solution with $a = 2.960$, $c = 4.831$. These lattice constants correspond to those of α-Ti saturated with oxygen in solid solution. The sample also contained an appreciable proportion of an impurity which could not be identified.

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Decontamination of equipment is identical to that described in the synthesis of calcium metal. A similar procedure can be used to produce powders of zirconium, chromium, vanadium, thorium, uranium, and other refractory metals from their oxides; the reductant/metal oxide ratio, however, differs for each metal in order to avoid formation of oxygenated metal by-products and ensure maximum product purity.

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15. CESIUM TITANIUM ALUM

$$TiOSO_4 + 2CsNO_3 + 2H_2SO_4 \rightarrow Ti(SO_4)_2 + Cs_2SO_4 + 2HNO_3 + H_2O$$

$$2Ti(SO_4)_2 + Zn \rightarrow Ti_2(SO_4)_3 + ZnSO_4$$

$$Ti_2(SO_4)_3 + Cs_2SO_4 + 24H_2O \rightarrow 2CsTi(SO_4)_2 \cdot 12H_2O$$

Submitted by Burl E. Bryant* and Edward Paul*
Checked by L. A. Hiller, Jr.† and Ernesto Giesbrecht†

Cesium titanium alum may be prepared by reduction of titanium(IV) compounds, using either electrolysis[1] or a chemical reducing agent.[2] The latter method, using zinc as the reducing agent, does not require the elaborate apparatus of the electrolytic reduction, and yet gives high yields.

* University of Utah, Salt Lake City, Utah.
† University of Illinois, Urbana, Ill.

Procedure

To 30 ml. of dilute sulfuric acid (1:1) is added 36.3 g. of basic titanium(IV) sulfate and 10 g. of cesium nitrate. The mixture is heated until sulfur trioxide fumes are given off, cooled, 20 ml. of concentrated sulfuric acid added, and the mixture fumed again. After cooling, the solution is diluted with 300 ml. of water and filtered to remove any insoluble material. The filtrate is passed through a Jones reductor and allowed to cool for 2 days in an ice chest. This solution should be exposed to air as little as possible to prevent oxidation of titanium(III).

The mother liquor is decanted and the solid recrystallized from 40 ml. of 2 *N* sulfuric acid (cooling at 0° for at least 24 hours is required for complete crystallization). The crystals are shaken with 100 ml. of cold ethanol, then 100 ml. of ether, and filtered. They are pressed between filter paper and stored under a nitrogen atmosphere. The yield is 25.5 g. (83%). *Anal.* Calcd. for $CsTi(SO_4)_2 \cdot 12H_2O$: Ti, 8.13; $SO_4^=$, 32.60. Found: Ti, 8.29; $SO_4^=$, 31.94.

Properties

Cesium titanium alum forms violet octahedral crystals which are sparingly soluble in cold water, more soluble in hot. These crystals belong to the β-type alum crystal structure, or those alums that contain a large unipositive ion. The compound is oxidized rapidly in air, and water solutions become turbid on exposure to air, precipitating titanic acid.

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16. TITANIUM(III) CHLORIDE

(Titanium Trichloride)

$$H_2 \rightarrow 2H$$
$$H + TiCl_4 \rightarrow TiCl_3 + HCl$$
$$Ti + 3TiCl_4 \rightarrow 4TiCl_3$$
$$TiCl_3 + HCl \rightarrow TiCl_4 + \tfrac{1}{2}H_2$$

SUBMITTED BY T. R. INGRAHAM,* K. W. DOWNES,* AND P. MARIER*
CHECKED BY Z. Z. HUGUS, JR.,† AND STANLEY STEIGER†

Titanium trichloride has been prepared by reducing titanium tetrachloride with metals such as aluminum,[1] antimony, lead, sodium amalgam,[2] and titanium,[3] and also by reduction with hydrogen.[4] Hydrogen reduction is preferred to metal reduction in producing a pure product because the low volatility and the tendency to disproportionation of titanium trichloride make the clean separation of titanium trichloride from other metal chlorides difficult. The procedure here described utilizes a closed Pyrex-glass apparatus into which titanium tetrachloride is fed at its vapor pressure at room temperature, and from which titanium trichloride is recovered as a fine brownish-purple powder. The hydrogen required for the arc-induced reduction is continuously regenerated over warm metallic titanium from the hydrogen chloride product of the arc reaction.[5] The apparatus is simple to construct and operates almost continuously, unattended, to produce about 1 g. of titanium trichloride per hour.

Procedure

The apparatus is shown in Fig. 7. It is constructed principally of 25-mm. Pyrex-glass tubing with packless Hoke

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† University of Minnesota, Minneapolis, Minn.

valves number 482, 7 and 9, joined to the Pyrex by a brass-to-Pyrex seal. One valve, 7, serves to control the access of titanium tetrachloride, 5, to the system; the other, 9, seals the system from vacuum, helium, and hydrogen sources.

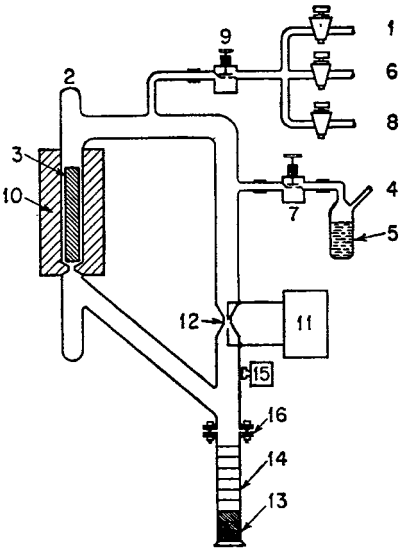

FIG. 7. Apparatus for the preparation of $TiCl_3$.

KEL-F gasket seals are used in the valves. When it is necessary to open the apparatus for the discharge of product, a Pyrex-glass pipe fitting with a Teflon gasket, 16, is used.

The electrode section of the apparatus, 12, is its most critical part. It consists of Pyrex tubing reduced from 25 mm. to 6.5 $\pm$ 1.0 mm. i.d. over a length of 11 $\pm$ 1 mm. Tungsten electrodes are sealed into the Pyrex in such a way that the space through which the arc passes is 22 $\pm$ 5 mm. in length. The top electrode is placed deeper within the constricted zone than the bottom electrode, to aid in directing the reaction product downward through the arc. In this way, the rapidly expanding gases from the arc force the titanium trichloride product, 13, preferentially in the direction of the collection container, 14.

High voltages to produce the required arc within the gas are provided by a Tesla coil leak tester, 11, connected to one electrode. The other electrode is grounded. For long operations, it is convenient to remove the outer casing of the Tesla leak tester to assist in the dissipation of heat. A titanium coupon, 3, of dimensions 1 by 15 by 120 mm. is used for the regeneration of hydrogen and is heated by an external tube furnace, 10, fitted with suitable controls to maintain a temperature of 460 ± 10°. Hydrogen absorption by the titanium does not occur at the temperatures and pressures of the operation.[6]

To begin a run, the apparatus is evacuated to a pressure of 10^{-4} mm. of mercury and checked for leaks. When the apparatus is found to be free from leaks and from any moisture introduced during construction, helium is admitted through 1, and an opening is made with a torch at 2 through which the titanium coupon is placed at 3. It should be clean and free of surface oxide coatings. The system is then sealed with a torch at 2 and an opening made at 4. Through this opening, against a gentle countercurrent of helium, 50 ml. of purified titanium tetrachloride is admitted to the apparatus at 5. The opening at 4 is then sealed with a torch, the helium supply cut off, and the titanium tetrachloride frozen with liquid air.* When freezing is complete, the apparatus is thoroughly evacuated through 6, and then valve 7 is closed. The titanium tetrachloride at 5 is then melted rapidly and brought to room temperature. While this is taking place, hydrogen is admitted through 8 to 4 ± 2 mm. of mercury with the use of a McLeod gage, then valve 9 is closed and the furnace 10 surrounding the titanium is brought up to 460 ± 10°. When this temperature is attained, the Tesla coil is started, and valve 7 is opened to admit titanium tetrachloride vapor to the system. This results immediately in the production of finely powdered titanium trichloride which collects on the inside of orifice 12 and is blown down the tube by the circulating

* Because of its lower freezing temperature, helium is preferred to argon.

gas stream. The powdered titanium trichloride, 13, settles in the graduated container, 14. Because the powder is electrostatically charged, some of it is attracted to the glass walls of the vertical tubing. It may be continuously dislodged by a mechanical vibrator, 15.

At the end of a run, when reservoir 14 is filled with titanium trichloride, valve 7 is closed and the gaseous atmosphere of the apparatus is removed by pumping through 6. Helium is then admitted through 1, and clamp 16 loosened. Against a gentle countercurrent of helium, container 14 is removed and replaced by a duplicate container, previously flushed with helium. After the clamps are tightened at 16, the system is again evacuated to 10^{-4} mm. of mercury and cylinder hydrogen admitted through 8 to 4 ± 2 mm. of mercury. Valve 9 is closed and valve 7 opened. When the arc is struck again, the reaction is resumed. The run may be continued without further interruption or attention until another container has been filled with titanium trichloride, or the titanium or the titanium tetrachloride supply is exhausted. Occasionally it may be necessary to replenish the hydrogen in the system when a large amount of titanium trichloride has been formed, owing presumably to the adsorption of hydrogen on the finely divided titanium trichloride.

As an alternative to the injection of hydrogen into the system at the beginning of an experiment, a solution of hydrogen chloride in titanium tetrachloride may be substituted for the titanium tetrachloride. This can be prepared by the addition of a small amount of water to titanium tetrachloride. The amount of the solution used is chosen so that when the hydrogen is liberated from it during the run, the pressure of hydrogen in the system will be approximately the same as that obtained by hydrogen injections. A convenient method of determining the amount of hydrogen chloride in the titanium tetrachloride has been published.[7]

The yield of titanium trichloride from the arc, based on

the consumption of metallic titanium, is over 90%. The titanium trichloride, with the exception of adsorbed hydrogen, hydrogen chloride, or titanium tetrachloride, which may be removed by a vacuum treatment, is pure and free from titanium dichloride and other metallic chlorides.

Properties

Titanium trichloride, as prepared by this method, is a brownish-purple powder with a bulk density varying from 0.07 to 0.25 g./cc. The particles vary in size from a few microns to aggregates of several hundred microns. The material is very reactive, being immediately hydrolyzed by moisture and pyrophoric in air. Any transfer or handling of the powder must be done in a dry box under nitrogen or an inert gas, if contamination is to be prevented.

Titanium trichloride is stable up to temperatures of about 500°. Above this temperature, under vacuum, it disproportionates quantitatively to titanium dichloride and titanium tetrachloride. Some of the dichloride disproportionates to metal under these conditions.

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17. TITANIUM(III) CHLORIDE AND TITANIUM(III) BROMIDE

(Titanium Trichloride and Titanium Tribromide)

$$TiCl_4 + \tfrac{1}{2}H_2 \rightarrow TiCl_3 + HCl$$
$$TiBr_4 + \tfrac{1}{2}H_2 \rightarrow TiBr_3 + HBr$$

SUBMITTED BY J. M. SHERFEY*
CHECKED BY ROLF B. JOHANNESEN†

Titanium trichloride has been prepared by saturating a stream of hydrogen with titanium tetrachloride and passing the mixture through an annular space formed by two concentric tubes. The inner tube is electrically heated, and the outer wall is cooled by a water jacket, with the mixture reacting at the hot surface and the resulting trichloride collecting on the cold surface.[1] However, the rate of production of titanium trichloride in this apparatus is only a few grams per hour and the yield, particularly with regard to the hydrogen used, is very poor. Also the product was contaminated with tetrachloride, especially when the temperature of the tetrachloride saturator was high.

The apparatus described below, utilizing the same reaction, produces 150 to 200 g. per day of a product that is 98% pure and can be further purified.

Procedure

The essential parts of the apparatus are shown in Fig. 8. The 4-l. reaction kettle, *A*, has a flanged top with four female standard-taper openings, one (34/45) centrally

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† Division of Chemistry, National Bureau of Standards, Washington, D.C.

located with three (24/40) joints symmetrically spaced around it. For simplicity these are shown in the drawing as if they were in a straight line.

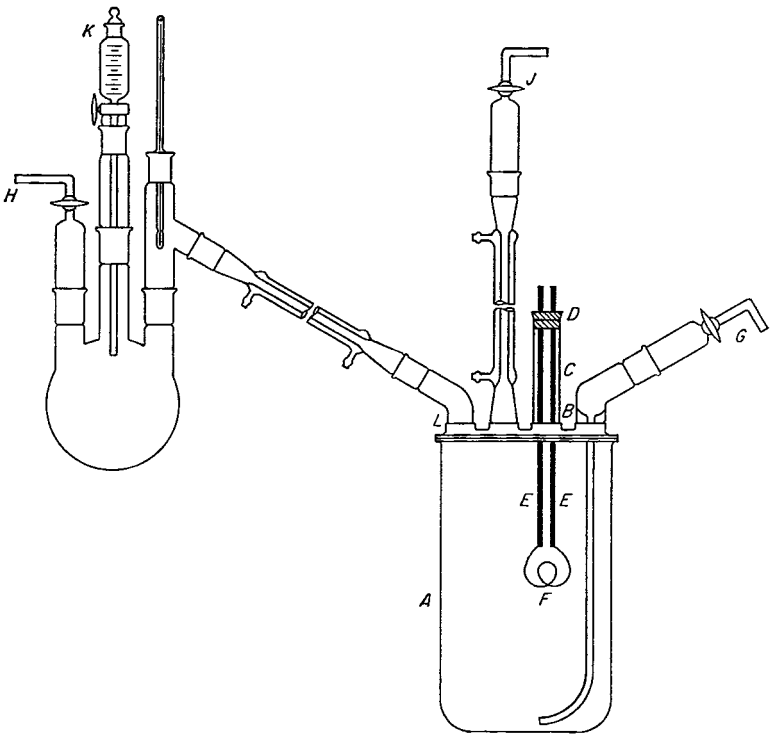

FIG. 8. Apparatus for the preparation of $TiCl_3$.

The center joint, *B*, of the reaction kettle is fitted with a chimney, *C*, in the top of which is a rubber stopper, *D*. Two tungsten rods, *E*, about 6 mm. in diameter, pass through this stopper and support a tungsten filament, *F*, which is capable of being heated to 1000 to 1100°.* The

* The diameter and length of this filament are fixed by the power supply available. A filament 1 mm. in diameter and 30 cm. long requires 38 amp. at 8.6 volts to heat it to the required temperature range. Thinner filaments should not be used because they are apt to burn out during a run. If iridium wire is available, it is preferable to tungsten as it is not attacked during the preparation of titanium trichloride, and a source of metallic

filament is attached to the rods by a stainless-steel sleeve. A milled slot about 1.5 mm. wide is cut longitudinally in the rod and the sleeve is placed over the slot, leaving both ends of the slot free. The wire is passed into the slot, under the sleeve, and then out of the slot at the other end and the sleeve is pushed along the rod until the filament is tightly wedged in place.

A run is started by flushing the entire apparatus with dry, oxygen-free hydrogen which is purified by passing it over hot copper turnings and then over a desiccant such as magnesium perchlorate.* After purification the hydrogen is passed through copper tubing or, if necessary, a minimum length of sound rubber tubing. The purified hydrogen is introduced at *G* and passes through the distillation assembly and out through the stopcock, *H*, until all the air has been removed. This also removes moisture and thus prevents the formation of hydrolysis products. While the hydrogen stream is continued, the stopcock *H* is closed and that at *J* is opened. About 1500 ml. of titanium tetrachloride is run into the distilling flask through the buret, *K*, and distillation is started. After 1000 to 1500 ml. of titanium tetrachloride is distilled into the reaction kettle, the distilling apparatus is removed from the reaction kettle and the opening, *L*, is quickly stoppered. The hydrogen stream is very rapid during this operation.

A hemispherical heating mantle is used to reflux the tetrachloride over the tungsten filament.† Jets of air are

contamination is thus avoided. The dimensions of the filament can be about the same. Iridium can be welded to the tungsten lead-in rods if an intermediate bead of nickel is used. Platinum wire is not suitable for a filament, since it is rapidly corroded during a run.

* The checker reports that satisfactory results may be obtained by passing electrolytic hydrogen through a "De-Oxo" cartridge and then through magnesium perchlorate.

† A heating mantle that entirely encloses the reaction kettle is unsatisfactory in that condensation of the refluxing tetrachloride takes place almost entirely in the condenser. As a result, when reduction is started, the solid trichloride tends to clog the condenser and some will be carried out of the apparatus by the hydrogen stream.

directed against the upper part of the flask to allow most of the tetrachloride to condense on the walls and top of the reaction flask.

When the boiling of the tetrachloride has reached a steady state, the filament is turned on and brought to a bright red heat. Reduction begins with the formation of a dark purple smoke of titanium trichloride which collects on the walls of the reaction vessel.* Most of these particles are washed down to the bottom by the refluxing tetrachloride.

If for any reason the vessel is cooled, for instance by turning off the filament, the hydrogen flow is momentarily increased to prevent influx of air as a result of the partial vacuum formed. This influx would cause hydrolysis and oxidation. A length of rubber tubing on outlet *J* minimizes this danger.

The reaction is continued until the tetrachloride no longer refluxes freely down the sides of the vessel. The filament is then turned off, and the whole reaction kettle is heated to drive off the residual tetrachloride, which tends to be absorbed in the cake of solid trichloride. To condense and remove the tetrachloride, a still head and horizontal condenser are substituted for the reflux condenser.

The hydrogen stream is continued while the apparatus cools. The flask is then opened in an inert atmosphere and the product bottled. The yield is 154 g. (10%) when 1000 ml. of titanium tetrachloride are used.† *Anal.* Calcd. for $TiCl_3$: Ti, 31.0; Cl, 69.0. Found: Ti, 31.9; Cl, 67.6.‡

Titanium tribromide has been prepared in the same apparatus. As the tetrabromide is solid at room temperature, hot water or steam is used as a coolant for the condensers

* The rate of formation of titanium trichloride is largely determined by the size of the filament. This limitation could be circumvented if a sheet of tungsten in the shape of a cylinder were heated by induction.

† The checker reports a yield of 6% based on initial titanium tetrachloride used.

‡ The titanium tetrachloride used as a starting material was an unpurified commercial product. A method for purifying this reagent is now available.[2] The purity of the product could also be improved by sublimation.

(instead of the cold water used in the preparation of trichloride). The tetrabromide is poured hot into the distilling flask and allowed to solidify before flushing with hydrogen. The yield and purity of the product are very similar to those reported for the trichloride.

Properties

Titanium trichloride and titanium tribromide are both purple crystalline solids, the latter being a good deal darker with a reddish cast. They are both soluble in water and other polar solvents and neither can be recovered unchanged from these solutions. When heated, these two halides decompose before melting to the di- and tetrahalides. It has been reported that dichloride of high purity can be produced by this method.[3]

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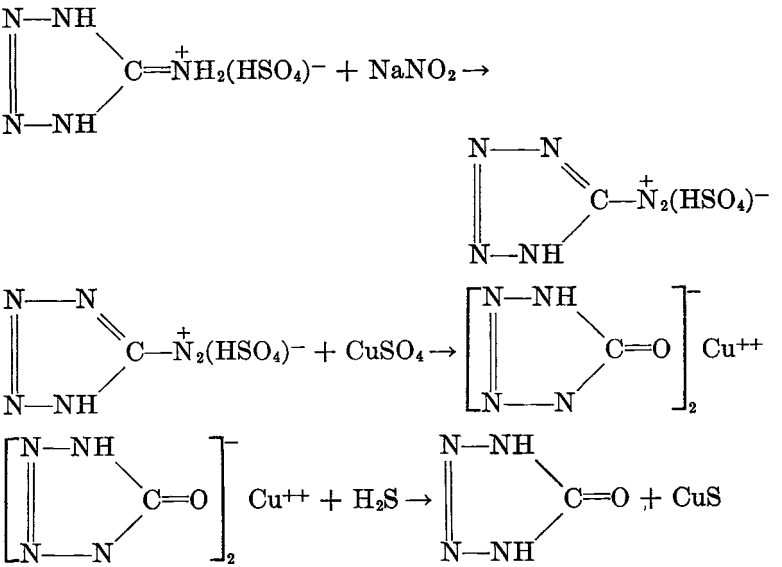
CHAPTER VA

18. TETRAZOLONE

(5-Hydroxytetrazole; Cyclic Azourea)



SUBMITTED BY EUGENE LIEBER* AND TASKASHI ENKOJI*
CHECKED BY RAYMOND C. BURROWS†

Tetrazolone (generally recorded in the literature as 5-hydroxytetrazole) has been prepared by the potassium

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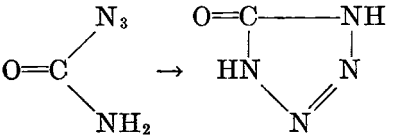
hydroxide fusion of tetrazole-5-sulfonic acid;[1]* by the acid hydrolysis of 5-methoxytetrazole;[3,4] by the basic hydrolysis of 5-iodotetrazole;[3,4] and by the diazotization of 5-aminotetrazole and subsequent replacement of the diazonium group by a hydroxyl group.[3] The last procedure, as modified by Hattori, Lieber, and Horwitz,[5] is the basis for the present procedure. While Wieland[6] has reported that carbamyl azide is easily cyclized to 5-hydroxytetrazole:

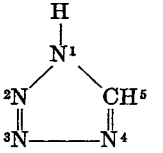


subsequent studies[5,7] have failed to verify this, the reaction leading only to the decomposition of the carbamyl azide. An improved method for the syntheses of 1-substituted 5(4*H*)-tetrazolones by the reaction of organic isocyanates with aluminum azide in anhydrous tetrahydrofuran has recently been reported.[9] The procedure described is at present the only practical method for making tetrazolone.

Procedure†

A mixture consisting of 10.3 g. (0.1 mol) of 5-aminotetrazole 1-hydrate‡ in 200 ml. of water, 10 ml. of concentrated sulfuric acid, and 100 g. of ice was cooled by stirring to below 5° by completely immersing the reaction

* The parent of this heterocyclic system has the ring index number[2] 52 and the following numbering for substituents:



† Melting points are uncorrected. Microanalyses are by Dr. G. Weiler and Dr. F. B. Strauss, Oxford, England.

‡ The commercial product as supplied by Fairmount Chemical Co., Inc., Newark, N.J., was used without further purification.

vessel in crushed ice.* A solution of 7.6 g. (0.11 mol) of sodium nitrite in 50 ml. of water, cooled to 5°, was added to the stirred solution at a fairly rapid rate. Very little, if any, temperature rise was observed. The reaction mixture was stirred at 5° for 30 minutes and a cooled solution of 37.0 g. (0.15 mol) of copper(II) sulfate 5-hydrate in 200 ml. of water was added. Stirring was continued for an additional 30 minutes and the reaction mixture was refrigerated overnight at 5°.

A small amount of precipitate which had separated was collected by filtration, dissolved in 10 ml. of concentrated hydrochloric acid, and added to the original filtrate. Hydrogen sulfide was bubbled through the solution for 10 minutes and the precipitated copper(II) sulfide was removed by filtration. The hydrogen sulfide treatment was twice repeated to remove any residual copper ions. The filtrate was heated on the steam bath and 81.0 g. (0.33 mol) of barium chloride 2-hydrate was added with rapid stirring. The precipitated barium sulfate was removed by filtration and the filtrate was evaporated to dryness on the steam bath with the aid of an air stream. The residue was further dried to yield 4.78 g. of product, melting point 250 to 251° (dec.).† Two more recrystallizations from water gave 3.25 g. (38%) of tetrazolone having a melting point of 257 to 258° (dec.).‡ Three subsequent recrystallizations from water did not raise the melting point. The following analysis was obtained for this final purifica-

* The solution of 5-tetrazole diazonium sulfate must not be allowed to spatter on the sides of the reaction vessel, since the dried material tends to detonate. This was avoided by stirring at a constant moderate speed of about 120 r.p.m., by completely surrounding the reaction vessel with crushed ice, and by washing down the sides of the flask after addition of the sodium nitrite to the sulfuric acid–5-aminotetrazole mixture and subsequently after 15 minutes of stirring. For safety, 5-tetrazol diazonium sulfate should always be handled in a hood with a safety shield.

† The literature[5] reports a value of 260° dec. (uncorrected).

‡ The following analysis was obtained for the product at this stage of the purification: *Anal.* Calcd. for CH_2ON_4: C, 13.95; H, 2.34; N, 65.10. Found: C, 14.33; H, 2.61; N, 65.20.

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tion: *Anal.* Calcd. for CH_2ON_4: C, 13.95; H, 2.34; N, 65.10. Found: C, 14.09; H, 2.25; N, 65.45.

Properties

A detailed study of the crystal morphology, optical properties, x-ray diffraction data, and fusion data has been reported[8] for tetrazolone.

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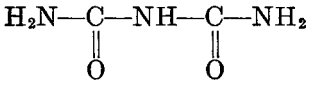
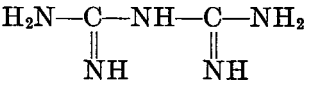
19. METAL BIGUANIDE COMPLEXES

Submitted by Priyadaranjan Rây*
Checked by W. Conard Fernelius†

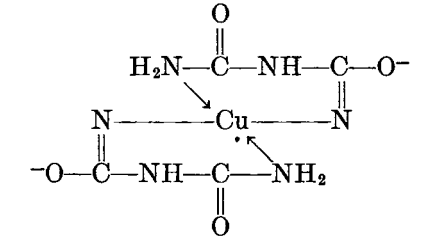
Chemically and structurally biguanide[1] is closely related to biuret, for it may be viewed as derived from the substitution of both the oxygen atoms of the biuret by imino (NH) groups.


Biuret

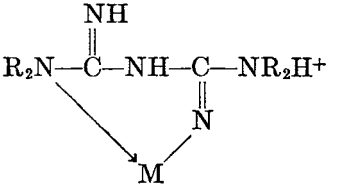

Biguanide

* University College of Science, Calcutta, India.
† The Pennsylvania State University, University Park, Pa.

In the familiar biuret reaction the copper ion[2] forms the center of a violet-red, anionic complex:



Similarly, biguanide and its substituted derivatives have been found to give rise to numerous complexes with many bivalent and trivalent metals of the transitional elements which are characterized by brilliant colors. Compounds of bivalent metals such as copper, nickel, and cobalt with biguanides, both as free bases and their salts, have long been known.[3–5] Besides the simple biguanide, many of its substituted products, such as methyl, ethyl, diethyl, and phenyl derivatives, may be employed. There was, however, a considerable difference of opinion regarding the constitution of these interesting compounds. A systematic investigation of the preparation and properties of these complexes containing not only the bivalent metals copper and nickel, but also those of cobalt(II), palladium(II), chromium(III), cobalt(III), silver(III), etc., has been made by Rây and coworkers.[6–27] These investigations have disclosed many interesting facts and led to many illuminating conclusions on the problem of valency and the structure of chemical compounds. Rây and Saha[6] suggested the following configuration:



($\frac{1}{2}M^{II}$ or $\frac{1}{3}M^{III}$)

R=H, alkyl, or aryl
M^{II}, M^{III}=central atom

The bivalent metals, as usual, combine with two molecules of biguanide to form 4-coordinated planar complexes, while the trivalent cobalt and chromium combine with three molecules of the ligand to produce a 6-coordinated octahedral configuration. The only exception is the trivalent silver which yields, however, a 4-coordinated planar complex. The preparation of the free tris(biguanidato)chromium, $Cr(C_2N_5H_6)_3$, in the anhydrous state,[6] as well as of the corresponding anhydrous cobalt(III),[8] copper(II), cobalt(II), palladium(II), and nickel(II) compounds, provides indisputable evidence for the structure proposed. Similar anhydrous metallic complexes with numerous substituted biguanides also have been included in the above-mentioned studies.

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20. CHROMIUM(III) BIGUANIDE COMPLEXES

SUBMITTED BY PRIYADARANJAN RÂY*
CHECKED BY W. CONARD FERNELIUS†

A. TRIS(BIGUANIDATO)CHROMIUM(III) 1-HYDRATE

$$2KCr(SO_4)_2 \cdot 12H_2O + 6C_2N_5H_7 \cdot H_2SO_4 \cdot 2H_2O + 18NaOH \rightarrow 2[Cr(C_2N_5H_6)_3] \cdot H_2O + K_2SO_4 + 9Na_2SO_4 + 52H_2O$$

The following procedure is that given by Rây and Saha.[1]

Procedure

Two solutions are prepared: (*a*) 5 g. (0.01 mol) of potassium chromium alum is dissolved in 20 ml. of water and (*b*) 21 g. of sodium hydroxide (0.50 mol) and 10 g. of biguanide sulfate 2-hydrate‡ is dissolved in 50 ml. of water. Solution *b* is heated to 75°, and solution *a* is added drop by drop with constant stirring. As each drop strikes the alkaline solution, there is a momentary formation of green chromium hydroxide which dissolves to form a dark red solution. As the reaction progresses, bright red, prismatic crystals separate from the solution. After all of solution *a* has been added, the mixture is cooled in ice water until no more solid separates. The crystals are filtered on a fritted-glass funnel§ and washed with 5 ml. of cold water.

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‡ Biguanide sulfate 2-hydrate may be obtained from the American Cyanamid Company, New York.
§ The strong alkali readily attacks ordinary filter paper.

For purification, the crystals are dissolved in 100 ml. of hot water containing 0.5 g. of sodium hydroxide and 1 g. of biguanide sulfate and recrystallized by cooling in ice water. The crystals are washed first with 3 ml. of ice water and then with 3 to 5 ml. of alcohol.* Finally, the crystals are dried, either in a desiccator or in air, but must be protected from carbon dioxide. The yield is 3.3 g. (0.009 mol.; 89% of chromium taken).

Properties[1]

Tris(biguanidato)chromium(III) 1-hydrate forms beautiful, crimson-red crystals which are mdoerately soluble in water to give a strongly alkaline solution. The substance liberates ammonia from ammonium salts, precipitates hydroxides of heavy metals from solutions of their salts, and behaves as a triacidic base in aqueous solution. It decomposes on prolonged boiling with mineral acids to form chromic salts. Strong boiling alkalies precipitate chromium hydroxide with evolution of ammonia. On keeping a cold, alkaline solution of tris(biguanidato)chromium hydroxide for some time, the red color of the solution gradually turns reddish violet, and rose-red, silky crystals of a hydrolyzed product are occasionally deposited from the solution. A similar change occurs with dilute aqueous solution of the base itself. When the solid hydrate is heated to 150 to 160°, it forms the anhydrous complex. The magnetic susceptibility of the substance is $\mu_B = 3.83$, almost identical with that for all simple and complex chromium compounds.

B. TRIS(BIGUANIDE)CHROMIUM(III) CHLORIDE

$$[Cr(C_2N_5H_6)_3]\cdot H_2O + 3HCl \rightarrow [Cr(C_2N_5H_7)_3]Cl_3 + H_2O$$

The preparation of this compound is described by Rây and Saha.[1]

* The greatest loss occurs at this point because of the solubility of the product. If any quantity of the material is to be made, it is preferable to recrystallize a second batch from the mother liquor of the first batch.

Procedure

Three grams of tris(biguanidato)chromium(III) 1-hydrate is triturated in a mortar with 3 *N* hydrochloric acid in the cold (10°) until the mixture gives a slight acid reaction (8 ml. of acid is required). The red 1-hydrate is converted completely into yellow crystals of the hydrochloride which are filtered and washed with 3 to 5 ml. of cold water. The crystals are purified by recrystallizing from 38 ml. of water, filtering, and washing, first with 3 ml. of ice-cold water and then with 5 ml. of alcohol. The mother liquor is treated with a saturated solution of ammonium chloride to complete precipitation, and the second crop of crystals is treated as the first. The total yield is 2.45 g. (0.0053 mol or 66%).

Properties[1]

Tris(biguanide)chromium(III) chloride forms yellow, octahedral crystals soluble in water. This solution on keeping for a long time slowly turns violet and deposits rose-red crystals of a hydrolysis product, but finally decomposition to chromium hydroxide takes place.

C. HYDROXOAQUOBIS(BIGUANIDE)CHROMIUM(III) SULFATE

$$[Cr(C_2N_5H_6)_3]\cdot H_2O + (NH_4)_2SO_4 + 2H_2O \rightarrow [Cr(C_2N_5H_7)_2OH(H_2O)]SO_4 + 2NH_3 + [C_2N_5H_8]OH$$

The following procedure is that of Rây and Saha.[2]

Procedure

Five grams (0.0135 mol) of tris(biguanido)chromium(III) 1-hydrate is dissolved in 200 ml. of water and treated with a solution of 5.7 g. (0.043 mol) of ammonium sulfate in 10 ml. of water. The sparingly soluble tris(biguanide)-chromium sulfate is precipitated with liberation of ammonia. The mixture is heated on the water bath, whereby

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the precipitate goes into solution and almost simultaneously is hydrolyzed to the sparingly soluble, red-violet hydroxyaquobis(biguanide)chromium sulfate. Heating is continued for 12 to 15 hours with frequent stirring. Then the mixture is cooled and the crystals filtered. They are washed first with 5 ml. of hot water and then with 5 ml. of alcohol and dried in air. The yield is 3.7 g. (0.0096 mol or 74%).

Properties[2]

Hydroxoaquobis(biguanide)chromium(III) sulfate forms violet crystals which are sparingly soluble in water and do not lose any water even when heated to 120°. On treatment with hot caustic solution the substance is converted into tris(biguanidato)chromium which separates as ruby-red crystals. The chloride of the hydroxoaquo compound may be prepared as rose-red crystals by treating the sulfate with the calculated amount of barium chloride.

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21. TRIS (1-PHENYLBIGUANIDE)COBALT(III) SALTS

SUBMITTED BY PRIYADARANJAN RÂY*
CHECKED BY W. CONARD FERNELIUS†

Phenylbiguanide, $C_6H_5NHC(NH)NHC(NH)NH_2$, combines with trivalent cobalt, as does biguanide itself, to form complex tris(phenylbiguanido)cobalt(III), its hydroxide, and tris(phenylbiguanide)cobalt salts.[1] All of these resem-

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ble in composition and properties the corresponding chromium complexes.[1] The tris(phenylbiguanide)cobalt(III) ion has been resolved through fractionation of its chloro-*d*-tartrate. The following preparations are those of Rây and Bhattacharya.[1]

A. TRIS(PHENYLBIGUANIDE)COBALT(III) HYDROXIDE

$$CoCl_2 + 2C_6H_5C_2N_5H_6\cdot HCl + 4NaOH \rightarrow [Co(C_6H_5C_2N_5H_6)_2](OH)_2 + 4NaCl + 2H_2O$$

$$4[Co(C_6H_5C_2N_5H_6)_2](OH)_2 + 4C_6H_5C_2N_5H_6\cdot HCl + 4NaOH + O_2 \rightarrow 4[Co(C_6H_5C_2N_5H_6)_3](OH)_3 + 4NaCl + 2H_2O$$

Procedure

A solution of 15 g. of phenylbiguanidinium chloride in 200 ml. of 10% sodium hydroxide solution is treated gradually with constant stirring with a solution of 5 g. of cobalt(II) chloride 6-hydrate in 10 ml. of water. Yellow bis(phenylbiguanide)cobalt(II) hydroxide is precipitated immediately. The volume of the mixture is made up to 250 ml. and a vigorous current of air is passed through the mixture. The solid is warmed on a water bath for $\frac{1}{2}$ hour. The red, pasty mass which results hardens on cooling. It is powdered in a mortar and washed with water until free of alkali. The filtered product is then digested with 150 ml. of absolute alcohol, whereupon a dark red solution is obtained with little or no residue. The solution is filtered, mixed with 75 ml. of water, and kept overnight in the cold. The shining red crystals which separate are filtered and washed with cold water. The yield is 6.3 g. When the mother liquor is concentrated to a volume of 100 ml. on the water bath and then kept in the cold, a further crop of crystals is obtained. The filtrate from the second crop on further evaporation to 50 ml. gives a third crop. The second and third crops are contaminated with carbonate and are not used for analysis. All the crops of crystals are dried in vacuum over calcium chloride and lime. The combined

yield is 11.2 g. (81% on the basis of the cobalt taken). *Anal.* Calcd. for $[Co(C_6H_5C_2N_5H_5)_3]\cdot 3H_2O$: N, 32.76; Co, 9.20. Found: N, 32.77, 32.98; Co, 9.25, 9.31.

Properties

Tris(phenylbiguanido)cobalt(III) hydroxide, $[Co(C_6H_5C_2N_5H_5)_3]\cdot 3H_2O$ or $[Co(C_6H_5C_2N_5H_6)_3](OH)_3$, forms rose-red crystals which melt with decomposition near 200° and are insoluble in water and alcohol. The compound absorbs carbon dioxide from the atmosphere and liberates ammonia from solutions of ammonium salts on boiling. Boiling water and alkali have no action upon the complex base, but concentrated acids decompose it. The anhydrous material may be obtained by heating the hydrate to 145 to 150° for 24 hours, but it readily absorbs water on exposure to air. The substance is preserved in an atmosphere free from carbon dioxide.

B. TRIS(PHENYLBIGUANIDE)COBALT(III) CHLORIDE

$$[Co(C_6H_5C_2N_5H_6)_3](OH)_3 + 3HCl + 2.5H_2O \rightarrow [Co(C_6H_5C_2N_5H_6)_3]Cl_3\cdot 2.5H_2O$$

Procedure

In a chilled mortar 5 g. of tris(phenylbiguanide)cobalt(III) hydroxide is triturated with cold (10°) 2 *N* hydrochloric acid, drop by drop, until the mixture becomes slightly acid (approximately 15 ml. is required). From the clear red solution which first forms, orange crystals gradually separate. Cooling is essential, because otherwise the chloride tends to separate as an oil. After further cooling of the solution the crystals are separated by filtration and washed with 3 ml. of ice water. The crystals are dried over calcium chloride, dissolved in 6 ml. of dry alcohol, and precipitated by the slow addition of 90 ml. of cold (10°) acetone with stirring. The purified product is filtered, washed with

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acetone, and dried over concentrated sulfuric acid. The yield is 1.87 g.

The mother liquor from the crude crystals is evaporated to dryness on the water bath and the residue extracted with 6 ml. of alcohol. The alcoholic extract in turn is evaporated to dryness and washed three times with 4 ml. of anhydrous ether. The additional yield thus obtained is 1.8 g., while the total yield is 3.67 g. (63%). *Anal.* Calcd. for $[Co(C_6H_5C_2N_5H_6)_3]Cl_3 \cdot 2.5H_2O$: N, 28.32; Cl, 14.36; Co, 7.96. Found: N, 28.13; Cl, 14.40; Co, 7.98.

Properties

Hydrated tris(phenylbiguanide)cobalt(III) chloride forms needle-shaped, red crystals which are soluble in water and alcohol but insoluble in ether and acetone. When heated to 110° for 15 hours, the hydrate loses the whole of its water to form the red anhydrous salt. The solution of the complex chloride gives colored precipitates with a number of complex anions such as hexacyanoferrate(II), hexacyanoferrate(III), nitroprusside, hexacyanocobaltate(III), and chloroplatinate.

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22. ETHYLENEBISBIGUANIDESILVER(III) COMPOUNDS

SUBMITTED BY PRIYADARANJAN RÂY*
CHECKED BY W. CONARD FERNELIUS† AND SAM N. HOLTER†

Ethylenebisbiguanide is an interesting coordinating ligand because it stabilizes the oxidation state of three in

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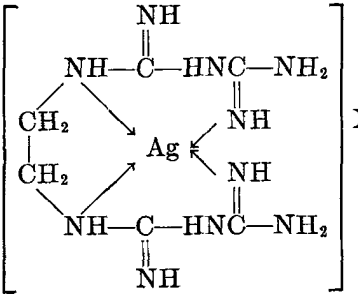
silver.[1] Although many instances are known in which silver(II) is stabilized by complex formation, only a few anionic complexes of silver(III) are known: diperiodatoargentate(III)[2] and ditelluratoargentate(III).[3] Ethylenebisbiguanide forms a series of compounds in which the quadricovalent central silver ion rather strikingly shows a positive valency of three:



X_3 or $[Ag\{en(big\ H)_2\}]X_3$ (where $X = \frac{1}{2}SO_4^-$, NO_3^-, ClO_4^-, or OH^-)

The following procedures for the preparation of ethylenebisbiguanidinium hydrogen sulfate and silver(III) complexes of ethylenebisbiguanide are taken from Rây and Chakravarty.[1,4]

A. ETHYLENEBISBIGUANIDINIUM HYDROGEN SULFATE

$$H_2NCH_2CH_2NH_2 + 2NCNHC(NH)NH_2 + CuSO_4 \cdot 5H_2O \rightarrow [Cu\{-CH_2NHC(NH)NHC(NH)NH_2\}_2]SO_4 + 5H_2O$$

$$[Cu\{-CH_2NHC(NH)NHC(NH)NH_2\}_2]SO_4 + 2H_2SO_4 + 1.5H_2O \rightarrow CuSO_4 + \{-CH_2NHC(NH)NHC(NH)NH_2\}_2 \cdot 2H_2SO_4 \cdot 5H_2O$$

Procedure

The following amounts of materials in finely divided condition are thoroughly mixed together: 10 g. (0.075 mol) of ethylenediamine dihydrochloride, 12.5 g. (0.1485 mol) of dicyanodiamide, and 3 g. (0.012 mol) of copper(II) sulfate 5-hydrate. The mixture is melted with continuous stirring at a temperature of 140 to 145° and maintained at this

temperature with continued stirring for 1 hour in order to obtain a perfectly homogeneous, blue-colored mass. The temperature must not rise above 145°, because at or above 150° decomposition takes place. After cooling, the mixture is treated with 200 ml. of water and 3 g. of ammonium sulfate. The blue mass disintegrates on standing to give a blue solution and a rose-red, insoluble, silky residue. The mixture is neutralized with ammonia and the residue filtered and washed with three 10-ml. portions of cold water. The yield is 3.9 g. (75% on copper used).

The copper salt is decomposed in the cold with 8 ml. of 1:1 (by volume) sulfuric acid by mixing in a mortar and then treated with 32 ml. of cold water. The resulting mixture is filtered from any residue and the filtrate kept in the cold (10°) overnight. Practically the whole of the ethylenebisbiguanide separates, particularly on stirring, in large, rectangular, prismatic crystals. For purification the crystals are moistened with 5.5 ml. of 3 *N* sulfuric acid and then dissolved in 350 ml. of water by boiling. The solution is filtered and kept in the cold (10°) overnight with occasional stirring. The crystals that separate are filtered and washed three times with 3 to 4 ml. of cold water (10°). The yield is 3.2 g.* (79% on the copper complex used). *Anal.* Calcd. for $(C_6H_{16}N_{10})\cdot 2H_2SO_4\cdot 5H_2O$: C, 15.96; H, 4.20; N, 31.04; $SO_4^=$, 42.57; H_2O, 6.0. Found: C, 16.10, 15.85; H, 4.70, 5.31; N, 30.40, 31.0; $SO_4^=$, 42.50, 42.50; H_2O, 5.90.

Properties

Ethylenebisbiguanidinium hydrogen sulfate is a white, crystalline material which is difficultly soluble in cold water but moderately soluble in hot water. Despite its sparing solubility, this compound requires a long time to crystallize

* If 4 g. of copper(II) sulfate is used, the yield increases to 4.5 to 5.0 g., but the product becomes somewhat impure; moreover, the larger quantity of copper(II) sulfate necessitates a longer time for fusion. With quantities larger than 4 g. of copper(II) sulfate fusion does not occur even at 150°.

out of the solution. It is perfectly stable in air and melts at 263.5°.

B. ETHYLENEBISBIGUANIDESILVER(III) SULFATE

$$6(-CH_2NHC(NH)NHC(NH)NH_3)_2(HSO_4)_2 + 3Ag_2SO_4 + 6K_2S_2O_8 \rightarrow 3[Ag\{-CH_2NHC(NH)NHC(NH)NH_2\}_2]_2(SO_4)_3 + 12KHSO_4 + 6H_2SO_4$$

Procedure

Three solutions are prepared: (*a*) 0.3 g. of silver sulfate in 50 ml. of water; (*b*) 1 g. of ethylenebisbiguanidinium hydrogen sulfate in 200 ml. of water and contained in a 600-ml. beaker; and (*c*) 1 g. of potassium peroxydisulfate in 20 ml. of water. Solution *a* is added to *b* and the resulting mixture cooled to 10°. Then *c* is added and the mixture kept in ice water (10° or less) for several hours with frequent stirring. After about 2 hours, beautiful red, silky crystals of the silver complex commence to separate. The mixture is kept in a refrigerator overnight and then filtered through a sintered-glass crucible. The crystals are washed with three 3-ml. portions of cold (10°) water and dried over calcium chloride. The yield is 0.65 g. (65%). *Anal.* Calcd. for $[Ag^{III}en(Big\ H)_2]_2(SO_4)_3 \cdot 7H_2O$: C, 13.31; H, 4.44; N, 25.88; Ag, 19.96; $SO_4^=$, 26.61; O(active), 2.95; H_2O, 11.65. Found: C, 13.60; H, 4.30; N, 26.30; Ag, 19.86; $SO_4^=$, 27.00; O(active), 2.94; H_2O (by loss at 80°), 10.40.

Properties

Ethylenebisbiguanidesilver(III) sulfate forms red, silky crystals which are sparingly soluble in water. In the solid state it can be heated to 30° without appreciable decomposition. A solution of the pure substance in water or dilute sulfuric acid can be heated on the water bath without any detectable change. In concentrated sulfuric acid it dissolves to form a red solution. The salt remains unchanged

at ordinary temperatures for a fairly long time but gives out an odor of ozone. It has a diamagnetic susceptibility of $X_g = -0.394 \times 10^{-6}$. A trivalent silver atom should possess an electronic configuration similar to that of bivalent nickel and palladium, and hence its complexes would be diamagnetic like those of nickel and palladium, if the coordination bonds be of planar, hybrid dsp^2 type. Trivalent silver thus resembles trivalent gold of the same periodic group in forming quadricoordinate, planar complexes.

C. ETHYLENEBISBIGUANIDESILVER(III) HYDROXIDE

$$[Ag\{-CH_2NHC(NH)NHC(NH)NH_2\}_2]_2(SO_4)_3 + 6NaOH \rightarrow 3Na_2SO_4 + 2[Ag\{-CH_2NHC(NH)NHC(NH)NH_2\}_2](OH)_3$$

Procedure

To 10 ml. of a cold 15% solution of sodium hydroxide is added 0.5 g. of ethylenebisbiguanidesilver(III) sulfate and the mixture is thoroughly stirred. The resulting solid is washed several times by decantation, first with 8-ml. portions of cold water to which has been added 2 drops of 15% sodium hydroxide through a sintered-glass funnel until free from sulfate and then three times with 3-ml. portions of cold water. The product is dried over calcium chloride and lime. The yield is quantitative. *Anal.* Calcd. for $[Ag^{III}(en\text{-}big\ H)_2](OH)_3 \cdot 3H_2O$: N, 31.75; Ag, 24.49. Found: N, 31.95; Ag, 24.45.

Properties

Ethylenebisbiguanidesilver(III) hydroxide forms violet-red microcrystals resembling permanganate in color. It is sparingly soluble in water, gives a strongly alkaline reaction to litmus, and decomposes on heating with water. It has a diamagnetic susceptibility of $X_g = -0.393 \times 10^{-6}$. From the complex base the corresponding nitrate and perchlorate can be prepared by treatment with 1 *N* nitric acid

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or 60% perchloric acid. The complex nitrate forms orange-red crystals which can be recrystallized from hot, dilute nitric acid.

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23. TRIMETAPHOSPHIMIC ACID

$$K_3(PO_2NH)_3 + 3HClO_4 \rightarrow H_3(PO_2NH)_3 + 3KClO_4$$

SUBMITTED BY MORRIS L. NIELSEN*
CHECKED BY OSCAR T. QUIMBY†

Procedure

To an ice-cold solution of 35.1 g. (0.1 mol) of tripotassium trimetaphosphimate in 95 ml. of water is added, slowly, 62 ml. of 72% perchloric acid so that the temperature does not exceed 25°. The potassium perchlorate is filtered off and washed with 15 ml. of 5% perchloric acid. The combined filtrates are transferred to a 200-ml. round-bottomed flask and evaporated at reduced pressure. A Dry Ice trap and potassium hydroxide pellets are used before the oil pump. The solution is stirred with a magnetic stirring bar and is heated in a water bath at not over 31°. When nearly but not quite dry, the solids are slurried in ethyl acetate–methanol (80/20 by volume) to remove any crystallized potassium perchlorate, transferred to a Büchner funnel and rinsed, using a total of 125 ml. of the above solvent, then

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quickly rinsed with 25 ml. of ethyl ether, and air-dried briefly to constant weight. The yield of the 2-hydrate is 25.1 g. (92%). *Anal.* Calcd. for $H_3(PO_2NH)_3 \cdot 2H_2O$: N, 15.39; P, 34.03. Found: N, 15.40; P, 33.89. It is advisable to store the product in a refrigerator to delay hydrolysis and decomposition.

The anhydrous acid is obtained if the evaporation is done above 33°. *Anal.* Calcd. for $H_3(PO_2NH)_3$: N, 17.73; P, 39.21. Found: N, 17.91; P, 38.30. If desired, the acid can be recrystallized as the 2-hydrate from a cold-water solution by adding ethanol to turbidity and enough hexane to maintain two layers.

Properties

Trimetaphosphimic acid, as the 2-hydrate, crystallizes as rectangular platelets which melt at 105 to 110° by a rapid determination. The solubility in water is approximately 111 g./100 g. of water at 35°, and 48 g./100 g. of water at 25°. The transition from 2-hydrate to anhydrous acid occurs at 33°. In the anhydrous form the acid crystallizes in characteristic rhombs which do not melt at 110° but decompose at higher temperatures. The crystals are not noticeably hygroscopic. Both forms are practically insoluble in alcohols, ethyl acetate, ether, or hexane. The x-ray diffraction patterns have been reported.[1]

Trimetaphosphimic acid is a strong acid with three replaceable hydrogens, giving a single deflection in the electrometric titration curve. By progressively neutralizing it with sodium hydroxide the corresponding monosodium, disodium, and trisodium salts may be prepared and isolated as crystalline solids.[1] With excess sodium hydroxide a compound corresponding to $Na_3(PO_2NH)_3 \cdot NaOH \cdot 7H_2O$ has been prepared.

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24. ANHYDROUS DEUTEROPHOSPHORIC ACID

$$P_2O_5 + 3D_2O \rightarrow 2D_3PO_4$$

SUBMITTED BY N. N. GREENWOOD* AND A. THOMPSON*
CHECKED BY HENRY F. HOLTZCLAW, JR.,† GORDON A. GALLUP,† AND JACK L. SWANSON†

Anhydrous deuterophosphoric acid can be prepared by condensing the stoichiometric amount of heavy water onto phosphorus(V) oxide in a vacuum line. The mixture is warmed to complete the reaction and fractionally crystallized to constant melting point. The method can also be used to prepare crystalline orthophosphoric acid, H_3PO_4, and when only small quantities are required, is preferable to methods involving the dehydration of aqueous solutions of the acid.[1]

Procedure

Pure phosphorus(V) oxide is prepared by vacuum sublimation in a Pyrex-glass apparatus (Fig. 9) which has previously been dried and degassed by flaming it under dynamic vacuum. About 15 g. of reagent-grade phosphorus(V) oxide is placed in limb *A* which is then sealed at point 1. The glass near 1 should be kept clean from oxide, for otherwise it will devitrify when fused. The oxide is sublimed into section *B* under dynamic vacuum after which the apparatus is sealed at points 2 and 3 and the oxide resublimed into limb *C* which is then sealed at point 4. The sublimations are best carried out by wrapping asbestos paper around the glass and winding this roughly with an electrical resistance heater (500 watt) controlled by a Variac transformer. The constructions 2 and 4 should be as wide as possible to prevent plugging; they can be kept free from

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sublimed oxide by heating them intermittently with a Bunsen flame.

The oxide is sublimed to one end of tube *C* and a sharp file mark made near the clear end, after which the tube is weighed accurately, broken open, and quickly sealed into

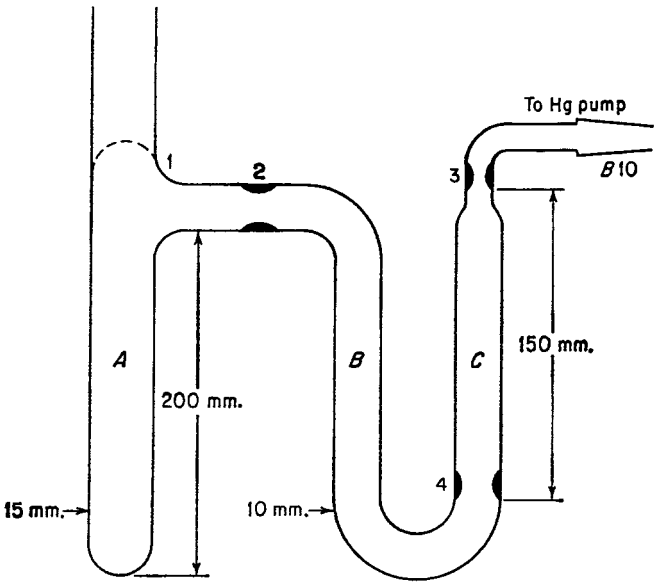

FIG. 9. Apparatus for the sublimation of phosphorus(V) oxide.

the open limb *D* of the apparatus shown in Fig. 10. The apparatus is evacuated and phosphorus(V) oxide quantitatively sublimed into limb *E*, care being taken to keep the oxide as much as possible in the lower section of the limb. The area around point 5 should be cleared of all traces of oxide by gentle heating with a Bunsen flame before tubes *C* and *D* are drawn off. The weight of oxide used is determined by reweighing the pieces of tube *C* and correcting for buoyancy (approximately 1.2 mg./ml. of internal volume of *C*).

The calculated amount of heavy water (4.2328 g./10 g. of P_2O_5) is weighed into tube *F* and transferred quantitatively

into *E*. A simple and accurate procedure which avoids buoyancy corrections is to weigh tube *F* when evacuated, let in dry air, pour in a slight excess of heavy water through a capillary funnel which passes through the barrel of the tap, reevacuate, reweigh, and then progressively adjust the weight by allowing heavy water to evaporate into the isolated section *G* of the vacuum line. When the correct

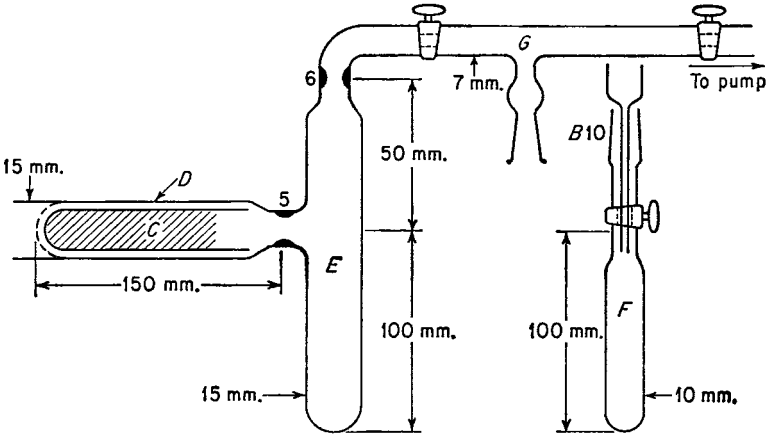

FIG. 10. Apparatus for the preparation of deuterophosphoric acid.

weight is obtained, tubes *E* and *F* are left in contact for a few hours (or overnight) to allow the first, highly exothermic absorption of heavy water to proceed spontaneously; the remaining water is quantitatively transferred into *E* by cooling it to −78° (solid CO_2/alcohol).

Tube *E* is drawn off at point 6 and immersed in a bath at 95 to 100° for 3 days to complete the hydrolysis. The product at this stage (m.p. 42.6°) has the stoichiometry D_3PO_4 but contains, besides deuterophosphoric acid, small equilibrium concentrations of polyphosphates such as D_3O^+-$D_3P_2O_7^-$.[2] These can be removed, if so desired, by sealing the compound into one limb of an evacuated U-tube and subjecting it to repeated, slow, fractional crystallization, the last fraction of liquid being decanted each time into the second limb before the bulk of the solid, except for a seed

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crystal, is remelted by warming at 48 to 50°. After several cycles the melting point reaches a maximum of 45.95°.

Properties

Pure deuterophosphoric acid is stable indefinitely as a solid but in the fused state always contains traces of pyro- and other polyphosphates which depress the freezing point of the compound. Its chemical properties are similar to those of phosphoric acid. The more important physical properties of the two compounds (supercooled) are compared in the following table.[3]

	m.p.	n_D^{20}	d_4^{25}	η_{25} poise	$10^2 \cdot \kappa_{25}$ ohm^{-1} cm.$^{-1}$
H_3PO_4	42.35°	1.4503	1.8634	1.775	4.68
D_3PO_4	45.95°	1.4430	1.9082	2.318	2.82

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25. PHOSPHORUS(III) CYANIDE

$$PCl_3 + 3AgCN \rightarrow P(CN)_3 + 3AgCl$$

Submitted by P. A. Staats* and H. W. Morgan*
Checked by Harvey M. Cohen†

A phosphorus cyanide compound was first reported in 1835 by Cenedella.[1] Hübner and Wehrhane expressed doubt that this compound was the tricyanide when they published their synthesis and purification of phosphorus-

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† Harvard University, Cambridge, Mass.

(III) cyanide in 1863.[2] A second article[3] by these authors discussed in some detail the chemical reactions of this substance. No further comment has appeared in the literature on the preparation or the properties of this compound until recently.[4] Synthesis was accomplished by mixing phosphorus(III) chloride and silver cyanide (in chloroform) and heating in a sealed tube for several hours at 120 to 140°. After cooling, the tube was opened and the chloroform and unreacted phosphorus(III) chloride removed by evaporation. The phosphorus(III) cyanide was then obtained from the residue by sublimation. The yield was reported to be about 85% by this method.

Procedure

The method described below is a modification of the above synthesis. Chloroform, carbon tetrachloride, and benzene have been found satisfactory as solvents. Twenty-five grams of dry silver cyanide and 25 ml. of solvent are placed in a 500-ml. round-bottomed flask* equipped with a side arm for admission of a dry, inert gas. A condenser is attached in reflux position and the system flushed to remove air. If standard taper glassware is used, it is not necessary to lubricate the joints. Thirteen grams of phosphorus(III) chloride, previously diluted with 25 ml. of solvent, is then added by momentarily removing the condenser, and the system is again flushed. A drying tube is mounted atop the condenser, and the contents of the flask are refluxed for a period of 18 to 20 hours. If the silver cyanide forms a cake when the refluxing is started, the flask should be cooled and the cake crushed to a fine powder. When reflux is finished, the remaining phosphorus(III) chloride and the solvent are evaporated, using the stream of dry gas or by vacuum distillation. To avoid sublimation of the phosphorus(III) cyanide as the flask goes to dryness, it is recommended that

* The checker has suggested the alternative use of a three-necked flask for the preparation.

the last traces of liquid be removed at room temperature using a vacuum pump and a cold trap.

The solid residue is transferred to a sublimation retort similar to that described by Kempf.[5,6] At this point the solid may exhibit blue-black specks from decomposition of the silver chloride formed during the synthesis (this may be prevented by covering the flask with a towel during the reflux period). The retort is evacuated to a pressure of less than 0.1 mm. and the phosphorus(III) cyanide sublimed into the neck. Sublimation proceeds rapidly at about 200°. At too rapid a rate, however, fine particles of silver chloride are carried into the neck, giving the product a grayish color. It may be necessary to renew the vacuum once or twice during the sublimation since there is a tendency for gas formation. The residue after sublimation will have a dark brown or black color, and the product will have a dirty white or pale yellow color. After cooling to room temperature the retort is opened in a dry box filled with an inert atmosphere and the crude product removed. When the retort is opened, there may be some evidence of smoke, depending on the dryness and the purity of the gas. The yield is 5.5 g. or approximately 81%. Further purification may be effected by a second sublimation.

Properties

Pure phosphorus(III) cyanide is a snow-white crystalline compound, having the form of needles and platelets. It reacts readily with water, or water vapor, to form hydrogen cyanide, phosphorous acid, and a yellow phosphorus compound. It can be kept indefinitely in a dry, airtight container. Reaction with water vapor during storage is shown by the development of a yellow tinge, due to the product mentioned above. Sublimation occurs in the range 160 to 180°. The melting point is close to 200°; however, prolonged heating above this temperature results in the formation of a reddish-brown solid. Purified crystals of phos-

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phorus(III) cyanide burn if heated in dry air. The compound is slightly soluble in chloroform, carbon disulfide, phosphorus(III) chloride, and ether.

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26. TRI-*n*-BUTYLPHOSPHINE

$$n\text{-}C_4H_9Br + Mg \xrightarrow{(C_2H_5)_2O} n\text{-}C_4H_9MgBr$$

$$3\ n\text{-}C_4H_9MgBr + PCl_3 \xrightarrow[NH_4Cl,H_2O]{(C_2H_5)_2O} (n\text{-}C_4H_9)_3P + 3MgBrCl$$

SUBMITTED BY GEORGE B. KAUFFMAN* AND LARRY A. TETER*
CHECKED BY E. O. BRIMM†

In contrast to the tertiary amines, trialkylphosphines have strong donor properties and form exceedingly stable coordination complexes with a wide variety of metal salts such as those of univalent copper and gold, and bivalent platinum, palladium, and mercury.[1] Like phosphine itself, many of these tertiary alkylphosphines are highly flammable, toxic, and extremely susceptible to air oxidation. Ease of oxidation first decreases and then increases as the alkyl group becomes larger.[2,3,4,5] The *n*-butyl compound is thus a convenient member of this group for preparation.

Tertiary alkylphosphines can be prepared by reaction of phosphonium iodide with alcohols[6] or by treatment of a

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† Tonawanda Laboratories, Linde Company, Tonawanda, N.Y.

phosphorus(III) halide with Grignard reagents.[2,3,4,5] The latter method is preferable and is used in this synthesis.

Procedure

A 1-l. three-necked round-bottomed flask is fitted with a Tru-bore paddle stirrer, a long water-cooled reflux condenser, a dropping funnel, and a gas inlet as shown in Fig. 11. The apparatus is dried by flaming with a Bunsen burner while being flushed with a stream of dry nitrogen.

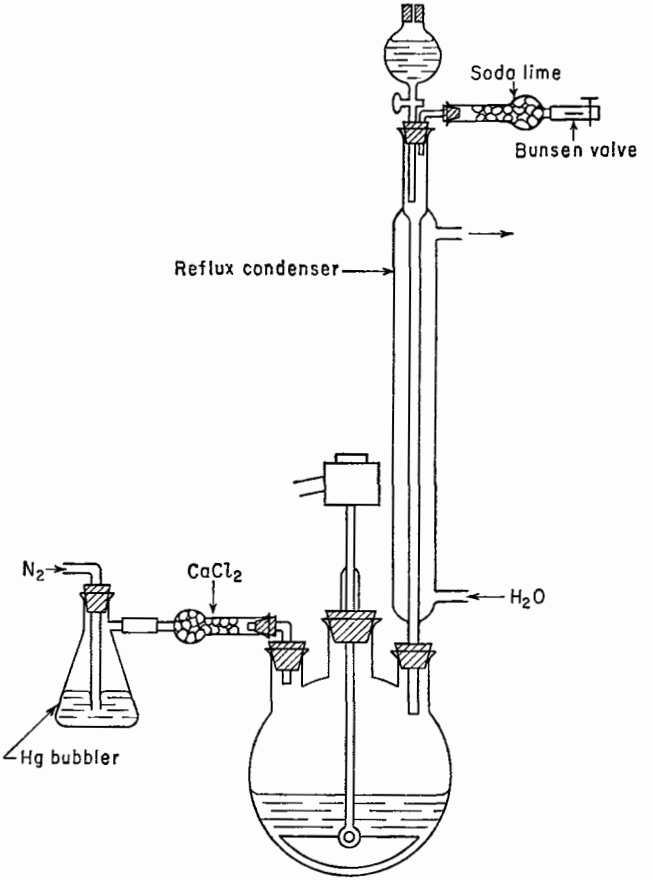

FIG. 11. Apparatus for the preparation of tri-*n*-butylphosphine.

This gas is passed through the apparatus throughout the course of the entire reaction.*

Ten grams (0.41 mol) of magnesium turnings and 150 ml. of anhydrous ethyl ether are placed in the flask, and through the funnel is added dropwise a solution of 42 ml. (53.8 g.; 0.39 mol) of *n*-butyl bromide (density, 1.28) in 100 ml. of anhydrous ethyl ether.† This dropwise addition takes place over a period of about 3 hours, during which time the mixture is continually stirred. The mixture is warmed until the reaction has started, and the rate of addition is adjusted so that the ether just refluxes.‡ The reaction mixture is light violet until the reaction is initiated, whereupon it becomes a turbid white and finally a dark gray.

The resulting solution of *n*-butylmagnesium bromide is cooled to 0° with an ice-salt bath, and a solution of 8.7 ml. (13.7 g.; 0.10 mol) of redistilled phosphorus(III) chloride (density, 1.57) in 50 ml. of anhydrous ethyl ether is added dropwise with stirring over a period of about an hour. The mixture is then refluxed by warming for ½ hour, cooled below 0° in an ice-salt bath (ca. ½ hour minimum) and treated with 250 ml. of an ice-cold aqueous solution containing 50 g. of ammonium chloride.§

After about ½ hour, when most of the precipitated magnesium salts have dissolved, the ether-water mixture is filtered through an 8½-in. funnel containing a large wad of glass wool into a 1-l. separatory funnel. The glass wool is washed with two 10-ml. portions of ethyl ether and the washings added to the mixture in the separatory funnel. The lower water layer is drawn off, and the remaining ethe-

* Care must be taken not to pass the gas too rapidly for excessive loss of ether may result. A slight positive pressure as indicated by the mercury bubbler is sufficient.

† The reaction, although exothermic, is difficult to start, but once started goes well. A granule of iodine dissolved in this solution appears to catalyze the reaction.

‡ Use of a long condenser permits more rapid addition.

§ This solution should be added very slowly (dropwise) at first since the reaction is quite vigorous.

real solution is dried by shaking with anhydrous sodium sulfate for about ½ hour and then filtered through glass wool. The ether is then distilled off in an atmosphere of dry carbon dioxide, and the solution is fractionally distilled under reduced pressure (50 mm.), the fraction boiling at 149 to 150° being collected. The yield is 11.5 g. or 14.2 ml. [57%, based on phosphorus(III) chloride].

Properties[2]

Tri-*n*-butylphosphine is a colorless, toxic liquid with a sickening odor which at high dilution smells like lilacs. It possesses a high boiling point (149.5° at 50 mm.) and low density (0.8118 at 25°). It is immiscible with water, but miscible in all proportions with alcohol, ether, and benzene. It combines with alkyl halides to form phosphonium halides. With carbon disulfide it yields a deep red crystalline addition compound, $(C_4H_9)_3P{\cdot}CS_2$. It also forms a characteristic addition product with alcoholic mercury(II) chloride. It is less readily oxidized than lower homologs and does not readily combine with atmospheric oxygen at room temperature. However, on boiling with access to air or on warming with 40% nitric acid it is converted to tri-*n*-butylphosphine oxide, $(n\text{-}C_4H_9)_3PO$ (b.p., 300° at 760 mm.).

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27. AN IMPROVED ALL-GLASS APPARATUS FOR THE PREPARATION OF PHOSPHONIUM IODIDE

$$10P_2I_4 + 13P_4 + 128H_2O \rightarrow 40PH_4I + 32H_3PO_4$$

SUBMITTED BY NICKY BEREDJICK*
CHECKED BY KIRBY SCHERER†

Phosphonium iodide was first prepared by Houton-Labillardière[1] by mixing phosphine and hydrogen iodide. Later, Baeyer[2] and Hoffmann[3] prepared it by hydrolysis of a mixture of diphosphorus tetraiodide and white phosphorus and used it as a source for pure, dry phosphine gas. It is also a useful reagent for hydrogenolysis of benzyl[5,6,7] and substituted[9] benzyl groups and other carbo alkyl or aryloxy groups.[8] It is particularly valuable because of the mild, nonhydrolyzing conditions under which it is effective.[5–9]

We have constructed an all-glass apparatus for the preparation of this compound (see Fig. 12). It embodies the features of Work's[10] apparatus and also has some modifications which make the preparation less hazardous and less cumbersome. Higher yields were also obtained.

Procedure

The mixture[10] of diphosphorus tetraiodide and white phosphorus is introduced into flask *A* of the apparatus, which has been previously swept with carbon dioxide. This flask is constructed so as to fit a Glas Col spherical heating mantle which enables even heating. The connections between flask *A* and the condenser and between the condenser and flask *B* are wrapped in electrical heating tape which is connected to a variable source of power.

* Technical Division, Visking Company, Chicago, Ill. The author is grateful to the National Science Foundation for financial support of this work.

† Harvard University, Cambridge, Mass.

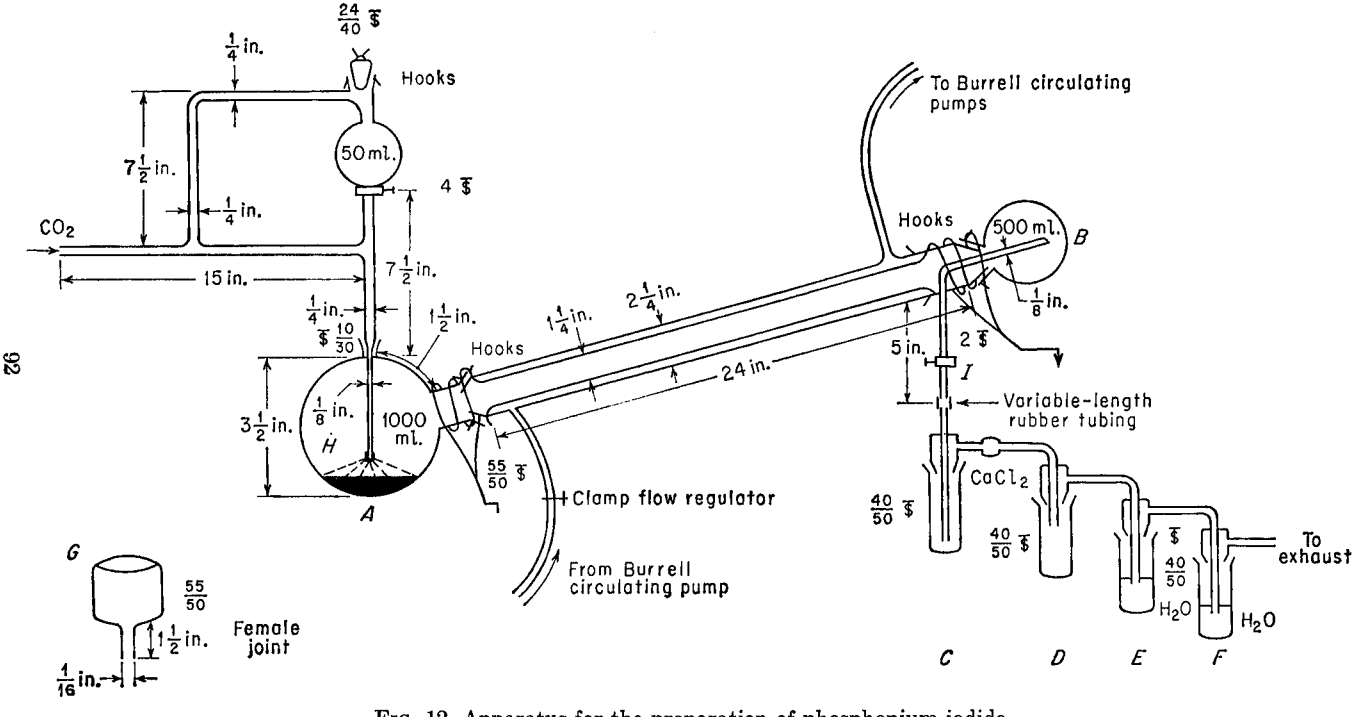

FIG. 12. Apparatus for the preparation of phosphonium iodide.

All glass joint connections are secured with rubber bands through the adjoining hooks. Cold water is circulated through the condenser. A slow stream of carbon dioxide is bubbled through the system, while flask *A* and the adjoining tape-wrapped glass joint are heated to about 10 to 20° above the temperature of the water circulating in the condenser. Jets of water are sprinkled periodically over the diphosphorus tetraiodide–white phosphorus mixture through *H* which is a gas dispersion tube (Fisher Scientific Company, Catalog No. 11-138). The phosphonium iodide sublimes into the cooled condenser as it is formed.

The dispersion of the water through a gas tube upon the whole surface of the diphosphorus tetraiodide–white phosphorus mixture appears to be more advantageous than dropwise addition, which may cause rapid local reaction while little reaction over the rest of the surface occurs. The overall even heating of the reaction flask *A* and connecting glass joint prevents any sublimation of the top part of *A* or plugging of the connecting joint, which may frequently occur in previously designed apparatus. After the addition of all the water the reaction flask *A* is heated to 100° for 1 to 2 hours to complete the sublimation of phosphonium iodide. It is then cooled to room temperature, rapidly removed, and replaced with adaptor *G* which is connected to the carbon dioxide supply. The flask *B* (500 ml. or less) is next lowered so as to become a receiver and the condenser is tilted upward, forming a new 30° angle. Flask *B* is cooled in Dry Ice. The condenser is connected to a Burrell vertical immersion agitating-circulating pump placed in a Pyrex (12 in. by 12 in.) glass jar in which water has been previously heated to about 95° by conventional constant-temperature bath heaters (nickel-chromium wire enclosed in copper sheathing).

Hot water is slowly circulated through the condenser and returned to the hot-water bath. The glass joint connection between flask *B* and the condenser is heated with the heating tape to about the same temperature as the circulating

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water. The phosphonium iodide resublimes into flask *B* in big white crystals. Yields as high as 72% were obtained (previously 50 to 60% yields were reported[10]).*

The variable-length rubber tubing enables easy manipulation when the apparatus has to be tilted. *C* and *D* are safety traps, whereas *E* and *F* are water traps for hydrogen iodide.

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28. TRIMERIC PHOSPHONITRILE CHLORIDE AND TETRAMERIC PHOSPHONITRILE CHLORIDE

$$3PCl_5 + 3NH_4Cl \rightarrow (PNCl_2)_3 + 12HCl$$
$$4PCl_5 + 4NH_4Cl \rightarrow (PNCl_2)_4 + 16HCl$$

Submitted by Morris L. Nielsen† and Garland Cranford‡
Checked by Oscar T. Quimby§

Trimeric and tetrameric phosphonitrile chlorides are among the products formed in the reaction of phosphorus-

* Substantial yields probably will result only after several trials with the apparatus.

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‡ Deceased.

§ Miami Valley Laboratories, The Procter & Gamble Company, Cincinnati, Ohio.

(V) chloride and ammonium chloride.[1–3] The use of an inert solvent to maintain a reaction temperature of 130 to 145° facilitates handling and improves the yield of distillable material.[4]

Procedure

This preparation is divided into three steps: (1) the reaction of phosphorus(V) chloride with ammonium chloride in an inert solvent, (2) the rapid distillation from the solvent and from the nondistillable, rubber-forming higher polymers, and (3) the fractionation of the trimeric and tetrameric compounds. The reaction apparatus consists of a 5-l. three-necked flask with standard-taper joints fitted with a thermometer and a motor-driven, heavy-duty stirrer, and heated by an electric mantle. For the preliminary removal of water from the solvent a Dean and Stark trap is used at a side joint in conjunction with a long water-jacketed condenser, the latter having a calcium chloride drying tube at its upper end.

The flask is filled half full with *s*-tetrachloroethane, and 300 g. of ammonium chloride is added. *Caution:* Use hood. As a typical chlorinated solvent, this is a toxic material. The mixture is heated to boiling while stirring so as to distill all water into the trap. When the volume of collected water shows no change in an hour's time, the mixture is cooled to about 60°, the trap and condenser are removed, and the condenser is dried and replaced on the flask. To the flask is added 900 g. of phosphorus(V) chloride and the mixture heated to reflux (128 to 143°) for 6 to 20 hours. It is cooled to about 40 to 60° and filtered on a Büchner funnel to remove solids (excess ammonium chloride), which can be rinsed with additional solvent and discarded.

The combined solutions are returned to a clean 5-l. flask fitted with a stirrer and suitable take-off adapter so that the solvent can be removed under reduced pressure (water aspirator). Distillation is made with the pot temperature

below 80°, and the residue is transferred while still warm to a 1-l. flask having a 24/40 standard-taper joint.

The rapid distillation is done at about 3 mm. pressure, using an oil pump protected by a Dry Ice trap and potassium hydroxide pellets. The take-off adapter is connected directly to a short air condenser (20 by 170 mm.) fitted with a male 24/40 joint. The receiver is a three-necked flask with one neck connected to a manometer and the other neck to a vacuum system in anticipation of plugging due to sublimation. The flask is cooled in an ice bath, and bumping is avoided by the use of wooden sticks in the distillation pot. It is advantageous to distill as rapidly as possible to attain maximum yield (280 to 360 g.) before the pot bottoms polymerize to a rubbery mass.

The trimer and tetramer are next separated by fractional distillation using a Vigreaux column 21 mm. o.d. by 12 in. long. The column is heated by a Nichrome-wound glass jacket to 100 to 125° for the trimer and to 180 to 190° for the tetramer. During this step the distillation head is kept warm with heating tape (E. H. Sargent and Co.) or by "flashing" with a soft gas flame so that no solids freeze on the walls. The receiver and accessory equipment are the same as described above except that it is desirable to use a manostat (Emil Greiner Co.) for maintaining a constant pressure. At 10 mm. the fraction distilling at 120 to 128° is essentially trimer (about 180 g. or 36% of theory). An intermediate fraction boiling at 128 to 180° is set aside (about 5 to 10 g.). The fraction at 180 to 187° is essentially tetramer (about 30 g. or 6% of theory).

Recrystallization of the trimer is accomplished by dissolving it in 350 ml. of warm ether per 100 g., stirring with decolorizing carbon, and filtering by gravity. After concentrating to half volume and chilling in an ice bath, about 85% of the crude solids are recovered as crystals (m.p. 113 to 115°; lit. 114°,[1] 114.9°[3]). The tetramer is recrystallized from benzene by using 100 ml. of benzene per 50 g. at 65°, stirring with decolorizing carbon, and filtering. By evapo-

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rating the benzene and chilling, two crops of crystals are obtained, representing 80% of the crude solids (m.p. 123.4 to 123.9°; lit. 123.5°[1]).

The x-ray powder diffraction patterns are available for comparison.[5] For the trimer, absence of a line at $d = 7.63$ A. can be interpreted as absence of the tetramer; for the tetramer, absence of a line at $d = 5.66$ A. shows absence of the trimer.

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29. TRIPOTASSIUM TRIMETAPHOSPHIMATE

$$(PNCl_2)_3 + 9CH_3COOK + 6H_2O \rightarrow K_3(PO_2NH)_3 + 6KCl + 9CH_3COOH$$

Submitted by Morris L. Nielsen* and T. J. Morrow*
Checked by Oscar T. Quimby†

Procedure

In a 1-l. flask fitted with a stirrer is placed a solution of 60 g. of trimeric phosphonitrile chloride in 240 ml. of dioxane and a solution of 300 g. of potassium acetate in 300 ml. of water. The temperature is held at 45 to 55°, cooling at first with a cold-water bath, later heating with a heating

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† Miami Valley Laboratories, The Procter & Gamble Company, Cincinnati, Ohio.

mantle or regulated water bath for 5 hours, while stirring the solution. The solids are filtered off, washed with methanol, and dried under vacuum, yielding about 100 g. of crude material. To remove potassium chloride by Soxhlet extraction with methanol it is necessary first to reprecipitate the solids in a very finely divided form. They are dissolved in about twice their weight of water* and poured quickly into 10 volumes of methanol with vigorous stirring to avoid formation of two liquid layers. The solids are filtered off and transferred to a Soxhlet extractor thimble. After about 15 hours extraction with methanol, a test of the solids probably will still show chloride.† Although continued extraction may remove the chlorides, it is advisable to dissolve the solids in water and reprecipitate again in methanol as described above. Additional extraction for 15 to 20 hours is sufficient to reduce the chloride content below 1%. The yield is 45 g. (74%). *Anal.* Calcd. for $K_3(PO_2NH)_3$: N, 11.96; P, 26.45; K, 33.39. Found: N, 11.71; P, 26.26; K (by flame), 31.3.‡ The crystals, as well as the silver salt prepared by reaction of the potassium salt with silver nitrate in dilute nitric acid solution, are useful for identification by x-ray diffraction.[1]

Reference

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* The approximate solubility of $K_3(PO_2NH)_3$ is 82 g./100 g. of water at 25°.

† Four tests have been useful: (1) release of hydrochloric acid by concentrated sulfuric acid, (2) precipitation of silver chloride, insoluble in dilute nitric acid, (3) heating the sample on copper wire, and (4) x-ray diffraction analysis for potassium chloride.

‡ The checker found that one methanol precipitation plus one methanol Soxhlet extraction for 16 hours reduced the potassium chloride content from 45 to 15%. Repetition of both steps reduced the potassium chloride to 1.4%. An additional methanol precipitation reduced the potassium chloride to 0.14%, but the yield was only 75% of that specified in the method given. *Anal.* Calcd. for $K_3(PO_2NH)_3$: N, 11.96; P, 26.45; K, 33.39. Found: N, 11.73; P, 26.0; K (tetraphenyl borate), 33.7.

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30. TRISODIUM TRIMETAPHOSPHIMATE 1-HYDRATE

$$(PNCl_2)_3 + 9CH_3COONa + 6H_2O \rightarrow Na_3(PO_2NH)_3 + 6NaCl + 9CH_3COOH$$

SUBMITTED BY MORRIS L. NIELSEN* AND T. J. MORROW*
CHECKED BY OSCAR T. QUIMBY†

The hydrolysis of trimeric phosphonitrile chloride dissolved in ether and shaken with aqueous sodium acetate solution was described by Stokes.[1] It is slow and uncertain, however, and the substitution of dioxane for ether, as practiced by de Fiequelmont in related preparations,[2] is preferred.

Procedure

The sodium salt is prepared in a manner similar to that for the potassium salt. A solution of 60 g. of trimeric phosphonitrile chloride in 240 ml. of dioxane is stirred with a solution of 300 g. of sodium acetate 3-hydrate in 480 ml. of water at 45 to 55°. After 3 hours, crystals amounting to 47 to 55 g. are recovered, and after an additional 16 hours a second crop can be recovered for a total of 59 g. (91%). The product is found to be free of sodium chloride by x-ray diffraction analysis. *Anal.* Calcd. for $Na_3(PO_2NH)_3 \cdot H_2O$: N, 11.22; P, 24.77; Na, 18.40. Found: N, 11.01; P, 24.99; Na, 18.2.

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† Miami Valley Laboratories, The Procter & Gamble Company, Cincinnati, Ohio.

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31. DISODIUM MONOAMIDOPHOSPHATE

(Disodium Phosphoramidate)

$$(C_6H_5O)_2PONH_2 + 2NaOH \rightarrow Na_2PO_3NH_2 + 2C_6H_5OH$$

SUBMITTED BY R. KLEMENT*
CHECKED BY OSCAR T. QUIMBY†

Disodium monoamidophosphate is formed when monoamidophosphoric acid diphenyl ester reacts with stoichiometric amounts of sodium hydroxide.[1]

Procedure

Twenty-five grams of monoamidophosphoric acid diphenyl ester is boiled for 10 minutes with 16 g. of sodium hydroxide dissolved in 60 ml. of water. Sometimes crystallization starts when the clear liquid is cooled down to 0°; however, it will start immediately when ice-cold ethanol is added. Two hundred milliliters is sufficient to precipitate the whole solution. The resulting disodium monoamidophosphate is already fairly pure. For recrystallizing or obtaining larger crystals, the salt is dissolved in a little water with two pellets of sodium hydroxide, filtered, and then ethanol is added at room temperature. A viscous liquid is formed first but after some stirring large crystals are formed. These are washed with alcohol and ether and dried under vacuum at 20° and 12 mm. The yield is approximately 20 g. of disodium monoamidophosphate 6-hydrate.‡

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‡ The method seldom gives a product of 100% purity because of the ease with which the amide group is converted to ammonia by hydrolysis. The checker reports the normal limits of amide nitrogen as a ratio relative to phosphorus to be 0.98 to 1.00.

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Properties

The crystals effloresce slowly when exposed to air and are decomposed by carbon dioxide. Consequently, they must be kept sealed off from air.* This compound is, moreover, very soluble in water.

Reference

1. R. KLEMENT and G. BIBERACHER: *Z. anorg. u. allgem. Chem.*, **283**, 246 (1956).

32. TETRASODIUM IMIDODIPHOSPHATE

$$2Na_2PO_3NH_2 \rightarrow Na_4P_2O_6(NH) + NH_3$$

SUBMITTED BY R. KLEMENT†
CHECKED BY OSCAR T. QUIMBY§

When anhydrous disodium monoamidophosphate is heated to 210° under vacuum, anhydrous tetrasodium imidodiphosphate is formed.[1]

Procedure

To get a good yield, the disodium monoamidophosphate has to be absolutely free from water. The freshly prepared, crystal, water-containing salt is kept at room temperature in a desiccator over sodium hydroxide or calcium chloride

* The crystals are unstable. This is shown by a faint ammonia odor above crystals stored in a closed container and by repeated analysis for amide (or ammonia) nitrogen. Therefore the checker advises that $Na_2PO_3NH_2$ be prepared only as needed from the diphenylester.

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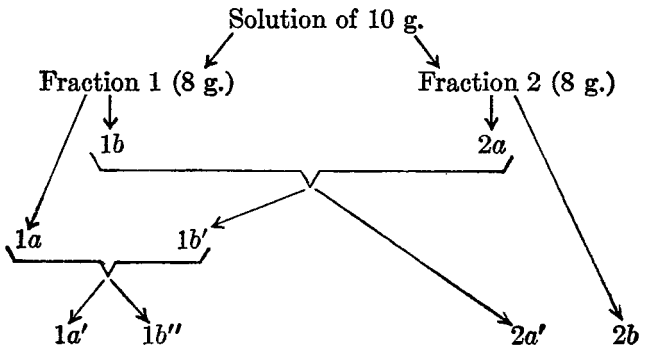
in vacuum for 2 days. Then the drying agent is replaced by phosphorus(V) oxide and the cover-rim of the desiccator is covered with a temperature-resistant grease, such as DC Silicone High Vacuum Grease. The air is pumped out and the desiccator is placed in an oven, heated to 70° over a period of 6 hours, and then allowed to stay there for another 3 days, replacing the phosphorus(V) oxide as necessary. If a tight desiccator is used, a completely dry product is obtained.

Then 10 to 15 g. of the anhydrous disodium monoamidophosphate is weighed in a 50-ml. flask with a glass joint. The flask is attached to a high-vacuum system, via a stopcock and a trap filled with solid sodium hydroxide, and evacuated. The flask is then heated in an oil bath to 80° and this temperature maintained for 6 hours. The temperature is then raised, and pressure builds up from the ammonia liberated. This gas is pumped off at intervals and the temperature increased to 210°. The formation of ammonia slows down after some time, and the reaction comes to an end after about 7 days.

In order to purify the crude product, tetrasodium imidodiphosphate, 10 g. of it is put in small portions into 100 ml. of ice-cold water with continuous stirring. Because of hydration the temperature of the solution goes up to 10 to 15°. The clear liquid is immediately precipitated in fractions by acetone. Schematically:



Then 1*a'* is discarded and the three fractions 1*b''*, 2*a'*, and 2*b*, which contain pure tetrasodium imidodiphosphate, are united. Finally, the crystals are washed with acetone and air-dried.*

Properties

Tetrasodium imidodiphosphate occurs as colorless crystals, easily soluble in water. It is isomorphous with $Na_4P_2O_7 \cdot 10H_2O$. The water solution has a pH of 11 (0.1 *M*). At the boiling point a cleavage into monoamidophosphate and monohydrogen phosphate occurs:

$$Na_4P_2O_6NH + H_2O \rightarrow Na_2PO_3NH_2 + Na_2HPO_4$$

In acidic solution mono phosphate is formed quantitatively. When heated under vacuum at 450° over a period of 7 days sodium nitridotriphosphate, $2N(PO_3Na_2)_3$, is formed.

Reference

1. R. KLEMENT and G. BIBERACHER: *Z. anorg. u. allgem. Chem.*, **283**, 246 (1956).

* The checker was able to recover 50% of the phosphorus taken as $Na_2PO_3NH_2 \cdot 6H_2O$. From qualitative neutral chromatograms the checker estimated the purity as falling between 70 and 85%; the major impurity was pyrophosphate, but 3 to 7% of the phosphorus was present as orthophosphate.

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33. PENTASODIUM DIIMIDOTRIPHOSPHATE 6-HYDRATE

$$Na_3P_3(NH)_3O_6 + H_3O^+ \rightarrow Na_3P_3(NH)_2O_7 + NH_4^+$$
$$Na_3P_3(NH)_2O_7 + 2NaOH + 5H_2O \rightarrow Na_5P_3(NH)_2O_8 \cdot 6H_2O$$

SUBMITTED BY O. T. QUIMBY* AND A. NARATH†
CHECKED BY ROBERT L. GERTEIS‡

The ring of the trimetaphosphate ion is so easily opened in alkaline solutions[1] that in warm concentrated sodium hydroxide solutions (20 to 30%) the phosphorus can be precipitated quickly and almost quantitatively as the chain compound pentasodium triphosphate 6-hydrate. The ring of the triimidotrimetaphosphate ion (usually called trimetaphosphimate) does not open in concentrated alkali even at the boiling point.[2,3] However, if an oxygen bridge is substituted for one of the three trimetaphosphimate imides, the alkaline hydrolysis readily breaks the P-O-P link of the ring ion to produce the chain ion diimidotriphosphate.[2] The preparation of the latter compound from trimetaphosphimate therefore involves two hydrolyses. The first is a mild acid hydrolysis to introduce the P-O-P link, the second is a strongly alkaline hydrolysis to break it and open the ring.

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‡ University of Illinois, Urbana, Ill.

Procedure

A. PURIFICATION OF SODIUM TRIMETAPHOSPHIMATE*

One hundred twenty and one-half grams of crude $Na_3P_3(NH)_3O_6 \cdot 4H_2O$ is dissolved in 850 ml. of water at 70° and stirred for 5 minutes. Eight hundred fifty milliliters of glycerol at 70° is added and the mixture is stirred for 1 hour. The hot solution is then filtered quickly.† Ethanol is added rapidly to the filtrate until precipitation starts. At this point it is added dropwise until the ethanol-to-water volume ratio is about 3:7. The mixture is stirred for 20 to 30 minutes, and the 4-hydrate crystals are filtered off and washed once by resuspending the crystals in 1000 ml. of 50% ethanol and again filtering. The crystals are then dried in air of 40 to 50% relative humidity at 25°. The yield is 107.0 g. (90%).

B. MILD ACID HYDROLYSIS OF SODIUM TRIMETAPHOSPHIMATE‡

One hundred grams of purified $Na_3P_3(NH)_3O_6 \cdot 4H_2O$ is dissolved in 1 l. of water containing 20 ml. of glacial acetic

* Work in this laboratory[3] has shown that all samples of sodium trimetaphosphimate made from $(PNCl_2)_3$, which has been separated from $(PNCl_2)_4$ by distillation, are contaminated to the extent of 2 to 10% with a difficultly soluble impurity of unknown nature. It is probably derived from higher phosphonitrile chloride polymers $(PNCl_2)_x$ (where $x > 4$) formed during the distillation.[4] To reduce the amount of such difficultly soluble impurity in the final product, one should remove as much of this as possible before the trimetaphosphimate is hydrolyzed. The trimetaphosphimate as $Na_3P_3(NH)_3O_6 \cdot 4H_2O$ can be leached away from the impurity.

† If necessary the leaching step can be repeated on the residue to reduce the loss of trimetaphosphimate. However, sacrifice of 10 to 20% of the trimetaphosphimate is necessary in order to remove a fairly large part of the impurity.

‡ This step is arranged so as to produce as much diimidotrimetaphosphate as possible without forming more than minor amounts of imidotrimetaphosphate. The latter must be avoided in order to obtain diimidotriphosphate containing little imidotriphosphate in the alkaline hydrolysis which comes later. A large amount of the trimetaphosphimate is necessarily left unconverted, but, since this will not be attacked by the concentrated sodium hydroxide, its presence will merely decrease the yield without contaminating the product.

acid, and the solution is then heated for 16 hours at 60 ± 2°. After being cooled to room temperature, the intermediate is precipitated by adding 1 l. of ethanol (rapidly at first, dropwise after precipitation starts). Stirring is continued for 20 to 30 minutes after all the ethanol has been added. The crystals are then filtered off, resuspended in 500 ml. of 50% ethanol, and refiltered.*

C. STRONGLY BASIC HYDROLYSIS OF THE DIIMIDOTRIMETAPHOSPHATE

The moist crystals from the mild acid hydrolysis are dissolved in 1 l. of water, and 430 g. of reagent-grade sodium hydroxide pellets are added during a 30-minute period so as to prevent the temperature from exceeding 75°. The reaction is then carried out by holding the temperature at 70 to 75° for 3 hours. To start the precipitation of $Na_5P_3(NH)_2O_8 \cdot 6H_2O$ it is often necessary, after 1 to 2 hours at 70 to 75°, to cool the mixture (or a portion of it) to a temperature of 20 to 35° for a short time. Restoration of the mixture to 70 to 75° then ensures precipitation of the desired species. The precipitated crystals are recovered by hot filtration. If it has been necessary to let the sample cool, e.g., by standing overnight, it is reheated before filtering to avoid contamination of the precipitate by trimetaphosphimate. The precipitate is removed from the filter, mixed intimately with 400 ml. of 50% ethanol at room temperature, and refiltered. A second such washing is given with 400 ml. of 100% ethanol and the product is air-dried at 25° and 40 to 50% relative humidity. The crude pentasodium diimidotriphosphate is dissolved in 100 ml. of 0.1 *N* NaOH and

* The moist crystals so recovered are in the form of mixed crystals[2] of 1-hydrates of the sodium salts. That this intermediate contains considerable unconverted trimetaphosphimate, considerable diimidotrimetaphosphate, and a little imidotrimetaphosphate can be shown conveniently by alkaline paper chromatography[5,6] with the Biberacher solvent II. The degradation products from the mild acid hydrolysis are largely removed during the precipitation by ethanol. The orthophosphate in particular is less easily removed after the alkaline hydrolysis.

precipitated by adding 80 ml. of ethanol. The system usually separates into two liquid layers as the ethanol is being added, but continued stirring brings about formation of fine crystals within a few minutes after the ethanol addition is complete. Stirring is continued for 30 minutes after crystallization starts, the precipitate is removed by filtration, and it is then washed successively with 100 ml. of 50% ethanol, 100 ml. of 100% ethanol, and 100 ml. of diethyl ether. The yield is 37 to 51 g. (29–41%).* *Anal.* Calcd. for $Na_5P_3(NH)_2O_8 \cdot 6H_2O$: P, 19.60; N, 5.91; H_2O, 22.80. Found: P, 18.92; N, 5.68; H_2O, 23.93.†

Properties

Although no solubility measurements have been made, the experience in its preparation and purification shows that pentasodium diimidotriphosphate is considerably more soluble than ordinary pentasodium triphosphate. Both crystallize from water as the 6-hydrates, which have very similar x-ray diffraction patterns. Along with the 6-hydrate of pentasodium imidotriphosphate they form a solid solution. The crystals of $Na_5P_3(NH)_2O_8 \cdot 6H_2O$ are hygroscopic enough to gain weight upon exposure to relative humidities of 40 to 50%. The pH of a 1% solution of $Na_5P_3(NH)_2O_8$ is near 11. Its titration curve with acid shows a vague end point near 11 and sharp end points at pH 8.6 and 5, the last two corresponding to the monohydrogen and dihydrogen diimidotriphosphate ions, respectively.

The diimidotriphosphate ion is much less stable toward hydrolysis than ordinary triphosphate. At pH values of 3 to 9 and at 60°, the ratio of the quarter-life of diimidotri-

* The reasons for the wide variation in the yield have not been determined.

† The crystals tend to contain a little more than the theoretical 6 mols of water. The sample chromatographed as a single species in neutral chromatograms,[6] which shows that an undetectable amount of imidotriphosphate, the most likely impurity, is present.

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phosphate to that of triphosphate falls in the range 0.02 to 0.002. Even at room temperature and the pH of the pentasodium salt, the hydrolysis rate is considerable. For example, a 1% solution of $Na_5P_3(NH)_2O_8 \cdot 6H_2O$ stored at room temperature (25 to 30°) for 1 week already had 2% of its total phosphorus present as orthophosphate.

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34. PHOSPHORYL TRIAMIDE

$PO(NH_2)_3$

Submitted by R. Klement*
Checked by Morris L. Nielsen†

Phosphoryl triamide is formed when ammonia reacts with phosphoryl trichloride in chloroform under good cooling:[1]

$$POCl_3 + 6NH_3 \rightarrow PO(NH_2)_3 + 3NH_4Cl$$

Separation of the reaction products is accomplished by reaction of ammonium chloride with diethylamine to form ammonia and diethylammonium chloride, which is soluble in chloroform:

$$NH_4Cl + NH(C_2H_5)_2 \rightarrow NH_3 + (C_2H_5)_2NH_2Cl$$

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† Monsanto Chemical Co., Dayton, Ohio.

The remaining unchanged, chloroform-insoluble phosphoryl triamide is readily recrystallized from methanol.[2]

Procedure

A 2-l. three-necked flask is fitted with a glass joint-type mechanical stirrer, a dropping funnel which can be cooled, and a glass joint through which an insertion tube (for gases) leads and to which a drying tube filled with sodium hydroxide is attached. In this flask is placed 1500 ml. of freshly distilled chloroform dried over calcium chloride, which is then cooled down to −15° with a butanol–Dry Ice bath. The liquid is then saturated with ammonia by passing a fast stream of dry ammonia through the chloroform for 3 hours. The cooling mantle of the dropping funnel is next filled with an ice–sodium chloride mixture, and 100 ml. of freshly distilled phosphoryl trichloride dissolved in 60 g. (37 ml.) of chloroform is brought into the funnel itself.

While the mixture is stirred well, a steady stream of ammonia maintained, and the temperature held at −15°, the phosphoryl trichloride solution is allowed to drip into the ammonia-saturated chloroform over a period of 2 hours. The stream of ammonia is maintained for another hour. Then the cooling mixture is removed and the reaction mixture may remain overnight. The precipitate formed is sucked off rapidly by means of a Büchner funnel, washed with dry chloroform, and dried under vacuum. The yield is approximately 110 g.

The compound is next placed in a round-bottomed flask fitted with a reflux condenser, mixed with 225 ml. of dry chloroform, and 160 g. (230 ml.) of diethylamine, and the mixture kept at 60° for 9 hours. A higher temperature is to be avoided because of decomposition. Then 200 ml. of chloroform is added and the remaining oxyphosphorus triamide filtered off. It is washed with dry chloroform until the chloride reactions in the product and wash solution are

negative. The product is dried under vacuum, giving a yield of 34 g.

To recrystallize,* the crude product is heated with 150 ml. of anhydrous methanol on a water bath. The solution is filtered hot, and after cooling, the precipitated phosphoryl triamide is sucked off. The mother liquid is discarded as it always contains some chloride. The remaining, undissolved crude material is next treated in the same manner with another 200 ml. of anhydrous methanol. The mother liquid of this run is retained to recrystallize the rest of the crude product. The collected precipitates are dried under vacuum. Paper chromatography shows the product to be pure. The yield is 26 g.; 70% calculated for phosphoryl trichloride.

Properties

Phosphoryl triamide forms colorless crystals, probably monoclinic. It is readily soluble in methanol, very soluble in water, but unstable in this solution as it is transformed into orthophosphate via amidophosphates; it is insoluble in ethanol. When heated with sodium hydroxide diamidophosphate is formed.

When hydrogen chloride is passed into a suspension of phosphoryl triamide in ether at $-15°$ imidodiphosphoric acid tetramide, $(NH_2)_2P(O)—NH—P(O)(NH_2)_2$, is formed; at $+30°$ diimidotriphosphoric pentamide is formed. Both these compounds are formed simultaneously when phosphoryl triamide in toluene is heated to 120°. After some weeks in humid air phosphoryl triamide forms ammonium hydrogen monoamidophosphate. For storage the compound must be sealed off in a glass tube. With

* The checker has found that recrystallization is unnecessary if ammonium chloride is adequately removed. Two treatments with diethylamine in chloroform, carefully grinding up lumps between each, gave 29 g. of product free of ammonium chloride. *Anal.* Calcd. for $PO(NH_2)_3$: N, 44.21; P, 32.59. Found: N, 43.94; P, 32.74.

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phosphoryl trichloride a chlorine-containing intermediate is formed, which is changed into the amide-imide of the monophosphorous acid, $[H_2N—P(O)=NH]_n$, when treated with ammonia.*

References

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2. R. Klement and O. Koch: *Chem. Ber.*, **87**, 333 (1954).

35. THIOPHOSPHORYL TRIAMIDE

$PS(NH_2)_3$

Submitted by R. Klement†
Checked by Morris L. Nielsen‡

Thiophosphoryl triamide is prepared in a manner analogous to that of phosphoryl triamide, involving the reaction of ammonia with thiophosphoryl trichloride in chloroform while cooling:[1]

$$PSCl_3 + 6NH_3 \rightarrow PS(NH_2)_3 + 3NH_4Cl$$

The separation of the reaction products is accomplished by the use of ethylamine.

Procedure

In the reaction apparatus described in the previous synthesis, the solution of ammonia in chloroform is dropped into 60 g. of freshly distilled thiophosphoryl trichloride while stirring and carefully cooling to −15° for a period of

* The checker reports that the melting-point determination, run by inserting a capillary tube into a hot bath, gave a liquid at 170° which evolved a gas. X-ray diffraction data showed the absence of imidodiphosphoric acid tetramide, $(NH_2)_2P(O)—NH—P(O)(NH_2)_2$.

† The University, Munich, Germany.
‡ Monsanto Chemical Co., Dayton, Ohio.

2 hours. The reaction product (105 g.) is treated with 225 ml. of dry chloroform and 100 g. of diethylamine as given before. The yield of crude thiophosphoryl triamide is approximately 32 g. It, too, is recrystallized from methanol but as it is soluble in methanol to a greater extent than phosphoryl triamide, only 150 ml. instead of 200 ml. is required. The yield is 26 g., 66% of the theoretical.*

Properties

The crystals are colorless and rhombohedric. They are readily soluble in methanol and water, but insoluble in ethanol. When thiophosphoryl triamide is heated with sodium hydroxide, sodium diimidothiophosphate is formed:

$$PS(NH_2)_3 + NaOH \rightarrow NaPOS(NH)_2 + NH_3$$

When the compound is exposed to humid air over a period of some weeks, diammonium hydrogen monothiophosphate is formed:

$$PS(NH_2)_3 + 3H_2O \rightarrow (NH_4)_2HPO_3S + NH_3$$

Thiophosphoryl triamide must be stored in a sealed-off glass tube.†

Reference

1. R. Klement and O. Koch: *Chem. Ber.*, **87**, 333 (1954).

* The checker reports: *Anal.* Calcd. for $PS(NH_2)_3$: N, 37.82; P, 27.88; S, 28.86. Found: N, 37.92; P, 28.06; S, 29.18.

† The checker notes that the melting point of this compound is 118 to 119°.

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36. METHYLDIIODOARSINE

$$As_2O_3 + 6NaOH \rightarrow 2Na_3AsO_3 + 3H_2O$$
$$Na_3AsO_3 + CH_3I \rightarrow Na_2(CH_3AsO_3) + NaI$$
$$Na_2(CH_3AsO_3) + 2HCl + 2NaI + SO_2 \rightarrow CH_3AsI_2 + 2NaCl + Na_2SO_4 + H_2O$$

SUBMITTED BY I. T. MILLAR,* H. HEANEY,* D. M. HEINEKEY,* AND W. CONARD FERNELIUS†
CHECKED BY LUDWIG MAIER‡ AND E. G. ROCHOW‡

Methyldiiodoarsine has been prepared in a variety of ways: treatment of an alcoholic solution of methylarsenic oxide, CH_3AsO, with an excess of hydriodic acid,[1] passing methylarsine into an alcoholic solution of iodine,[2] the action of sulfur dioxide on methylarsenic tetraiodide,[3] the action of methyl iodide on arsenic,[4] and treatment of a solution of disodium methanearsonate and potassium iodide with hydrochloric acid and sulfur dioxide.[5] The following directions are essentially the last method combined with the preparation of the disodium methanearsonate *in situ*.[6,7] The use of an alcoholic medium greatly facilitates the reaction between sodium arsenite and methyl iodide.

Procedure

Caution. This preparation should be performed in a good hood. Contact of all solutions with the skin should be avoided not only because haloarsines have a vesicant action but also because many organoarsenicals can produce allergic contact eczema if contact is frequent.

To 300 ml. of water contained in a 3-l. Erlenmeyer flask fitted with a stirring motor is added 110 g. of arsenic(III)

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‡ Harvard University. Cambridge, Mass.

oxide (0.556 mol) and 194 g. of sodium hydroxide (4.849 mols). Stirring is begun, and when the mixture has cooled nearly to room temperature (by ice bath if desired), 1600 ml. of methylated spirit is added (two liquid layers are formed) and finally 227.5 g. (110 ml.) of methyl iodide (1.6 mols). Some evolution of heat accompanies the addition of methyl iodide so that further cooling in an ice bath is desirable. After stirring the mixture for about 20 hours the solution is evaporated to dryness under reduced pressure, taking care that the temperature does not rise above 50°. The residue is dissolved in 400 ml. of water, warming if necessary. While the solutions are stirred mechanically, concentrated hydrochloric acid is added from a dropping funnel to pH 3 (Universal paper) (ca. 135 ml.).* Stirring of the warm solution is continued and sulfur dioxide is then passed into the mixture for ca. 1½ hours while a solution of 210 g. of sodium iodide in 200 ml. of water is added from a dropping funnel. This addition should be complete before or at the end of the period of addition of sulfur dioxide. Then the warm mixture is filtered through a sintered-glass funnel and the solid washed twice with 100 ml. of water.† (If a heavy oily lower layer is not present before filtration, the solution is warmed to 50°.) The solid is pressed out and discarded. The lower liquid layer of methyldiiodoarsine is separated from the filtrate and allowed to crystallize spontaneously or by stirring quickly into a small quantity of ice water (m.p. 27 to 28°; yield 165 to 170 g.).

The crude product is purified by washing with a small quantity (2 × 50 ml.) of ice water and vacuum-dried for 2 hours. The yield is 150 g. (78%). The product forms clean yellow crystals (m.p. 29 to 30°). For further purifi-

* Higher acidity in the sulfur dioxide reduction leads to separation of a white solid which is not reducible to CH_3AsI_2. It is best separated by warming the mixture to 70° and filtering through a sintered-glass filter. Very high acidities lead to the precipitation of some arsenic(III) iodide.

† This solid is insoluble in ether and soluble in hot water. It melts above 350° and contains arsenic and iodine; however, the structure is unknown.

cation the product may be distilled under reduced pressure [b.p. 128° (16 mm.)].

Properties

Methyldiiodoarsine [m.p. 30°; b.p. 128° (16 mm.)] forms odorless yellow needles which melt to a red liquid and volatilize without decomposition at 200°. The compound is somewhat soluble in water and moderately soluble in alcohol, ether, and carbon disulfide; the solubility is increased by the presence of hydrogen iodide. Hydrogen chloride or bromide converts the diiodoarsine into the corresponding chloro or bromo compound, while iodine oxidizes the compound to methylarsenic oxide.[8] When boiled with dry sodium carbonate in the presence of benzene, methyldiiodoarsine forms the corresponding oxide.[5]

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37. DIMETHYLIODOARSINE

$$CH_3AsI_2 + 4NaOH \rightarrow Na_2(CH_3AsO_2) + 2NaI + 2H_2O$$
$$CH_3I + Na_2(CH_3AsO_2) \rightarrow Na(CH_3)_2AsO_2 + NaI$$
$$Na(CH_3)_2AsO_2 + HCl + NaI + SO_2 \rightarrow (CH_3)_2AsI + NaCl + NaHSO_4$$

SUBMITTED BY I. T. MILLAR,* H. HEANEY,* D. M. HEINEKEY,* AND W. CONARD FERNELIUS†
CHECKED BY LUDWIG MAIER‡ AND E. G. ROCHOW‡

Dimethyliodoarsine has been prepared by the distillation of cacodyl oxide with concentrated hydriodic acid,[1] by the interaction of cacodyl and methyl iodide,[2] and by distillation of the periodide, $(CH_3)_4AsI \cdot I_2$.[3] Dimethyliodoarsine, among other products, results from the interaction of methyl iodide and powdered arsenic[3] and may be obtained by the reaction between potassium iodide and dimethylchloroarsine.[4,5] When a solution of cacodylic acid, $(CH_3)_2AsO(OH)$, and potassium iodide is treated with hydrochloric acid and sulfur dioxide, dimethyliodoarsine settles out as an oil and may be recovered in 90% yield.[6,7] The following directions are taken from an improvement of the last method and do not require the isolation of the cacodylic acid.[6,8]

Procedure

Caution. This preparation should be performed in a good hood. Contact of all solutions with the skin should be avoided not only because haloarsines have a vesicant action but also because many organoarsenicals can produce allergic contact eczema if contact is frequent.

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† The Pennsylvania State University, University Park, Pa.
‡ Harvard University, Cambridge, Mass.

The methyldiiodoarsine obtained from the previous synthesis (150 g. or 0.436 mol) is dissolved in 800 ml. of methylated spirit. To this is added a solution of 208 g. of sodium hydroxide (5.199 mols) in 300 ml. of water, and after the mixture has attained room temperature (cooling in an ice bath, if desired) 185 g. (81.5 ml.) of methyl iodide (1.303 mols) is added. After standing with stirring for 16 hours,* the mixture is evaporated nearly to dryness under reduced pressure with slight heating if necessary. The residue is dissolved in 300 ml. of water (clear solution) and concentrated hydrochloric acid added to pH 3 (Universal paper) (ca. 200 ml.). *Caution.* Excess acid is to be avoided. The mixture (not a clear solution) is saturated with sulfur dioxide (ca. 1 hour).† The crude dimethyliodoarsine separates as a dark red oil. This mixture is filtered through a sintered-glass funnel and the solid washed with ether (200 to 300 ml.). The filtrate and ether washings are combined, the ethereal layer separated, and washed twice. The ethereal solution is dried for 6 hours over 20 g. of anhydrous sodium sulfate. The solution is evaporated, the dry oil distilled under nitrogen, and the fraction boiling at 154 to 166° collected. On refractionation the material boiling between 154 to 157° is collected. The yield is 50 g. (50%).

Properties

Dimethyliodoarsine (m.p. ca. −35°; b.p. 154 to 160°) is a yellow oil of penetrating odor, soluble in organic solvents but insoluble in water. It is volatile with steam and inflames when heated in air with the liberation of iodine vapors. Dimethyliodoarsine is decomposed by both nitric and sulfuric acids with the separation of iodine.

* If the mixture tends to overheat during the early stages of this period, stirring is discontinued temporarily.

† Prolonged passage of SO_2 is deleterious since it leads to the precipitation of sulfur.

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CHAPTER VB

38. VANADIUM OXYTRICHLORIDE

[Vanadyl(V) Chloride]

$$V_2O_5 + 2AlCl_3 \rightarrow 2VOCl_3 + Al_2O_3$$

SUBMITTED BY ROLF B. JOHANNESEN*
CHECKED BY GUY H. DORITY† AND J. BROWN GOEHRING†

Vanadium oxytrichloride has usually been prepared by the chlorination of vanadium(III) oxide, either alone or mixed with a reducing agent such as carbon.[1] The method of preparation described below avoids the use of free chlorine and the potentially hazardous distillation from sodium, which are the most undesirable features of the classical method; further, it requires only a minimum amount of apparatus.

Preparation

A distilling apparatus is set up for distilling from a 200-ml. flask into a 200-ml. receiver. The equipment is all glass, assembled by means of ground joints which may be lubricated with glassy phosphoric acid. The receiver must be protected by a drying tube (calcium chloride is a suitable desiccant). After assembling the apparatus, 35 g. of vanadium(V) oxide (dried at 110°) and 50 g. of anhydrous aluminum chloride are weighed out, both in the form of fine

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

powders (the aluminum chloride must be completely anhydrous; it is recommended that a freshly opened bottle be used). Then the two powders are mixed thoroughly but rapidly, minimizing exposure to the atmosphere. The dry mixture is transferred to the distilling flask and then the distilling flask is heated, cautiously at first, but eventually to about 400°. Vanadium oxytrichloride begins to distill soon after heat is applied and continues to distill during the course of the heating. Heating is discontinued when no more vanadium oxytrichloride distills over, or when aluminum chloride begins to sublime into the condenser. The vanadium oxytrichloride is a yellow liquid which may be clear or slightly cloudy. It is redistilled once to remove most of the accompanying aluminum chloride. The yield is about 39 g. (60%). This method of preparation does not produce any vanadium(IV) chloride; therefore the product need not be distilled from sodium. Spectrographic analysis shows that the vanadium oxytrichloride contains about 0.1% of aluminum. It is probable that this could be removed by an efficient fractional distillation, if its presence is undesirable.

Properties

Vanadium oxytrichloride is a lemon-yellow liquid with a boiling point of 127°[1,2] and a freezing point of −79.5°.[2] Vapor-pressure data are also given in reference 2. Its chemical properties are those to be expected of a covalent, anhydrous metallic halide. It is very readily hydrolyzed and should be protected from moisture at all times. If the liquid has been exposed even briefly to moisture, its color will be orange or red, and it will contain an orange-red precipitate.

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CHAPTER VIA

39. ANHYDROUS DEUTEROSULFURIC ACID

$$SO_3 + D_2O \rightarrow D_2SO_4$$

SUBMITTED BY N. N. GREENWOOD* AND A. THOMPSON*
CHECKED BY HENRY F. HOLTZCLAW, JR.,† ROBERT H. HARRIS,† AND LAWRENCE RAKESTRAW†

Deuterosulfuric acid can be prepared by condensing the stoichiometric amount of heavy water onto sulfur(VI) oxide in an apparatus similar to that described on page 83.

Procedure

About 10 g. of pure sulfur(VI) oxide is prepared in the apparatus shown in Fig. 13. Concentrated oleum is placed in flask *A* which is cooled, evacuated, and sealed at point 1. Tube *B* is cooled in liquid air until the required amount of sulfur(VI) oxide has distilled over; it is then sealed at point 2. Further purification of the trioxide by vacuum distillation is usually unnecessary. The procedure for reaction of the oxide with the required amount of heavy water (2.5018 g./10 g. SO_3) is similar to that described in the preparation of deuterophosphoric acid except that sulfur(VI) oxide, being more volatile than phosphorus(V) oxide, should be cooled to $-78°$ before being placed in the side arm of Fig. 14. An inert Fluorlube tap grease is recommended. Limb *E* is cooled and the apparatus evacuated slowly to prevent volatilization and entrainment of sulfur(VI) oxide in the vacuum line. When the oxide has been completely

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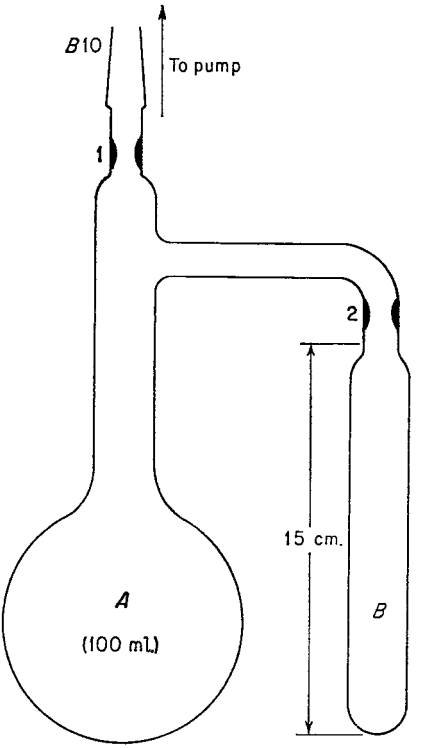

FIG. 13. Apparatus for the preparation of sulfur(VI) oxide.

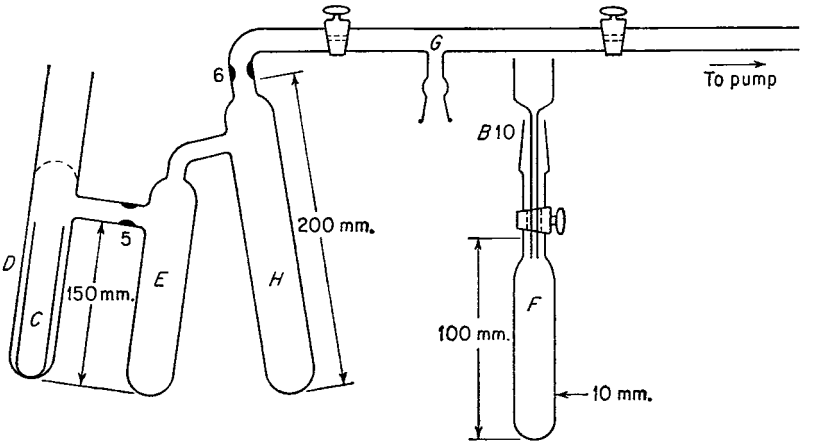

FIG. 14. Apparatus for the preparation of deuterosulfuric acid.

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transferred to *E*, the apparatus is sealed at 5 and the stoichiometric amount of heavy water is transferred into *H* as described in the deuterophosphoric acid preparation. Seal 6 is closed and the two reactants allowed to warm. With experience limb *E* can be omitted and both the sulfur(VI) oxide and heavy water distilled directly into *H*.

Deuterosulfuric acid prepared in this way melts at about 11°. It can be purified if necessary by fractional freezing to maximum melting point (14.10° after 5 cycles).

Properties

The physical properties of anhydrous sulfuric and deuterosulfuric acids are compared in the following table.[1,2]

	m.p.	d_4^{25}	η_{25} poise	$10 \cdot \kappa_{25}$ ohm^{-1} cm.$^{-1}$
H_2SO_4	10.36°	1.8266	0.246	1.044
D_2SO_4	14.35°	1.8572	0.249	0.257

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40. SULFUR NITRIDES

Submitted by Margot Becke-Goehring*
Checked by William L. Jolly,† Ulrich de la Camp,† James D. Macomber,† and H. Fritz Woeller†

The following procedures give the synthesis of tetrasulfur tetranitride, disulfur dinitride, polymeric sulfur nitride, and tetrasulfur dinitride.

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† University of California, Berkeley, Calif.

Procedure

A. TETRASULFUR TETRANITRIDE (S_4N_4)

For the preparation of this compound the reaction between ammonia and disulfur dichloride, S_2Cl_2, is employed. Besides tetrasulfur tetranitride, sulfimide, S_7NH, some sulfur, and ammonium chloride also are formed.

A 6-l. round-bottomed flask is used as the reaction vessel. This is fitted with a cork stopper, bored to carry a gas inlet tube, a reflux condenser, and an efficient mechanical stirrer. The inlet tube should penetrate as far as possible into the flask and is best fitted with a T-piece above the stopper, so that in case the end of the tube becomes blocked during the reaction a wire may be pushed through to free it. The other arm of the T is connected to an ammonia cylinder via a safety valve and a long potassium hydroxide drying tube, the latter being unnecessary when dry ammonia is used.

Four liters of carbon tetrachloride (dried over P_4O_{10}) and 250 ml. of freshly distilled disulfur dichloride are mixed in the flask and the solution saturated with chlorine at room temperature. The apparatus is connected to the ammonia supply and a fast stream of ammonia (about 50 l./hr.) is passed through the solution as rapidly as possible without causing solid and liquid material to belch from the top of the reflux condenser. The solution is briskly stirred, and if the stirrer is insufficient to cope with the thick mass which forms, a more dilute solution of disulfur dichloride in carbon tetrachloride may be used. To prevent the temperature from rising above 50°, it is necessary to cool the flask in ice water for the first couple of hours.

A thick, red-brown mass is rapidly formed, which slowly becomes gray-green. The color gradually brightens, however, until after 6 hours the product is salmon red. The time of appearance of this final color depends on the ammo-

nia flow rate and the efficiency of stirring. At this stage, the ammonia supply should be disconnected, since further passage of the gas causes sulfur nitride ammoniate to be formed.

The mixture is filtered, after which the solid material is wet with carbon tetrachloride. The damp material is slurried with 3 l. of water for about 15 minutes. When the precipitate is separated in a sintered funnel and dried on a porous plate or a watch glass, the product appears bright yellow. To remove sulfimide the dried residue is shaken with 750 ml. of ether in a 1-l. wide-necked reagent bottle. After 1 hour the residue is again isolated and washed further with ether. Then by the evaporation of the filtrate sulfimide may be obtained.

Tetrasulfur tetranitride is next dissolved out of the residue by treatment with dry dioxane, which has been dried with sodium followed by calcium hydride. Either a Soxhlet extractor or an extraction tube is used for this, the extraction being continued until the eluate is only weakly colored orange-yellow. The eluate is cooled and the solution is decanted from the crude tetrasulfur tetranitride, which has crystallized out, and evaporated in an evaporating dish at 50°.

The red-brown residue from this treatment is dissolved in hot benzene, and on cooling of this solution orange-red needles of tetrasulfur tetranitride crystallize out. The crude tetrasulfur tetranitride may also be put in an extraction thimble and extracted with benzene. When all the tetrasulfur tetranitride is extracted, the extraction pot is cooled to 0° and pure tetrasulfur tetranitride filtered off. Yields of 90 to 100 g. of material melting at 178° can be obtained in both ways. Further purification may be effected by sublimation in high vacuum with a bath temperature of about 100°.*

* *Note:* All operations should be carried out with caution, since tetrasulfur tetranitride is liable to decompose explosively on striking or at temperatures much above 100°.

B. DISULFUR DINITRIDE

(S_2N_2)

This compound is formed by thermal splitting of tetrasulfur tetranitride. The apparatus is shown diagrammatically in Fig. 15. The tube A is 320 mm. long and made of quartz. The diameter of the lower half is 11 mm., that of the upper part about double. C is a water-cooled "glass finger." The quartz tube is heated by the two ovens, H_1 and H_2; H_1 should produce a temperature of 80°, while H_2

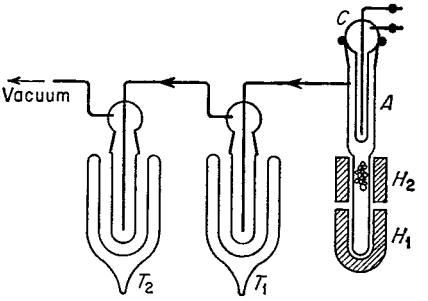

FIG. 15. Apparatus for the preparation of disulfur dinitride.

should heat the contents of the tube to 300°. This means that the inside of A should be heated to temperatures of 300 and 80°, respectively. Instead of the oven H_1, an oil bath may be used as well.

One to two grams of tetrasulfur tetranitride is placed in A, and a 7-cm.-long plug of finely pressed silver wool is pushed into that part of the tube which is to be heated by H_2. Silver-plated glass wool or copper wool may be used, but the yield will be much lower. The apparatus is then evacuated, trap T_1 (200 ml. content) is cooled with a methanol–carbon dioxide mixture to −80°, and trap T_2 is surrounded with liquid nitrogen. H_2 may then be heated, and when this has attained 300°, H_1 may be heated as well.

In a short while C becomes covered with a blue film and colorless to pale crystals are seen to form in the colder parts of the inlet tube of T_1 (size about 2 mm.). With a vacuum

of 0.005 atm. all the tetrasulfur tetranitride is decomposed after 6 to 8 hours. The ovens are then switched off, the coolants for T_1 and T_2 removed, and the apparatus aerated with dry air or nitrogen. Trap T_1 is found to contain a light grey, crystalline substance which in the higher warmer parts of the trap is tinged with red and has a blue edge. This product is extracted with ether until only a dark blue, metallic film remains on the walls of the trap. Initially, the ethereal solution is colored deep red from tetrasulfur dinitride which is simultaneously formed. It is filtered and transferred to a flask which has a ground-glass neck and a pointed bottom. This is fitted with a filter tube which extends to the base of the flask. The solution is cooled to $-80°$, whereupon white crystals of disulfur dinitride separate; these are filtered off. In this way 0.8 g. of disulfur dinitride is readily obtained from 1 g. of tetrasulfur tetranitride. Sublimation in high vacuum at room temperature effects further purification of disulfur dinitride, whereupon fine, large crystals may be obtained, which are quite colorless.

As with the preparation of tetrasulfur tetranitride, caution must be observed; tetrasulfur dinitride decomposes explosively at temperatures of ca. 30°, and on grinding with only slight pressure very violent detonations can occur. It should also be noted that at room temperature the substance undergoes appreciable polymerization in a short time.

C. POLYMERIC SULFUR NITRIDE

$[(SN)_x]$

For the transformation, disulfur dinitride is allowed to stand in a vacuum desiccator for ca. 30 days, after which time all the disulfur dinitride has polymerized to polymeric sulfur nitride. The progress of the reaction may easily be told by the disappearance of the characteristic smell of disulfur dinitride. The product is a dark substance with a metallic luster.

D. TETRASULFUR DINITRIDE

(S_4N_2)

This compound is prepared by the reaction of tetrasulfur tetranitride with sulfur. An autoclave, fitted with a magnetic stirrer and capable of being heated to 100°, is used as the reaction vessel. A mixture of 24 g. of tetrasulfur tetranitride and 50 g. of sulfur is suspended or, respectively, dissolved in 380 ml. of pure carbon disulfide. The mixture is heated in the autoclave for 2 hours at 110° and then cooled rapidly. It is then filtered from the polythiocyanogen which is formed under these conditions, and the residue washed well with carbon disulfide. These washings are added to the original filtrate, and this is then evaporated in vacuum. The red residue after removal of carbon disulfide is distilled in high vacuum with a bath temperature of 60 to 65°, whereupon dark red crystals separate in the receiver (f.p. 23°). It is found that the best yields are obtained when the walls of the autoclave are soiled from a previous preparation, in which case about 4 g. of tetrasulfur dinitride is usual.

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CHAPTER VIB

41. ANHYDROUS CHROMIUM(III) CHLORIDE

$$Cr_2O_3 \cdot xH_2O \rightarrow Cr_2O_3 + xH_2O$$
$$Cr_2O_3 + 3CCl_4 \rightarrow 2CrCl_3 + 3COCl_2$$

SUBMITTED BY A. VAVOULIS,* T. E. AUSTIN,* AND S. Y. TYREE, JR.*
CHECKED BY CHARLES W. HOPPESCH† AND R. J. TRIMBLE, JR.†

The earlier synthesis of chromium(III) chloride[1] has been used by graduate students at Chapel Hill for a decade with varying degrees of success. The alternate synthesis, herein described, has been found to be more reliable in the hands of graduate students. In particular the product has been used as the starting material in satisfactory syntheses of organochromium compounds.

Procedure

The apparatus is shown in Fig. 16. A heavy-wall Vicor glass tube 100 cm. long (i.d. 25 mm.) is used for the reaction tube. The exit tube *Q*, held in place with asbestos tape *P*, should have an inside diameter of 14 mm. or larger. A tube of smaller diameter will become plugged during the reaction and stop the flow of gases. The exit gases contain phosgene and chlorine. Between 4.5 and 6.0 g. (larger amounts than this will cause plugging of the reaction tube) of chromium-(III) hydroxide (J. T. Baker Chemical Co.) is placed in porcelain boats and the boats are placed in the reaction tube

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† Southern Illinois University, Carbondale, Ill.

so that they are approximately in the center of the hinge-type sleeve heating unit M (30 cm. long) when the reaction tube is in place. About 4 cm. of pyrex glass wool is introduced at L, just filling the space between the heating unit M and the rubber stopper K. Then 150 to 200 ml. of dry carbon tetrachloride is introduced into the 300-ml. flask G through tube H, after which H is closed off. With stopcock I closed and stopcock J in the proper position, tank nitrogen is admitted through alkaline pyrogallol (tower C), a safety trap (tower D), sulfuric acid (tower E), and phosphorus(V) oxide (tower F) into the reaction tube. Tank

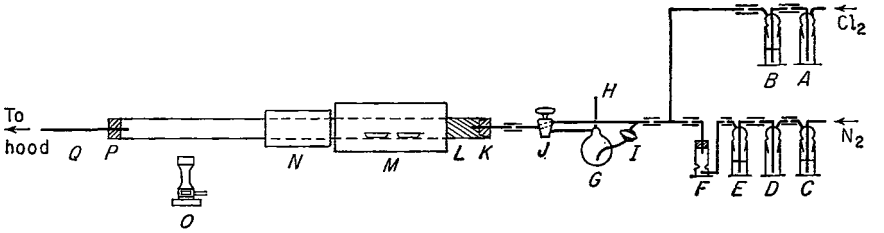

FIG. 16. Apparatus for the preparation of anhydrous chromium(III) chloride.

chlorine is admitted through a safety trap (tower A) and sulfuric acid (tower B) into the reaction tube also. The chlorine is allowed to pass slowly for ½ hour and the nitrogen for 1 hour in order to flush the system of air. After 1 hour (with the chlorine turned off), both M and sleeve heating unit N (15 cm. long) are turned on and the nitrogen is allowed to bubble through the carbon tetrachloride (stopcock I opened and stopcock J in the proper position) at a rate of 80 to 120 bubbles/min. M is allowed to reach 620 to 630° (higher temperatures cause decomposition of the carbon tetrachloride with a resulting carbon deposit in the desired product).* N is kept between 475 to 500°, which is not high enough to sublime the anhydrous chromium(III) chloride, but does sublime impurities away from the anhydrous chloride. These temperatures are measured by

* The checkers used a higher gas flow rate of 200 to 250 bubbles/min. (using 4-mm.-i.d. tubing) and found it necessary to raise the furnace temperature to 700° in order to complete the reaction in 5 hours.

means of thermocouples. The gas burner *O* is used to keep the part of the reaction tube past the furnaces warm enough so that volatile by-products will be vaporized and carried out at *Q*. When the heating units reach 110 to 115°, some water condenses in the reaction tube from the dehydration of the oxide. At about 300° solid chlorocarbons begin to deposit on the walls of the reaction tube. At about 450° a light brown coloration appears on the reaction tube wall past the heating units. Four hours after the heating units are turned on, *M* is opened to see if the porcelain boats are empty. If the boats are not empty, heating is continued. When the boats are empty, both heating units are turned off, stopcock *I* is closed, and stopcock *J* reversed. Chlorine gas is allowed to flow at a rate of 60 to 80 bubbles/min. and the nitrogen is almost stopped. Using the burner *O*, the part of the reaction tube past the heating units is flamed completely in order to remove volatile material that condensed on this portion of the reaction tube.

The chlorine gas is allowed to flow until the heating unit *M* has cooled to 300 to 350° at which time it is replaced by nitrogen gas. When the heating units and the reaction tube reach room temperature, the nitrogen flow is stopped. Most of the product is found between *N* and *M*. The reaction tube is removed, the porcelain boats drawn from the reaction tube, and the violet, crystalline solid pushed from the reaction tube by means of a glass plunger inserted from the end *P*. There is some difficulty in scraping the part of the product that has fused next to the wall of the reaction tube. Most of this can be loosened by the plunger and pushed out of the tube. The reaction tube is cleaned with a stiff brush and soapy water prior to reuse. If such a procedure does not suffice, it is washed with a 10% solution of hydrofluoric acid. The yield of anhydrous chromium(III) chloride, based on $Cr(OH)_3$, is 65 to 75%. *Anal.* Calcd. for $CrCl_3$: Cr, 32.84; Cl, 67.16. Found: Cr, 32.86; Cl, 67.19.

The properties of chromium(III) chloride have been

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described.[1] The substance prepared by the present method has been used successfully to obtain good yields of bisbenzenechromium.[2] (See next synthesis.)

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42. BISBENZENECHROMIUM(0) AND BISBENZENECHROMIUM(I) IODIDE

Submitted by E. O. Fischer*
Checked by Roy Pruett†

Sandwich compounds like ferrocene, $Fe(C_5H_5)_2$, are known in which either the benzene ring or its alkyl or aryl *derivatives may be bonded to different metals. Bisben*zenechromium(0), $Cr(C_6H_6)_2$, the first compound recognized as such a π complex, is obtainable through the yellow bisbenzenechromium(I) cation, which is formed according to the reaction:

$$3CrCl_3 + 2Al + AlCl_3 + 6C_6H_6 \rightarrow 3[Cr(C_6H_6)_2][AlCl_4]$$

This method utilizes aluminum as a reducing agent and aluminum chloride as both a reactant and a catalyst, and it is a very convenient reaction for the preparation of such aromatic, six-ring complexes. It is not necessary to conduct the reaction in a sealed tube if a trace of mesitylene is employed as a starting agent. The complex cation bisbenzenechromium(I) also is formed by the reaction of chromium(III) chloride with phenylmagnesium bromide at low temperatures.

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† Union Carbide Chemicals Co., South Charleston, W.Va.

The direct disproportionation of the bisbenzenechromium(I) ion to bisbenzenechromium(0) and higher oxidation levels of the uncomplexed metal ion is not complete in alkaline medium, and is also undesirable because some of the metal is lost for further complexing. The quantitative reduction of the cation with dithionite ion according to the reaction:

$$2[Cr(C_6H_6)_2]^+ + S_2O_4^= + 4OH^- \rightarrow 2Cr(C_6H_6)_2 + 2SO_3^= + 2H_2O$$

is preferable.*

Sparingly soluble salts of the complex cation, such as the iodide, the picrate, the reineckate, the perchlorate, and the tetraphenylborate, are prepared in pure form by air oxidation of bisbenzenechromium(0) in a mixture of benzene and water according to the reaction:

$$2Cr(C_6H_6)_2 + \tfrac{1}{2}O_2 + H_2O \rightarrow 2[Cr(C_6H_6)_2]OH$$

followed by precipitation out of the concentrated aqueous solution. Potassium iodide, for instance, precipitates yellow bisbenzenechromium(I) iodide, which is slightly sensitive to light.

A. BISBENZENECHROMIUM(0)

Seven-tenths gram (0.026 mol) of aluminum powder, 5 g. (0.031 mol) of powdered anhydrous chromium(III) chloride, 12 g. (0.09 mol) of sublimed and quickly ground aluminum chloride, and 25 ml. of dry and pure benzene are placed in a sealed tube of approximately 60 ml. volume. After cleaning the neck of the tube, a stopcock is attached to it by means of a short piece of rubber tubing. The tube is carefully evacuated, and benzene is allowed to boil off for some minutes at room temperature. Then the stopcock is closed and the tube is sealed *in vacuo*. The contents are

* The checker experienced difficulty with the dithionite reduction but obtained good results using metallic aluminum powder in aqueous alkali in the reduction step. It is suggested that a difference in purity of the reagent sodium dithionite, as obtained in the two countries, may account for the differing results.

thoroughly mixed, and the tube is inserted in a protecting pipe and heated for 6 hours at 140° while being rotated in a horizontal position at 50 r.p.m. After cooling, the tube is carefully opened and the yellow-green contents are poured onto a small, sintered-glass funnel equipped with a nitrogen inlet at the top and a stopcock at the bottom, air contact being avoided as much as possible by handling the solution in a countercurrent of dry nitrogen. The reaction mixture is filtered into a 100-ml. dropping funnel equipped with a side arm. To prevent the complex salt from crystallizing (which would plug the filter), the stopcock between the filter funnel and the dropping funnel is opened only for a short moment every time to suck off the liquid collected above it. The same applies to the stopcock at the side arm of the dropping funnel which is attached to the vacuum line. Cleaning of the sealed tube is accomplished by rinsing it twice with 10 ml. of dry benzene saturated with nitrogen. Next, the residue is washed three times with 10 ml. of dry benzene and kneaded thoroughly with a glass rod. Two layers are formed in the dropping funnel; the lower, orange-colored phase contains the chromium complex, while the upper phase consists of slightly yellow-colored benzene.* Meanwhile, in a three-necked 1-l. flask equipped with a sealed stirrer and stopcock outlets and filled with dry nitrogen there is prepared a solution of 40 g. of potassium hydroxide in 250 ml. of water, 100 ml. of methanol, and 450 ml. of benzene. To this is added 30 g. of sodium dithionite with stirring. Then the contents of the dropping funnel are added to this mixture (kept at 10° with running cold water), while vigorous stirring and passage of a slow stream of dry nitrogen through the flask are maintained. Afterward

* The checker's procedure involved use of 0.4 mol of chromium(III) chloride, 0.4 mol of aluminum bromide, 1.2 mol of aluminum powder, and a large excess of benzene as starting materials. These were caused to react as above and the total mixture then hydrolyzed and reduced with aluminum and 8.6 mols of sodium hydroxide in 1.5 l. of water, the temperature being held at 10° by use of an ice bath. Recovery of the product proceeded as above, and yields up to 70% were obtained.

the nitrogen tank is shut off and stirring continued for 2 hours at room temperature in the closed system. At the end of this time the benzene layer must appear dark brown while the aqueous layer has turned nearly colorless. The benzene layer is then sucked carefully into an evacuated separating funnel equipped with a side arm. The remaining mixture is again stirred for a few minutes with a small portion of benzene, which is then added to the bulk of the benzene solution. After drying with solid potassium hydroxide for a short time, the solution is transferred to a distillation apparatus. All operations with the dissolved bisbenzenechromium(0) must be carried out under dry nitrogen with exclusion of air. The solvent is distilled off on a steam bath in a stream of nitrogen, vacuum being applied at the end of the distillation. The black, solid residue can be scratched easily from the walls of the flask with a spatula. The yield is 6.2 to 6.4 g. (95 to 98% of theory calculated from $CrCl_3$). To remove organic impurities, the substance is extracted three times with 20 ml. of dry ether and sublimed in high vacuum at 160°.

The following method is convenient for the preparation of larger amounts of bisbenzenechromium(0): into a 250-ml. three-necked flask, equipped with a stopper in the ground-glass joint in the middle, and two stopcock standard-taper joints, is weighed 25 g. (0.16 mol) of ground, anhydrous chromium(III) chloride, 3.5 g. (0.13 mol) of aluminum powder, and 60 g. (0.45 mol) of sublimed and quickly ground aluminum chloride. After having evacuated and then filled the apparatus with dry, oxygen-free nitrogen, 100 ml. of benzene is added in a counter current of nitrogen. As a precaution the apparatus is evacuated again for some minutes until about 10 ml. of benzene has distilled off. Then 10 drops (0.3 ml.) of dry mesitylene is added, one of the stopcock outlets is exchanged for a reflux-condenser equipped with a mercury bubbler excess-pressure gage, and a close-fitting stirrer is inserted in the middle. Once the apparatus is closed, the stream of nitrogen is shut off after

having flushed the flask several times. All standard-taper joints which come in contact with hot benzene vapor should be tightly fitted, well greased, and clamped together with springs. The mixture is stirred vigorously and refluxed for 30 to 35 hours, periodic checking of the apparatus being made to ensure its remaining tight. In the meantime a 5-l. three-necked bottle with stopcock outlets and stirrer is filled with a solution of 220 g. of potassium hydroxide in 1300 ml. of water, 500 ml. of methanol, and 2 l. of benzene. After the flask is filled with nitrogen, 140 g. of sodium dithionite is added with stirring. The cool, yellow-green contents of the reaction flask are stirred under nitrogen into the prepared reducing solution contained in the 5-l. three-necked flask while cooling with running water. Then the solid material is transferred to the hydrolysis bottle with a spatula, air being excluded as much as possible. Next the mixture is stirred intensely for 2 hours at room temperature in the closed system. As before, the benzene solution is decanted, dried, and evaporated. The yield of the crude product is 31 g. (95% of the theory).* For purification the material is again washed with ether and sublimed in high vacuum.

B. BISBENZENECHROMIUM(I) IODIDE

Five grams (0.025 mol) of finely ground bisbenzenechromium(0) is shaken with 100 ml. of benzene and 50 ml. of water in a separating funnel, air being bubbled through the mixture until all the bisbenzenechromium(0) is dissolved and the benzene phase is only slightly yellow colored. The yellow-brown, aqueous layer is treated with an aqueous

* Very good reactions with yields of 95% and more are obtained only with very pure and absolutely dry chemicals. The aluminum chloride being used must necessarily be freshly sublimed; it must be ground and filled in as fast as possible. The benzene used must be free of other aromatic impurities. To avoid already hydrolyzed salt, the chromium(III) chloride is treated with boiling 2 *N* hydrochloric acid and washed with water, methanol, and ether. The aluminum powder is purified from organic impurities by washing it with benzene.

solution of potassium iodide with stirring until no further yellow precipitate separates. After cooling with ice the precipitate is filtered and washed with 5 ml. of ice water, 5 ml. of ethanol, and finally several times with ether. Then the precipitate is dried *in vacuo*. The yield is 5 g. (62% as calculated from $Cr(C_6H_6)_2$).

Properties

Bisbenzenechromium(0) is somewhat unstable in air. It sublimes at about 150° in high vacuum, melts under nitrogen at 284 to 285°, and decomposes at 300°. It is somewhat soluble in organic solvents such as benzene, sparingly in ether and petroleum ether, and insoluble in water. The dipole moment at 25° in benzene is 0 ± 0.37 D. Bisbenzenechromium(0) is diamagnetic, showing respective molar susceptibilities of $\chi_{mol}^{291°K} = -150.7 \times 10^{-6}$ cm.^{3}/mol and $\chi_{mol}^{90°K} = -154.8 \times 10^{-6}$ cm.^{3}/mol. It crystallizes in the cubic system and belongs to the space group $Pa3 - T_h^6$. Its heat of combustion at 20° is $H_c = 1723.7 \pm 1.4$ kcal./mol. According to this the heat of formation in the gas phase from benzene and chromium is $H_{298°K} = -58.3$ kcal./mol. Bisbenzenechromium(0) iodide forms a yellow paramagnetic salt, stable in air, but somewhat sensitive to light. It is soluble in water and alcohol with yellow color.

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43. CHLOROPENTAMMINECHROMIUM(III) CHLORIDE

(Purpureochromic Chloride)

$$4CrCl_2 + 18NH_3(aq.) + 2NH_4Cl + O_2 \rightarrow 2[(NH_3)_5Cr{-}\overset{H}{\underset{|}{O}}{-}Cr(NH_3)_5]Cl_5$$

$$[(NH_3)_5Cr{-}\overset{H}{\underset{|}{O}}{-}Cr(NH_3)_5]Cl_5 + HCl \rightarrow 2[Cr(NH_3)_5Cl]Cl_2 + H_2O$$

SUBMITTED BY G. SCHLESSINGER*
CHECKED BY RICHARD L. SOUTH† AND MARK M. CHAMBERLAIN†

Chloropentamminechromium(III) chloride serves as a convenient starting material for all syntheses in the pentammine and tetrammine series of trivalent chromium complexes. It was originally prepared by Jørgensen[1] by the air oxidation of chromium(II) chloride in the presence of ammonia and much ammonium chloride. Christensen[2] shortly afterward introduced a slight modification of this method by first reducing a chromium(VI) solution to the trivalent stage and then further to the chromium(II) salt with metallic zinc in the absence of air. The basic salt rhodochromic chloride,‡ initially formed by oxidation in both cases, was decomposed by hot hydrochloric acid to give the desired product. The salt may also be prepared from anhydrous chromium(III) chloride and liquid ammonia, yielding a mixture with the corresponding hexammine salt[3,4] which is separated by its greater solubility from the purpureo chloride. Other methods of preparation involve

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‡ This is more properly called μ-hydroxobis[pentamminechromium(III)] chloride.

boiling aquopentammine,[5] hexammine,[6] nitropentammine,[7] or nitratopentammine[8] chromium(III) salts with hydrochloric acid.

The method outlined below is essentially that of Christensen except that chromium(III) chloride is the starting material and amalgamated zinc is used in the reduction to the bivalent stage in order to give a smoother and more easily controllable reaction. Care should be taken to achieve as complete a reduction as possible, since the yield of product is dependent solely on this step in the synthesis.

Procedure

Fifteen grams of pure zinc is shaken for a short time with 100 ml. of 1 *N* hydrochloric acid to which a trace of copper sulfate has been added. When the metal surface has become thoroughly clean, 50 ml. of a saturated mercury(II) chloride solution is added and the mixture is shaken until the zinc is well covered with a deposit of mercury. The metal is quickly washed by decantation, 50 ml. of clean mercury is added, and the solution is covered with more dilute acid. After a few hours the zinc dissolves and the 2% (by weight) amalgam is ready for use. It may be preserved under 0.1 *N* hydrochloric acid in a loosely stoppered bottle.

Twenty-nine grams of green chromium(III) chloride 6-hydrate (0.11 mol) is dissolved in a warm mixture of 25 ml. of concentrated hydrochloric acid and 45 ml. of water. The filtered solution is poured into a 250-ml., round-type, long-stemmed dropping funnel containing 35 ml. of the zinc amalgam and equipped with a two-hole rubber stopper carrying an inlet and outlet for a source of carbon dioxide or nitrogen.* With a good gas current circulating through the reduction apparatus the funnel is swirled

* The inert atmosphere can be illuminating gas from a laboratory tap. It is as safe as nitrogen if the excess gas is led out to open air through an outside window.

continuously until the solution is a clear blue with no green tint (about ½ hour). When reduction appears to be complete, the gas flow is increased and the amalgam is drained rapidly into a suitable receptacle. Any drops of mercury adhering to the inside of the funnel stem are tapped out. Then, placing the end of the stem well under the surface of a cold mixture of 300 ml. of concentrated ammonia and 150 g. of ammonium chloride (2.18 mols) contained in a 500-ml. Erlenmeyer flask, the chromium(II) chloride solution is run in as quickly as possible while swirling well. It should be noted that while the draining of both the amalgam and the solution should be performed as rapidly as possible in order to keep reoxidation at a minimum, once the solution has been run under and mixed with the ammonia no further protection from atmospheric oxygen is necessary.

The well-mixed ammonia solution is next transferred to a 1-l. suction flask fitted with a stopper and glass tube reaching almost to the bottom of the flask, and a vigorous stream of air is sucked through the mixture for ¼ hour. *Caution.* Use hood. The red suspension of the rhodo chloride and ammonium chloride is slowly poured into 1 l. of ice-cooled, concentrated hydrochloric acid contained in a 2-l. Erlenmeyer flask. The mixture is heated for 10 to 20 minutes over a small flame or hot plate and then allowed to stand until the solid in the flask is well settled. The clear, supernatant liquid is carefully decanted until the residual volume of the suspension is about 500 ml. A similar volume of water is then added and the flask is well shaken to dissolve as much ammonium chloride as possible. The suspension is filtered with suction, preferably on a sintered-glass funnel of medium porosity, while the flask is swirled gently to separate the product from any residual ammonium chloride. The product is stirred up on the filter with two 50-ml. portions of 1:1 hydrochloric acid* to remove any ammonium salt, is sucked dry, and is washed with alcohol

* The wash must be cold and a third or fourth portion of acid may be necessary to remove all the ammonium chloride.

and ether or acetone. The bright red product is air-dried, and the yield is 20 to 24 g. (76 to 91%).

Ammonia is determined by the Kjeldahl method and chromium by the process of decomposing the complex salt with alkali, making the mixture acid to phenolphthalein, filtering, igniting, and weighing as chromium(III) oxide. *Anal.* Calcd. for $[Cr(NH_3)_5Cl]Cl_2$: Cr, 21.5; NH_3, 35.0. Found: Cr, 21.5; NH_3, 34.7.

Properties

The product consists of small, carmine-red crystals belonging to the orthorhombic system and appearing as well-developed octahedra under the microscope. Heating an aqueous solution of the compound produces aquopentamminechloride, while dilute sodium hydroxide precipitates hydrated chromium(III) oxide on prolonged boiling. Silver nitrate precipitates only two-thirds of the chlorine in the cold. The material is quite stable in artificial light, but prolonged exposure to sunlight causes decomposition.

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44. CHROMIUM(III) (*O,O'*-DIETHYL DITHIOPHOSPHATE)

[Tris(*O,O'*-diethyl dithiophosphato)chromium(III)]

$$P_2S_5 + 4C_2H_5OH \rightarrow 2(C_2H_5O)_2P(S)(SH) + H_2S$$
$$3(C_2H_5O)_2P(S)(SH) + CrCl_3 \cdot 6H_2O \rightarrow Cr[S_2P(OC_2H_5)_2]_3 + 3HCl + 6H_2O$$

SUBMITTED BY DAVID E. COLDBERY,* W. CONARD FERNELIUS,* AND MAURICE SHAMMA*
CHECKED BY F. P. DWYER,† J. W. HOGARTH,‡ AND I. K. REID†

Salts of the ester *O,O'*-diethyl dithiophosphate have been prepared by two different methods. One involves the reaction of $(C_2H_5O)_2P(S)Cl$ with potassium hydrogen sulfide.[1] The other is the reaction of phosphorus(V) sulfide with ethanol followed by the addition of metal halide.[1–3] The second method is the basis for this preparation, although the chromium(III) compound has not previously been reported. Salts of cobalt(III), nickel(II), and lead(II) can be prepared by analogous reactions using cobalt(III) fluoride, nickel(II) chloride 6-hydrate, and lead(I) oxide, respectively.

Procedure

Caution. The apparatus should be set up in a hood, since hydrogen sulfide and hydrogen chloride are liberated during the reactions. The preparation of *O,O'*-diethyl dithiophosphate is done in a nitrogen atmosphere because of the reactivity of the acid toward air and water.

In a 200-ml., 3-necked, round-bottomed flask equipped

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with a nitrogen inlet, a motor stirrer, and a Liebig condenser open to the atmosphere is placed 22.2 g. (0.1 mol) of phosphorus(V) sulfide. Nitrogen, bubbled through anhydrous ethanol to presaturate the gas, is admitted into the flask. Then, while the stirrer and nitrogen flow are going, 50 ml. (0.856 mol, excess) of absolute ethanol is poured into the flask through the condenser. The flask is heated on the steam bath. When the phosphorus(V) sulfide has dissolved (15 to 30 minutes), 22 g. (0.075 mol, excess) of chromium(III) chloride 6-hydrate is added, which immediately causes the yellowish solution to turn purple. After the solution is heated for 10 minutes, the nitrogen flow, the heating, and the stirring are stopped. The reaction mixture, which is almost completely solid upon cooling, is filtered; the solid is washed with 75 ml. of 30% ethanol (to remove excess $CrCl_3 \cdot 6H_2O$ and an oily product) and dried in air. The yield of crude product is 25.7 g. (66%). Purification of the product is effected by crystallization from 95% ethanol or by solution in 200 ml. of boiling acetone followed by filtration through a hot filter and addition of 50 to 60 ml. of hot water. The yield of purified product is 20.3 g. (52%, m.p. 160°). *Anal.* Calcd. for $Cr[S_2P(OC_2H_5)_2]_3$: C, 23.72; H, 4.98. Found: C, 23.49; H, 4.92.

Properties

Chromium(III) (*O,O'*-diethyl dithiophosphate) forms beautiful flakes which are purple by reflected light and dichroic by transmitted light; they are purple at one angle and green at another. The salt is soluble in organic solvents but insoluble in water. It is stable toward air and water, but decomposes at temperatures above its melting point.

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45. PREPARATION OF LABILE COMPOUNDS UNDER PROTECTIVE CONDITIONS. CHROMIUM(II) SALTS

SUBMITTED BY MAKSYMIKIAN KRANZ* AND ANNA WITKOWSKA*
CHECKED BY JOHN T. YOKE†

Chromium(II) salts are extremely sensitive and when affected by the least traces of air are oxidized to form chromium(III) salts. Because of these circumstances research and preparation of such compounds is very troublesome. The difficulties arise both in the investigation of the product's purity and absolute dryness during preparation, and in the removal of the final product from the protective conditions of the reaction field. The methods of obtaining chromium(II) salts employed at present are based on a rather complicated apparatus with indirect control. Thus preparation procedure has to be fixed a priori. Our method, described below, has been adapted particularly to prepare extremely sensitive compounds such as the chromium(II) salts. Using our apparatus the experimenter is able to intervene at any time and to handle the contents of the box in the same manner as he would on laboratory tables.

The box,[1] made of transparent Plexiglas, is entirely airtight and resistant to pressures in the range of 10 mm. to 2 atm.‡ The handling gloves provided ensure free experimental work. While pressure is reduced, the gloves are protected by metallic covers. The apparatus consists of: an inert gas source (steel flask of nitrogen), purifying, washing, and drying towers, a reaction box, a spring vacuum meter, and two vacuum pumps (oil pump of the Pfeiffer type 400 r.p.m. and a Bunsen water pump). The various segments

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‡ This pressure range is not necessary if the alternate procedure for obtaining an inert atmosphere is followed.

of the apparatus are joined by means of plastic hoses in order to avoid air diffusion. The main compound obtained in the above described manner is chromium(II) acetate by the reaction:

$$Cr^{3+} + H \rightarrow Cr^{++} + H^{+}$$
$$CrCl_2 + 2CH_3COONa \rightarrow (CH_3COO)_2Cr + 2NaCl$$

Procedure

The air is removed* (pressure about 10 mm.) from the box and is replaced by purified nitrogen. After having performed tests for the absence of traces of oxygen inside the box, 17.0 g. (0.26 mol) of zinc is placed in a 400-ml. beaker.† To this is added a solution of 10.0 g. (0.0376 mol) of chromium(III) chloride 6-hydrate‡ in 11.6 ml. of water.§ To the mixture so formed is added 23.0 ml. (0.27 mol) of concentrated hydrochloric acid. Then the beaker is covered with a watch glass. After about 15 minutes the zinc is largely dissolved and the solution is robin's egg blue in color. Next the watch glass is rinsed, the solution filtered quickly into a Büchner funnel suction flask, and the beaker and residue of zinc rinsed off with water. This done, the filtrate is poured into another 400-ml. beaker and the suction flask rinsed briefly. To the solution of chromium(II) chloride is added at once a slurry of 27.5 g. (0.336

* The checker suggests that any good dry box of the ordinary type may be used and that the air be displaced from the box by maintaining a high flow rate of prepurified nitrogen through the box for about 1 hour with occasional collapse of the gloves.

† The following specific procedure is that given by the checker.

‡ The actual sample of chromium(III) chloride used was the green material crystallized from concentrated hydrochloric acid on the steam bath, having the composition $CrCl_3 \cdot 4.27H_2O$. Thus 8.84 g. of this material is equivalent to 10.0 g. of $CrCl_3 \cdot 6H_2O$.

§ Water is prepared by taking distilled water, boiling it, and allowing it to cool in a stream of nitrogen. This water is used in the wash bottle inside the box as well as to prepare solutions of chromium(III) chloride, sodium acetate, and silver nitrate. The ether and ethanol used are distilled in a nitrogen atmosphere.

mol) of sodium acetate in 35.5 ml. of water. The mixture is then stirred with a glass rod for a few moments, whereupon the red chromium(II) acetate precipitates rapidly.

The mixture is suction filtered, the precipitate being collected on a tared, Pyrex-glass filtering crucible of medium porosity. The product is next washed several times with small portions of water until the washings are free of chloride ion, as tested with silver nitrate solution. Finally, it is washed with a little ethanol followed by a little ether. The crucible containing the product is placed in a vacuum desiccator over concentrated sulfuric acid and dried for 1 day with occasional addition of nitrogen to the desiccator, followed by reevacuation. The yield of chromium(II) acetate is 6.1 g. (95% of theory).

The chromium(II) acetate thus obtained can be converted into other chromium(II) salts by observing the same conditions as those for the above synthesis. This general method finds wide application in the preparation and handling of compounds which are easily oxidized, reduced, or hydrolyzed.

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46. MOLYBDENUM(VI) DIOXYACETYLACETONATE

[Bis(2,4-pentanedionato)dioxomolybdenum(VI)]

$$MoO_3 + 2HC_5H_7O_2 \rightarrow MoO_2(C_5H_7O_2)_2 + H_2O$$

SUBMITTED BY W. CONARD FERNELIUS,* KAZUJI TERADA,† AND BURL E. BRYANT‡
CHECKED BY MARY L. MCGOWAN§ AND ROBERT WEST§

Molybdenum(VI) dioxyacetylacetonate (molybdenyl acetylacetonate) was first prepared by Gach[1] by the action of acetylacetone upon molybdenum(VI) oxide at room temperature. Since he also isolated a small quantity of the same compound by the reaction between molybdenum(II) hydroxide and acetylacetone, he believed the compound to be $Mo(C_5H_7O_2)_2$. Rosenheim and Bertheim[2] later prepared the compound by refluxing an ethanolic solution of acetylacetone with molybdic acid. They correctly identified the product as molybdenyl acetylacetonate. Morgan and Castell[3] later duplicated the preparation of Rosenheim and Bertheim and verified their formula.

Procedure

Ten grams of reagent grade molybdenum(VI) oxide¶ is refluxed for 18 hours with 50 ml. of acetylacetone. The resulting mixture, containing several grams of unreacted molybdenum(VI) oxide, is filtered rapidly and the warm solution poured into 150 ml. of ligroin with stirring.‖

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‡ The University of Utah, Salt Lake City, Utah.
§ The University of Wisconsin, Madison, Wis.

¶ Molybdic acid, H_2MoO_4, is not suitable for this synthesis; however, it may be converted to molybdenum(VI) oxide by gently heating (125°).

‖ The saturated solution mixes with the ligroin only slowly without stir-

The mixture is then chilled for 1 hour in an ice bath. The orange-yellow powder is filtered, washed several times with ligroin, and air-dried. The yield is 10 to 15 g. (44 to 66%). *Anal.* Calcd. for $MoO_2(C_5H_7O_2)_2$: Mo, 29.5; C, 36.8; H, 4.29. Found: Mo, 28.5; C, 37.23; H, 4.28. If required, the solid is dissolved in fresh, boiling acetylacetone and the precipitation repeated.

Properties

Molybdenyl acetylacetonate is an orange-yellow powder, melting with decomposition at about 185°. It dissolves in acetone to give a green solution from which the original material cannot be recovered. Addition of the orange-yellow powder to boiling benzene gives a green solution and a yellow-green powder of indefinite composition. Slow decomposition of the dry product takes place in the open air.

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ring, and may deposit large, impure crystals. If the mixture is stirred vigorously, the molybdenyl acetylacetonate is precipitated as an orange-yellow powder.

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47. TRIPOTASSIUM ENNEACHLORODITUNGSTATE(III) AND PENTAPOTASSIUM TETRADECACHLOROTRITUNGSTATE(III)

$$K_2CO_3 + H_2WO_4 \rightarrow K_2WO_4 + H_2O + CO_2$$

$$K_2WO_4 + (2 + x)HCl \rightarrow 2KCl + (WCl_x)^{(x-6)-} + 4H_2O + (x - 6)H^+$$

$$2(WCl_x)^{(x-6)-} + 3Sn \rightarrow (W_2Cl_9)^{3-} + 3Sn^{++} + (2x - 9)Cl^-$$

$$(W_2Cl_9)^{3-} + 3K^+ \rightarrow K_3W_2Cl_9$$

$$3(W_2Cl_9)^{3-} + Cl^- \rightleftharpoons 2(W_3Cl_{14})^{5-}$$

$$(W_3Cl_{14})^{5-} + 5K^+ \rightarrow K_5W_3Cl_{14}$$

SUBMITTED BY ROBERT A. LAUDISE* AND RALPH C. YOUNG*
CHECKED BY RONN N. MINNÉ†

A dilute solution of tungsten(VI), which may easily be reduced in a medium of concentrated hydrochloric acid by metallic tin, can be prepared by dissolving tungstic acid in a boiling aqueous solution of potassium carbonate. The resulting potassium tungstate is converted to a readily reducible mixture of complex chlorides by adding the solution to concentrated hydrochloric acid, through which hydrogen chloride gas is being continuously bubbled in order to prevent the precipitation of tungstic acid.

The reduction must be carried out under controlled conditions, and no undissolved solid materials should be present before the metallic tin is added, for otherwise undesired competing reactions will predominate. Tin is preferred as the reducing agent because its reaction with the acid is not too violent, its chloride is soluble in cold, concentrated hydrochloric acid and in ethyl alcohol, and it has a high enough reduction potential to effect the reduction. The reduction product is either $W_2Cl_9^{3-}$ or $W_3Cl_{14}^{5-}$.

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If, then, the solution is cooled, there will be a high enough concentration of potassium ion to cause the precipitation of tripotassium enneachloroditungstate(III). The procedure given below differs considerably from that recommended by O. Olsson,[1,2] who successfully prepared the potassium, ammonium, thallium(I), rubidium, and cesium salts. It has been found in this laboratory, however, that the conditions of reduction are of great influence in determining the ultimate yield and purity of the product. R. C. Young[3] prepared tripotassium enneabromoditungstate(III) by a method analogous to Olsson's. Since the chloride, $W_2Cl_9^{3-}$, and $W_3Cl_{14}^{5-}$ ions are involved in an equilibrium, it is possible to cause the precipitation of the more soluble pentapotassium tetradecachlorotritungstate(III) by adjusting the concentration of potassium chloride before the reduction.

Procedure

A. TRIPOTASSIUM ENNEACHLORODITUNGSTATE(III)

Five grams of anhydrous potassium carbonate is added to 15 ml. of distilled water in a 150-ml. beaker. The beaker is covered to prevent undue evaporation and the solution brought just to the boiling point. Six and six-tenths grams of tungsten(VI) oxide (WO_3), or 7.1 g. of tungstic acid (H_2WO_4), is added in 1-g. portions while the solution is maintained at the boiling point. Between additions the beaker is kept covered to prevent evaporation. After the addition of all the oxide or acid the suspension is digested at the boiling point until clear, or for at least 10 minutes. While the above solution is boiling, 165 ml. of concentrated hydrochloric acid is placed in a 250-ml. flask, and hydrogen chloride gas is bubbled through the acid at a moderate rate.* The flask of hydrochloric acid is placed in a beaker of cold tap water at a temperature of about 13°,

* A cylinder of compressed hydrogen chloride is useful, although a conventional hydrochloric acid–sulfuric acid generator will suffice.

and the potassium tungstate solution is added to the hydrochloric acid in 2-ml. portions from a pipet. After each addition the acid is stirred with the hydrogen chloride gas delivery tube to hasten solution. When all the potassium tungstate solution has been added, hydrogen chloride gas is bubbled through the acid solution until any remaining tungstic acid has dissolved. (A few small curds may be allowed to remain, as these will dissolve on standing.) This solution is then removed from the water bath and allowed to stand at room temperature for at least 1 hour, although overnight is preferable.

One hundred fifty grams of mossy tin is placed in a 1-l. Erlenmeyer flask, which is clamped in a water bath at 25°. This flask is provided with a loosely fitting, one-hole stopper. The solution of tungsten(VI) chlorides is filtered through a fritted-glass funnel or crucible as follows. The fritted-glass plate is washed with concentrated hydrochloric acid and the washings from the filter flask discarded. Moderate suction is used to avoid boiling off hydrogen chloride gas, and if boiling does occur, the filter flask is disconnected from the suction momentarily. Then the solution of tungsten(VI) chlorides and suspended potassium chloride is decanted into the funnel, the transfer of much solid material being avoided.

Next the material from the filter flask is poured over the tin and the 1-l. flask stoppered with the one-hole stopper. The temperature in the water bath is maintained at 25 $\pm$ 2° and the reduction continued for exactly 2 hours. During this time the reduction solution will go from blue to purple to reddish-brown or green. Shortly before the reduction is over, a stoppered, 500-ml. Erlenmeyer flask is packed in crushed ice in a Dewar jug. The air in the flask is displaced with hydrogen chloride gas to avoid air oxidation. When the reduction is finished, the solution is decanted into the 500-ml. flask, the remaining tin being drained. This tin can be washed and reused. The reduction solution is resaturated with hydrogen chloride gas. (This step requires

from 10 to 15 minutes of bubbling at a moderate rate.) Then the flask is stoppered and placed aside in ice to crystallize. If no crystals are apparent after 24 hours, the solution is resaturated with hydrogen chloride gas. The crystals can be collected in the following way. Bottles of absolute ethanol and ether are packed in ice together with a clean, dry, 150-ml. beaker. Then a fritted-glass crucible or funnel is assembled for filtering in such a way that the crucible can be packed in ice.* The fritted-glass plate is next rinsed with concentrated hydrochloric acid. About 50 ml. of mother liquor is decanted off the crystals into the small beaker packed in ice. Then the remaining mother liquor is swirled to suspend the crystals and transferred to the filtering crucible. While waiting for the liquid to run through the filter, the flask is returned to the Dewar jug. The decanted mother liquor is used to wash adhering crystals from the walls of the flask.

When all the mother liquor has passed through the filter, the filtrate is transferred to the crystallizing flask in the Dewar jug and the crystals washed by washing down the sides of the crucible with a pipet using iced absolute ethanol. If the product on superficial washing is green and homogeneous, it should be further washed with two or three additional 2-ml. portions of ethanol and the filter cake then covered with iced ethanol and sucked almost dry. Next the filter cake is covered with iced ether and sucked dry. At this point air is blown through the stem of the funnel or crucible holder to loosen the filter cake, after which the product is air-dried out of direct sunlight. The dry product is stable toward air oxidation, but if the humidity is high, or if residual moisture remains, the green crystals will turn blue due to air oxidation. This can be avoided by drying in a stream of inert gas, although it is not usually necessary.

* This can be conveniently done by cutting a hole $\frac{1}{8}$ in. larger than the mouth of the filtering flask in the bottom of a half-pound coffee can, and having placed this can on the flask, securing the neoprene adapter and crucible, and packing the can with ice.

If the product is contaminated with tin salts (white material in the green crystals of product), the crystals should be transferred to a beaker containing 30 ml. of concentrated hydrochloric acid, saturated with hydrogen chloride gas at 0°, and the whole packed in ice. Stirring is maintained until the tin salts are dissolved; then recovery and washing proceeds as above. If the yield is low, or a large percentage of tin salts come down, a second crop can be collected by resaturating the mother liquor with hydrogen chloride gas and allowing the solution to remain in ice for another 48 hours. The crystals of $K_3W_2Cl_9$ are medium green in color and form a deep green aqueous solution. The yield, based on tungsten(VI) oxide or tungstic acid, is 50 to 55%.

B. PENTAPOTASSIUM TETRADECACHLOROTRITUNGSTATE(III)

The procedure is the same as outlined above except that 1.0 g. of potassium chloride is added to the 150 g. of tin before reduction. Moreover, if the solution of tungsten(VI) chlorides is allowed to stand overnight, the filtration step can be omitted in this case and the supernatant liquor poured directly on the tin–potassium chloride. Transfer of solid material should be avoided, but a very small amount of potassium chloride in addition to that added will not be harmful as the 1-g. amount is an excess. Since $K_5W_3Cl_{14}$ is more soluble than $K_3W_2Cl_9$, the yield is somewhat lower, about 45 to 50%.

Properties

Tripotassium enneachloroditungstate(III), sometimes called tripotassium ditungsten(III) enneachloride, forms yellow-green hexagonal crystals, soluble in water, giving a yellow-green solution with absorption maxima at 462 and 625 mμ. In solution the compound is soon oxidized by air, but it is virtually insoluble and quite stable in concentrated acids. The crystal structure, as determined by Brosset[4]

and checked by Pauling,[5] of the $W_2Cl_9^{3-}$ ion consists of two octahedra joined on a face with chlorines attached at all the apices. It has been recommended as an analytical reducing agent[6] and is said to resemble titanium(III) chloride, but with the advantage of being more easily prepared in the pure state and of being stable in the solid state.

The complex salt $K_5W_3Cl_{14}$ gives a deep red solution in water or hydrochloric acid with an absorption maximum at 515 mμ. It is more soluble and more easily oxidized than $K_3W_2Cl_9$. The equilibrium between $K_3W_2Cl_9$ and $K_5W_3Cl_{14}$ has been studied spectrophotometrically, and the ratio of $W_3Cl_{14}^{5-}$ to $W_2Cl_9^{3-}$ has been found to vary with the chloride-ion concentration.[7]

X-ray powder pictures of $K_3W_2Cl_9$ prepared by this method have confirmed the work of Brosset[4] and Pauling.[5] Powder pictures of $K_5W_3Cl_{14}$ are different from those of $K_3W_2Cl_9$, but on account of the equilibrium some contamination by $K_3W_2Cl_9$ is evident.[7]

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CHAPTER VIIA

48. CARBONYL FLUORIDE

$$CO + 2AgF_2 \rightarrow COF_2 + 2AgF$$

SUBMITTED BY M. W. FARLOW,* E. H. MAN,* AND C. W. TULLOCK*
CHECKED BY RONALD D. RICHARDSON†

Carbonyl fluoride can be prepared by any of several methods, including the conversion of carbonyl chloride to the fluoride by such reagents as hydrogen fluoride[1] and antimony(III) fluoride.[2] The direct combination of carbon monoxide and fluorine is another route to this fluoride, but carbon tetrafluoride is a by-product of the reaction.[3] A particularly suitable laboratory preparation of carbonyl fluoride is the fluorination of carbon monoxide by silver(II) fluoride.[4] This method, described below, gives directly carbonyl fluoride of rather high purity without recourse to a low-temperature distillation.

Procedure

A schematic diagram of the apparatus used for preparing carbonyl fluoride from carbon monoxide and silver(II) fluoride is shown in Fig. 17. Cylinders of helium and carbon monoxide are connected through flowmeters and a pressure-release device to the copper reaction tube (47 in. long, $1\frac{1}{2}$ in. diameter). A smaller copper vessel containing sodium fluoride pellets is connected with copper tubing and rubber fit-

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tings to the reaction tube. The sodium fluoride removes hydrogen fluoride from the product. The liquid nitrogen traps may be glass; for the preparation described here the first trap should be of 1 to 1.5-l. capacity. Connecting tubing may be thick-walled rubber or Tygon polyvinyl chloride.

The copper reaction tube is charged with about 1 kg. of silver(II) fluoride. The entire system is evacuated to 0.1 mm., then filled to atmospheric pressure with helium.

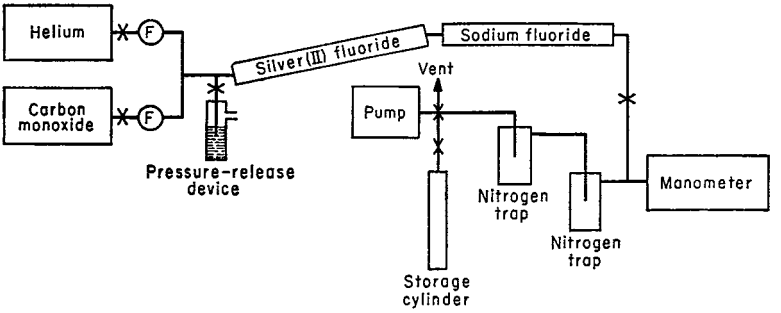

FIG. 17. Schematic diagram of the apparatus used for preparing carbonyl fluoride from carbon monoxide and silver(II) fluoride.

A slow stream of helium is maintained during the reaction to prevent access of moisture and the condensation of liquid oxygen in the liquid nitrogen traps. Carbon monoxide is admitted at a rate of about 10 l./hr., although this rate is not critical. An exothermic reaction takes place, as evidenced by a "hot zone" on the copper reactor. The progress of the reaction is readily determined by following the passage of the "hot zone";* the reaction is complete when the far end of the tube returns to room temperature. The

* The checker found that carrying out the reaction in a copper tube made the location of the "hot zone" impossible after the reaction had been running for a few minutes. Consequently, the gaseous reactant was admitted until the exit end of the reaction tube again approached room temperature. It was assumed that most of the excess carbon monoxide was swept through the liquid air trap by the flow of the inert gas.

carbonyl fluoride condenses as a solid in the nitrogen traps (about 10% of the total is caught in the second trap). When the reaction is complete, the gas flow is stopped, and the portion of the apparatus beyond the sodium fluoride scrubber is evacuated. The storage cylinder is cooled in liquid nitrogen, the line to the pump is closed, and the carbonyl fluoride is distilled *in vacuo* without the application of heat from the traps to the cylinder.

Yields of carbonyl fluoride obtained by this method range from 70 to 85%. The major contaminant in the frozen product is carbon dioxide. This substance may be present as an impurity in the carbon monoxide or may result from hydrolysis of carbonyl fluoride by traces of moisture in the apparatus. Carbonyl fluoride better than 99% pure is obtained if commercial carbon monoxide is purified before the reaction.*

Properties

Carbonyl fluoride is a colorless gas boiling at −83.1° at 760 mm. and freezing at −114.0°.[4] Its density is 1.388 as a solid in liquid air[4] and 1.139 as a liquid at its melting point.[4] The heat of formation of carbonyl fluoride has been calculated to be 166.6 kcal.[6] The carbon-fluorine bond in this molecule is highly reactive, resembling the carbon-fluorine bond of other acyl fluorides in chemical behavior. The dissociation value for the carbon-fluorine bond is −115 kcal./mol.[7] Hydrolysis proceeds rapidly, even in the atmosphere, to give carbon dioxide and hydrogen fluoride. The elements of hydrogen fluoride are split out by reaction of carbonyl fluoride with most other protonic substances. Reaction of carbonyl fluoride with trifluoromethyl hypofluorite at 250 to 300° produces perfluorodimethyl peroxide.[8]

* Carbon dioxide may be removed from commercial carbon monoxide by scrubbing with dry potassium hydroxide or a commercial carbon dioxide absorbent such as Caroxite. A procedure for the preparation and purification of carbon monoxide is given by W. L. Gilliland and A. A. Blanchard.[5]

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49. SULFURYL FLUORIDE

$$2AgF_2 + SO_2 \rightarrow SO_2F_2 + 2AgF$$

Submitted by E. L. Muetterties*
Checked by Ronald D. Richardson†

Sulfuryl fluoride has been prepared by a number of methods. Most of these consist of the fluorination of a sulfur-oxygen compound, as in the direct reaction of elemental fluorine with sulfur dioxide,[1] a metal sulfate, or a metal thiosulfate.[2] A well-known exception to this general method is the pyrolysis of barium fluorosulfate:[3]

$$Ba(SO_3F)_2 \xrightarrow{500 \text{ to } 800^\circ} BaSO_4 + SO_2F_2$$

Fluorination of sulfuryl halides by halogen exchange is apparently a very difficult process to force to completion; even at temperatures as high as 300° the usually effective Swarts reagent takes sulfuryl chloride only to the chloride

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fluoride, SO_2ClF.[4] Of all the reported syntheses the most convenient for the preparation of relatively small amounts of sulfuryl fluoride is the reaction of sulfur(IV) oxide and silver(II) fluoride,[5] and this procedure is described below.

Procedure

In brief, the procedure consists of passing sulfur(IV) oxide, diluted with an inert gas, through a metal or glass tube* packed with silver(II) fluoride. The product is collected in a glass trap cooled with liquid nitrogen. Purification is effected either by scrubbing the crude product with an aqueous solution of potassium iodide or by distillation at atmospheric pressure.

A copper, stainless-steel, or nickel tube is packed with 400 g. of silver(II) fluoride. One end of the reactor is connected (rubber or Tygon tubing is suitable) through a T-tube to a cylinder of sulfur(IV) oxide and to a cylinder of helium or nitrogen; these cylinders are fitted with proper regulatory valves and some type of flowmeter. Somewhere along the inlet line a blowoff valve, e.g., a mercury leg, should be inserted as a safety measure. The exit end of the reactor is connected by tubing to a glass trap fitted at both ends with stopcocks.†

The entire system is fully purged with the diluent gas and then the glass trap is cooled with a Dewar flask containing liquid nitrogen. A mixture of sulfur(IV) oxide and diluent gas containing about 80% sulfur(IV) oxide is then passed through the reaction system at a rate of 0.3 to 0.8 l./min. Neither the gas composition nor the gas flow rate is critical here. The course of the reaction is determined by following the relatively narrow "hot" reaction

* A glass reaction tube may be used but unless rigorous precautions are taken to avoid trace amounts of water, there is excessive etching of the glass and consequent lowering of yields. The use of a metal reactor tube is recommended.

† The stopcocks are not necessary but they do facilitate later operations of evacuation and transfer of product.

zone down the length of the metal reactor;* the reaction is essentially complete when the "hot zone" reaches the far end of the reactor. Sulfuryl fluoride, along with unreacted sulfur(IV) oxide, condenses as a solid in the cold trap. At the end of the reaction this trap is disconnected from the reaction system, and the crude product is vacuum-distilled into a cooled (solid carbon dioxide–acetone or liquid nitrogen) gas storage cylinder.

Distillation of the crude product in a glass column is the preferred purification procedure. In this manner 50 to 80 g. of sulfuryl fluoride of 98+% purity is obtained. The observed boiling point is −54.8° at 760 mm. Impurities detected in the distilled product by infrared and mass spectrographic analyses are silicon tetrafluoride, carbon dioxide, sulfur(IV) oxide, nitrogen, and oxygen. If equipment for a low-temperature distillation is not available, the crude product is purified by chemical means and a purity of 95% or better is achieved. In this latter method the crude product is passed through a series of three 500-ml. gas-washing bottles (fritted disk inlets) containing saturated solutions of potassium iodide, then through two drying columns packed with Drierite, into a gas storage cylinder cooled with liquid nitrogen (or, if the loss of a small amount of product can be tolerated, with solid carbon dioxide–acetone mixture).

Properties

Sulfuryl fluoride, a colorless gas at room temperature, melts at −136.7° and boils at −55.4°.[6] This oxyfluoride has C_{2v} symmetry and the bond distances and bond angles

* The checker carried out the reaction in a copper tube and experienced difficulty in determining the location of the "hot zone" after the reaction had been running for a few minutes. Consequently, the gaseous reactant was admitted until the exit end of the reaction tube again approached room temperature, which technique necessitated the removal of an appreciable quantity of excess sulfur(IV) oxide from the reaction products.

are: S—O = 1.405 A.; S—F = 1.530 A.; <OSO = 123°58′; <FSF = 96°7′.[7]

Chemically, the sulfur-fluorine bond in sulfuryl fluoride is intermediate in reactivity between the sulfur-fluorine bonds in thionyl fluoride and sulfur(VI) fluoride. Although hydrolysis is a thermodynamically favored process, it has been found that no hydrolysis occurs when sulfuryl fluoride and water are heated to temperatures as high as 150° in a sealed tube.[1] However, the more strongly nucleophilic hydroxyl ion can effect hydrolysis as demonstrated by the absorption of sulfuryl fluoride by aqueous bases at 25°.[1] Few reactions with electrophilic reagents have been carefully examined and most observations have been qualitative. Reaction with metals requires temperatures approaching red heat for measurable rates; and hydrogen and hydrogen sulfide convert sulfuryl fluoride to sulfur, hydrogen fluoride, and water only at temperatures of about 600°.[1,8] Thermally, sulfuryl fluoride appears to be very stable; it reportedly undergoes no decomposition up to 600°.[8]

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50. THIONYL FLUORIDE

$$3SOCl_2 + 2SbF_3 \xrightarrow{SbCl_5} 3SOF_2 + 2SbCl_3$$

SUBMITTED BY W. C. SMITH* AND E. L. MUETTERTIES*
CHECKED BY J. D. PARK† AND ROBERT SETTINE†

Thionyl fluoride can be prepared by the reaction of thionyl chloride with metal fluorides such as zinc(II) fluoride[1] and arsenic(III) fluoride,[2] and with metal fluorosulfites.[3] It is also obtained by the action of hydrogen fluoride upon a mixture of tetrasulfur tetranitride and copper(II) oxide[4] and by the reaction of hydrogen fluoride with thionyl chloride in the absence of[5] or in the presence of[6] antimony(V) fluoride as catalyst. Another method and the simplest on a laboratory scale involves the reaction of antimony(III) fluoride with thionyl chloride in the presence of antimony(V) chloride as catalyst.[7] This last procedure is described below.

Procedure

The reaction is carried out in a 500-ml. four-necked flask fitted with a mercury-sealed stirrer, thermometer, dropping funnel, and condenser. The condenser is connected in series to two glass traps,‡ fitted with stopcocks, and then to a calcium chloride drying tube.

The apparatus is thoroughly dried, and flushed with nitrogen; the reaction flask is charged with 280 g. (1.57 mols) of antimony(III) fluoride and 120 g. (0.524 mol) of antimony-

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† University of Colorado, Boulder, Colo.

‡ The traps are cooled in solid carbon dioxide–acetone baths. The first trap should have an inlet tube of such length that it will not extend below the surface of the condensed liquid product. All the product will condense in the first trap if the reaction temperature is controlled properly.

(V) chloride* under a blanket of nitrogen. The thionyl chloride (155 g., 1.30 mols) is placed in the dropping funnel under a nitrogen blanket. The slurry in the reaction flask is heated externally with stirring to 125° with a Glas Col mantle and the external heating is continued during the reaction period. The thionyl fluoride is generated readily by allowing the thionyl chloride to drop slowly into the reaction flask over about a 2-hour period, at such a rate that the temperature is kept at 125 to 150°. External heating is continued for an additional half hour with stirring to ensure complete reaction.

The colorless liquid product collected in the trap is purified by distillation in a glass still at atmospheric pressure. The yield is about 55%. Mass spectrometric analysis indicates that the product is 99.5% pure, with air and silicon tetrafluoride as the trace impurities present.

Properties

Thionyl fluoride, a colorless gas with an odor like phosgene, fumes mildly when exposed to moist air and is hydrolyzed very slowly by water. It is soluble in ether and benzene, melts at −129.5°, boils at −43.8°, and reaches the critical point at 89.0° and 55.3 atm.[7] In the absence of moisture, pure thionyl fluoride does not attack silicon, magnesium, nickel, copper, zinc, or mercury up to 125°.[7] It is reported to attack glass at 400°, but has no effect on iron at this temperature.[2]

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* The amount of antimony(V) chloride is such that the fluorinating mixture is fluid at the reaction temperature used.

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CHAPTER VIIB

51. MANGANESE(II) ACETYLACETONATE

[Bis(2,4-pentanedionato)manganese(II)]

$$MnCl_2 \cdot 4H_2O + 2HC_5H_7O_2 + 2NaC_2H_3O_2 \cdot 3H_2O \rightarrow Mn(C_5H_7O_2)_2 \cdot 2H_2O + 2NaCl + 2HC_2H_3O_2 + 8H_2O$$

$$NH_4OH + HC_2H_3O_2 \rightarrow NH_4C_2H_3O_2 + H_2O$$

SUBMITTED BY ROBERT G. CHARLES*
CHECKED BY SAM N. HOLTER† AND W. CONARD FERNELIUS†

Manganese(II) acetylacetonate 2-hydrate has been obtained by precipitation from aqueous solution.[1] The anhydrous product was prepared from the hydrate by allowing it to stand in a vacuum over phosphorus(V) oxide. Although the 2-hydrate, in solution or wet with solvent, is reported to oxidize rapidly in air, the dry material is reported to be stable.

Procedure‡

To a solution of 49.5 g. (0.25 mol) of manganese(II) chloride 4-hydrate in 250 ml. of water at room temperature is added a solution of 50 g. (0.5 mol) of acetylacetone in 100 ml. methanol. The mixture is stirred during the addition with a magnetic stirrer. A solution of 68.1 g. (0.5 mol)

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† The Pennsylvania State University, University Park, Pa.
‡ In order to receive satisfactory results with this preparation, the mixture should not be heated at any time. It is also necessary to minimize exposure to the air during the preparation.

of sodium acetate 3-hydrate in 150 ml. water is then added slowly with stirring, followed by 21 ml. of concentrated aqueous ammonia. The mixture is stirred about 10 minutes at room temperature and then placed for several hours in a refrigerator. The light yellow solid that forms is filtered off on a Büchner funnel under a stream of nitrogen and washed with several portions of cold water. The solid is dried in a vacuum desiccator at room temperature for 6 to 8 hours.* The yield is 18 to 20 g. (25 to 28%, based on manganese chloride used). *Anal.* Calcd. for $Mn(C_5H_7O_2)_2 \cdot 2H_2O$: Mn, 19.0. Found: Mn, 19.3.

If desired, the 2-hydrate can be purified by recrystallization. Sixteen grams of the dried material is stirred for a few minutes with 100 ml. of absolute ethanol, and the solution is then filtered with suction as rapidly as possible through coarse filter paper on a Büchner funnel. Sufficient ethanol is added to the filtrate to replace that lost by evaporation and to redissolve any solid which separates. Fifteen milliliters of water is added to the filtrate, and the solution is evaporated with a stream of nitrogen until reduced in volume by one-half. The mixture is then cooled for a few minutes. The yellow crystals are filtered off on a Büchner funnel and dried under the conditions specified for the unrecrystallized material. The yield is 30 to 50% of the quantity of unrecrystallized compound taken. *Anal.* Calcd. for $Mn(C_5H_7O_2)_2 \cdot 2H_2O$: C, 41.5; H, 6.3; Mn, 19.0. Found: C, 41.2; H, 6.1; Mn, 19.2.

The anhydrous compound may be formed as a tan powder by heating the 2-hydrate 2 to 4 hours at 100° in a drying pistol or vacuum oven at a pressure of several mm. Hg.

* The conditions used to dry the 2-hydrate are rather important. Pressures of the order of a few mm. Hg, in the absence of a drying agent, are suitable. Much lower pressures (a few microns) result in partial dehydration to the anhydrous compound. Prolonged drying (several days) at pressures of several mm. Hg also results in dehydration. The degree of hydration can be established by determining the weight loss of a 100 mg. sample after heating 4 hours at 100° at a pressure of several mm. Hg. The theoretical weight loss for the 2-hydrate is 12.5%.

Anal. Calcd. for $Mn(C_5H_7O_2)_2$: C, 47.4; H, 5.6; Mn, 21.7. Found: C, 46.7; H, 5.7; Mn, 22.0.

Properties

Manganese(II) acetylacetonate 2-hydrate is a light yellow crystalline material which easily loses the water of crystallization. The 2-hydrate is fairly soluble in most organic solvents but may appear to be insoluble if heated too much while effecting solution. The anhydrous material is obtained by mild heating of the 2-hydrate at a pressure of several mm. Hg or by allowing it to stand in high vacuum at room temperature. It is a tan material that does not melt when heated to 360°. In an inert atmosphere the anhydrous compound decomposes rapidly above about 250°. In a high vacuum (2 microns) it can be sublimed unchanged at 200°, but it does not sublime at atmospheric pressure. The anhydrous material is soluble in pyridine; slightly soluble in ethanol, methanol, and acetone; and nearly insoluble in benzene, toluene, and chloroform. Typical solubility data are given in Table I.

TABLE I

	$Mn(C_5H_7O_2)_2 \cdot 2H_2O$	$Mn(C_5H_7O_2)_2$
C_6H_6	0.057 g./10 ml.	$\ll$0.023 g./10 ml.
CH_3OH	1.79 g./10 ml.	0.69 g./10 ml.
C_2H_5OH	2.71 g./10 ml.	0.71 g./10 ml.

The dry compounds do not oxidize readily in air but the wet compounds do, more rapidly with higher temperature.

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52. POTASSIUM NITRIDORHENATE(VII)

$$Re_2O_7 + 3KNH_2 \rightarrow K_2ReO_3N + KReO_4 + 2NH_3$$

SUBMITTED BY A. F. CLIFFORD* AND R. R. OLSEN*
CHECKED BY SOTER G. KOKALIS† AND THERALD MOELLER†

Reports of nitridorhenic acid(VII) and its salts do not appear in the literature. The nearest analogs are the nitridoosmates(VIII),[1] such as $KOsO_3N$, and the nitridomolybdates(VI),[2] such as K_3MoO_3N. All three of these salts are characterized by having a nitrogen atom attached to only one atom. They thus are all true nitrides. The osmium salt, which is derived from a strong monobasic acid ($HOsO_3N$, cf. $HMnO_4$), is not hydrolyzed in aqueous solution. The molybdenum salt, which is the salt of a weak tribasic acid (H_3MoO_3N, cf. H_3VO_4), is hydrolyzed rapidly in aqueous solution and slowly in air with loss of ammonia. The rhenium compound, as might be expected of a salt of a dibasic acid intermediate in strength (H_2ReO_3N, cf. H_2CrO_4), is also hydrolyzed in water with loss of ammonia but is fairly stable in air. The colors of $KOsO_3N$, K_2ReO_3N, and K_3MoO_3N are very similar shades of yellow.

Procedure

Sixty-five hundredths gram (0.00134 mol) of rhenium(VII) oxide is put into one leg of a Faraday tube, such as that shown in Fig. 18, which has been flushed with dry nitrogen, and 0.300 g. (0.00767 mol) of clean, dry potassium metal is put into the other along with a short piece of iron wire. (Iron filings should not be used, because it is too

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difficult to decant the solution cleanly from them.)* Both legs of the tube are immersed in a Dry Ice bath, and ammonia is condensed until the tube is about half filled. The leg containing the potassium is then allowed to warm to the

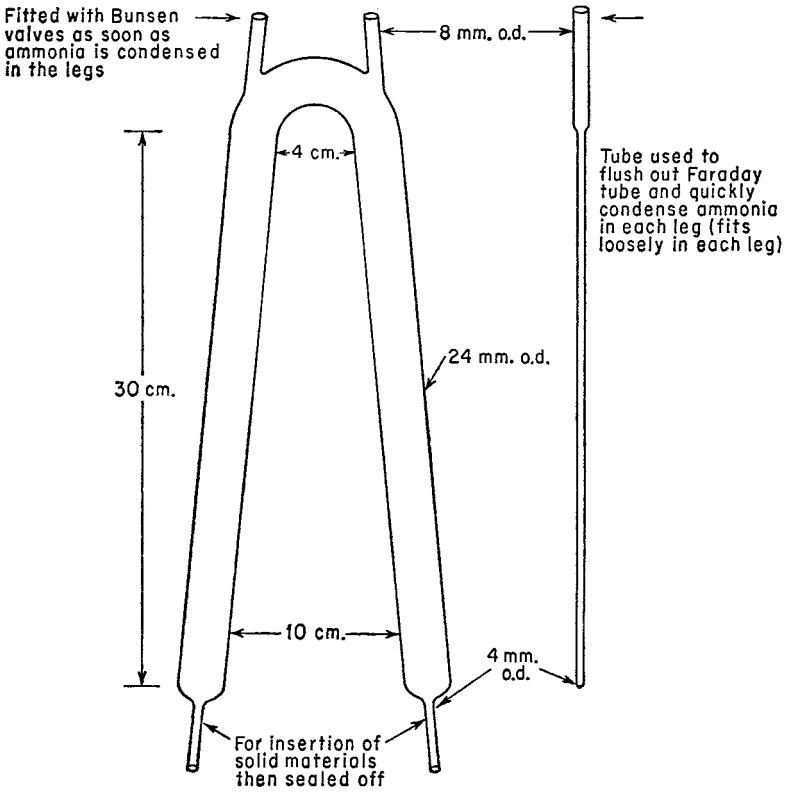

FIG. 18. Faraday tube.

boiling point (−33°) to cause the potassium to react with the ammonia;† it should be chilled occasionally if necessary to prevent undue loss of ammonia. This process is con-

* Since the product tends to adhere to the walls of the tube and the yields appear to be a function of the separation between the arms, the construction of the Faraday tube should not deviate greatly from that shown.

† Caution should be exercised during this step because of the possibility of violent bubbling and consequent spattering into the other leg.

tinued until all the initial blue color has been discharged to yellow and should take about 5 minutes.

$$K(\text{in } NH_3) + NH_3 \rightarrow KNH_2 + \tfrac{1}{2}H_2$$

Next the potassium amide solution is decanted away from the iron wire catalyst into the deep blue-green* solution of rhenium(VII) oxide in ammonia. Immediately upon mixing, a pale yellow precipitate of potassium nitridorhenate-(VII) is formed. The mixture is allowed to stand in a Dry Ice bath for an hour to ensure complete reaction. The tube is opened in a dry box or under a stream of dry nitrogen or ammonia gas and the contents poured into a sintered-glass funnel. Keeping the funnel in the dry box or under the gas stream, the pale yellow precipitate of potassium nitridorhenate(VII) is washed thoroughly with about 100 ml. of liquid ammonia to remove the soluble potassium perrhenate and excess soluble, deep yellow potassium amide. The pale yellow product is dried in a vacuum desiccator and stored in a sealed, evacuated ampoule. Yields as high as 89% of the theoretical have been obtained.

Properties

Potassium nitridorhenate(VII) is a pale yellow solid, insoluble in liquid ammonia but soluble in water with decomposition. When dry, it does not decompose rapidly in air but becomes white when heated. The infrared spectrum[3] of the solid has a strong peak at 1025 cm.$^{-1}$, attributable to rhenium-nitrogen stretching, and sharp peaks at 909 and 936 cm.$^{-1}$, attributable to rhenium-oxygen (cf. 912 cm.$^{-1}$ in ReO_4^-).

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* The checkers report a muddy brown, rather than a blue-green, solution of rhenium(VII) oxide.

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CHAPTER VIII

53. POTASSIUM DITHIOFERRATE(III)

$$6Fe + 4K_2CO_3 + 13S \rightarrow 6KFeS_2 + K_2SO_4 + 4CO_2$$[1]

SUBMITTED BY JOHN L. DEUTSCH* AND HANS B. JONASSEN*
CHECKED BY R. F. TRIMBLE, JR.†

Potassium dithioferrate(III) can be prepared by direct combination of iron, sulfur, and potassium carbonate at a temperature above that of the melting point of the carbonate.[1] This compound is also made by the heating of potassium thiocyanate and iron(III) oxide at a temperature above 400°, with iron(II) sulfide as a side product.[2] The former process has the advantage of separating the insoluble product from a soluble side product.

Procedure

Eight grams of iron powder, 45 g. of flowers of sulfur, 40 g. of potassium carbonate, and 8 g. of anhydrous sodium carbonate are very thoroughly mixed and put into a covered clay crucible. This mixture is then heated for a period of 1 to 1½ hours at 900°, at which temperature the reaction mixture is molten. On the completion of the reaction the crucible is allowed to come to room temperature and is then submerged in a beaker of water and the reacted mixture digested on a water bath. The supernatant liquid becomes dark green [the iron complex $Na_3FeS(OH)_3$][3]; it is then

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decanted, more water is added, and the digestion continued. This process is continued until the supernatant liquid is colorless. This assures the removal of any product sulfur, which appears as a scum during the first stages of the digestion. The residue is filtered, washed with water, ethanol, and diethyl ether, and then air-dried at room temperature. The yield is approximately 18.5 g. (82%).

Properties

The product consists of small, permanganate-colored crystals. The crystal is made up of infinite chains of FeS_2^- ions, formed of iron tetrasulfide tetrahedra sharing opposite edges. Between these lie the potassium ions surrounded by eight sulfur atoms.[4] The formula weight is 159.07; the density is 2.563;[5] the magnetic susceptibility is $+318 \times 10^{-6}$ e.m.u./mol (not corr.).[6] It is insoluble in both hot and cold water and dissolves in acid with the evolution of hydrogen sulfide and the separation of sulfur.[7] At room temperature the compound is stable in dry air but tends to disintegrate in moist air. In the absence of air it can be heated very strongly without decomposition, the crystals becoming darker in color; however, upon cooling they return to their original hue. If heated in the presence of air, iron oxide and potassium sulfate are formed.[8] In a hydrogen stream at red glow the compound loses a quarter of its sulfur content, with the color changing to black as the crystal structure alters. The product, potassium trithiodiferrate-(II), ($K_2Fe_2S_3$), is soluble in acids with the evolution of hydrogen sulfide and without the liberation of any sulfur.[9] Potassium dithioferrate(III) will form the corresponding silver salt, silver dithioferrate(III), if left in the presence of a silver nitrate solution.[10]

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54. IRON(II) CHLORIDE

$$C_6H_5Cl + 2FeCl_3 \rightarrow C_6H_4Cl_2 + 2FeCl_2 + HCl$$

SUBMITTED BY PETER KOVACIC* AND NEAL O. BRACE†
CHECKED BY T. M. STANLEY,‡ DAVID WILLIAMS,‡ AND A. L. ALLRED‡

Anhydrous iron(II) chloride has been prepared by passing hydrogen chloride over iron, by reducing iron(III) chloride with hydrogen, and by dehydrating one of the hydrates of iron(II) chloride. A new procedure is outlined here.[1,2]

Procedure

Two hundred and twenty-five grams (2 mols) of chlorobenzene and 162 g. (1 mol) of C.P. anhydrous iron(III) chloride are added to a three-necked, round-bottomed flask equipped with a thermometer, efficient paddle stirrer, and condenser. Arrangements are made to pass the hydrogen chloride which is evolved during the reaction through a

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safety trap and into a beaker of water where the acid is titrated with 2 *N* sodium hydroxide solution.

The mixture is stirred at a rapid rate and heated for 30 minutes to 126°, whereupon the black slurry thickens. Only approximately 1 ml. of the sodium hydroxide is consumed in this initial heating. The reaction is then allowed to proceed rapidly at 128 to 139° for 2 hours. In the course of the reaction the mixture becomes light tan and appreciably less viscous, and the theoretical amount of sodium hydroxide is required to neutralize the hydrogen chloride which is evolved. Very little additional hydrogen chloride is liberated during another hour of heating.

The solid is filtered, washed repeatedly with chloroform or benzene, and dried *in vacuo;* the yield is 99%. *Anal.* Calcd. for $FeCl_2$: Fe, 44.06. Found: Fe, 43.89.

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55. CARBONATOTETRAMMINECOBALT(III) NITRATE

$$2Co(NO_3)_2 + 6NH_3(aq.) + 2(NH_4)_2CO_3 + \tfrac{1}{2}O_2 \rightarrow 2[Co(NH_3)_4CO_3]NO_3 + 2NH_4NO_3 + H_2O$$

Submitted by G. Schlessinger*
Checked by John W. Simmons,† Gerhardt Jabs,† and Mark M. Chamberlain†

The first salts of this series were prepared by Vortmann[1] and later extensively investigated by Jørgensen,[2] who, however, gave only semiquantitative synthetic preparations.

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The method given below, which is a more exact procedure than given hitherto (and which may be significantly shortened by the use of hydrogen peroxide instead of air as oxidizing agent) may also be used, virtually without change, for the preparation of the chloride, bromide, iodide, sulfate, selenate, and oxalate of the carbonatotetrammine series simply by using an equivalent amount of the corresponding cobalt(II) salt as starting material.

Procedure

One hundred grams of cobalt(II) nitrate 6-hydrate (0.344 mol) is dissolved in 100 ml. of warm water and added to a mixture of 200 g. of ammonium carbonate (2.08 mols) in 1 l. of water and 500 ml. of concentrated ammonia. The resulting liquid is oxidized by sucking air through the solution contained in two 1-l. suction flasks fitted with stoppers and glass air-inlet tubes reaching almost to the bottoms of the vessels.* After $2\frac{1}{2}$ hours, when the oxidation is complete, the solution is evaporated on the steam bath to a volume of 500 ml. Any cobalt(III) oxide is filtered off while hot, and further evaporation to 350 ml. is carried out. During the course of the evaporation 50 g. of solid ammonium carbonate should be added in 5-g. portions at regular intervals.† The solution is next cooled in ice, filtered by suction, and the crystals pressed well dry. The crystals may be washed with 75 ml. of alcohol. The filtrate is evaporated down to 100 ml., with the addition of four 5-g. portions of ammonium carbonate, and more product is isolated as above. The first batch of product, 48 to 50 g., is analytically pure, but the second may be contaminated with a trace of carbonatopentamminecobalt(III) nitrate, which is

* A timesaving but more costly method of oxidation is to add 250 ml. of 3% hydrogen peroxide slowly to the well-stirred cobalt(II) ammine mixture. After standing 10 minutes the solution is evaporated as below. The yield is the same.

† The regular addition of the ammonium carbonate is emphasized.

removed by dissolving the salt in fifteen times its weight of water, filtering, and adding 2 to 3 volumes of alcohol. The product precipitates and is filtered off, giving a yield of 8 to 9 g. from the second evaporation.* *Anal.* Calcd. for $[Co(NH_3)_4CO_3]NO_3 \cdot \frac{1}{2}H_2O$: Co, 22.8; NH_3, 26.4. Found: Co, 22.7; NH_3, 26.2.

Properties

The salt crystallizes in violet-red to carmine-red prisms, depending on the crystal size. The solubility at room temperature is one part of the salt in fifteen parts of water. The aqueous solution has a basic reaction to litmus. Dilute acids form the diaquotetrammine salt, whereas concentrated acids form the diacido- or monoacidoaquotetrammine complex. Treatment of the salt with dilute acid, then with an excess of hot dilute ammonia, forms the aquopentamminecobalt(III) series of salts. The salt is stable indefinitely, samples 40 years old having yielded satisfactory synthetic results.

The carbonatotetrammine salts are assigned the *cis* configuration since they behave similarly in all respects to the more stable carbonatodiethylenediammine salts which have been resolved into optical isomers. They serve as excellent raw materials for syntheses in both the tetrammine and pentammine series.

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* The checkers obtained an over-all yield of 62.7 g., or 70%.

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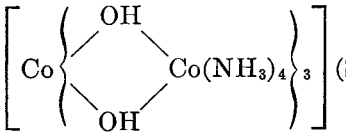
56. TRIS[TETRAMMINE-μ-DIHYDROXO-COBALT(III)] COBALT(III) SULFATE 4-HYDRATE

$$2CoCl_2 \cdot 6H_2O + 2(NH_4)_2CO_3 + 6NH_3 + H_2O_2 \rightarrow 2[Co(NH_3)_4CO_3]Cl + 2NH_4Cl + 14H_2O$$

$$[Co(NH_3)_4CO_3]Cl + 2HCl \rightarrow \textit{cis}\text{-}[Co(NH_3)_4(H_2O)Cl]Cl_2 + CO_2$$

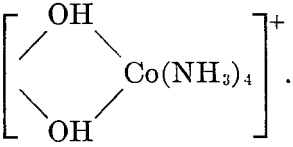
$$\textit{cis}\text{-}[Co(NH_3)_4(H_2O)Cl]Cl_2 + (NH_4)_2SO_4 \rightarrow \textit{cis}\text{-}[Co(NH_3)_4(H_2O)Cl]SO_4 + 2NH_4Cl$$

$$4\textit{cis}\text{-}[Co(NH_3)_4(H_2O)Cl]SO_4 + 2NH_3 + 6H_2O \rightarrow$$



$$(SO_4)_3 \cdot 4H_2O + 4NH_4Cl + (NH_4)_2SO_4$$

SUBMITTED BY GEORGE B. KAUFFMAN* AND ROBERT P. PINNELL*
CHECKED BY JACK K. CRANDALL† AND WILLIAM L. JOLLY†

Tris[tetrammine-μ-dihydroxo-cobalt(III)]cobalt(III) sulfate is analogous to the tris(ethylenediamine) compounds, with each ethylenediamine molecule replaced by the bidentate ligand  . It is easy to prepare in a pure state and can be readily converted into other members of the series by metathesis. It can be prepared by treating *cis*-chloroaquotetramminecobalt(III) sulfate with aqueous ammonia[1] or aqueous sodium hydroxide,[1] treating *cis*-diaquotetramminecobalt(III) sulfate with aqueous ammonia,[1] or by adding pyridine to a hot, dilute acetic acid solution of *cis*-diaquotetramminecobalt(III) sulfate.[2] It can also be prepared by heating *trans*-dibromotetramminecobalt(III) bromide with water until bromine is evolved and treating the resulting solution with ammonium sulfate solution.[2] In this synthesis, the compound is prepared by the first-

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mentioned method. The preparation of the *cis*-chloroaquotetramminecobalt(III) sulfate is a modification of a procedure given by Palmer[3] based upon the original work of Jørgensen.[4]

Procedure

Fifty grams of ammonium carbonate is dissolved in 150 ml. of water in a 600-ml. beaker, and 125 ml. of concentrated aqueous ammonia is added. Any undissolved solid will dissolve readily when the ammonia is added. A solution of 20 g. (0.084 mol) of cobalt(II) chloride 6-hydrate in 30 ml. of water is then added with continuous mechanical stirring. [A light blue precipitate of hydrated cobalt(II) hydroxide first forms, but dissolves as stirring is continued.] Fifty milliliters of 10% hydrogen peroxide are slowly added over a period of 10 to 15 minutes with continuous, rapid stirring, causing the color to change from a dull reddish brown to a deep purple. Stirring is continued until all effervescence ceases. The solution is then transferred to a 525-ml. evaporating dish and concentrated at 80° with continuous mechanical stirring to a volume of around 100 ml. During this time 2 to 3 g. of ammonium carbonate is added every 30 minutes to replace that lost by volatilization. The solution is then filtered through a Büchner funnel to remove any black hydrated cobalt(III) oxide that may have been formed from overheating, and then cooled in an ice bath. The cooled filtrate is transferred to a 400-ml. beaker, and a mixture of 62 ml. of hydrochloric acid with 62 ml. of water is added with continuous stirring over a period of 5 minutes. Seventy-five milliliters of concentrated hydrochloric acid is then added, whereupon carmine-red crystals of carbonatotetramminecobalt(III) chloride are deposited. The mixture is maintained at 60° on a hot plate with mechanical stirring for 45 minutes to 1 hour until the crystals have become deep purple. The mixture then is cooled in an ice bath until crystallization seems complete (around

12 hours). The small purple crystals are collected on an 8-cm. Büchner funnel, and this product is washed twice with 30 ml. of an equivolume mixture of hydrochloric acid and water and once with 30 ml. of ethanol. The crystals are then air-dried. The yield is 15.3 g. [72.4%, based upon cobalt(II) chloride 6-hydrate] of a product contaminated with small amounts of chloropentamminecobalt(III) chloride and *trans*-dichlorotetramminecobalt(III) chloride. Purification is effected by precipitation as the more insoluble sulfate.

Ten grams (0.0398 mol) of crude *cis*-chloroaquotetramminecobalt(III) chloride is added to a mixture of 300 ml. of water and 1 ml. of sulfuric acid, and the mixture is mechanically stirred until no more solid dissolves (around 15 to 20 minutes). The residual purple contaminants are removed by filtration through a small Büchner funnel, and 20 g. (0.151 mol) of ammonium sulfate is dissolved in the filtrate. Minute deep purple crystals start to form immediately. The mixture is then cooled with stirring in an ice bath until crystallization is complete (around 1 hour). The crystals are collected on a small Büchner funnel, washed twice with 10 ml. of ice water and once with 10 ml. of ethanol, and then air-dried. The yield is 9.9 g. (65.2% based on cobalt(II) chloride 6-hydrate).

Five grams (0.0181 mol) of finely ground *cis*-chloroaquotetramminecobalt(III) sulfate is dissolved in an ice-cold solution of 3 ml. of concentrated aqueous ammonia and 200 ml. of water. If the ammonia solution is not cold, premature precipitation of the product will result in a reduced yield. Any deep purple residue is removed by filtration, and the filtrate is allowed to stand for 24 hours in a stoppered 250-ml. flask.* The lustrous dark brownish-violet plates of the product are collected on a small Büchner funnel, washed free of chloride ion with three 10-ml. portions of ice-cold water, rinsed with one 10-ml. portion of

* The solution should not be cooled; crystals of the product form on warming to room temperature.

ethanol, and dried in a desiccator over sulfuric acid for several days. The yield is 3.00 g. [47.9%, based on cobalt(II) chloride 6-hydrate].

Properties

Tris[tetrammine-μ-dihydroxo-cobalt(III)] cobalt(III) sulfate occurs in several hydrated forms, all of them dark brownish-violet or black tabular crystals. Air-drying the compound results in the 9-hydrate, drying over calcium chloride results in the 6-hydrate, and drying at 98° or over sulfuric acid results in the 4-hydrate. Treatment with concentrated hydrochloric acid gives *cis*-diaquotetrammine-cobalt(III) sulfate as a product. Boiling in dilute sulfuric acid evolves oxygen, while boiling in concentrated sulfuric acid liberates oxygen and nitrogen. The compound is only very difficultly soluble in water and can be quantitatively precipitated from the resulting light brownish-violet solution by means of potassium chromate or dichromate (yellowish-gray needles) or hexachloroplatinic(IV) acid (gray crystals).

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57. DICHLOROAQUOTRIAMMINECOBALT(III) CHLORIDE

(Dichrochloride)

$$Co(NH_3)_3(NO_2)_3 + 3HCl + H_2O \rightarrow [Co(NH_3)_3H_2O(Cl)_2]Cl + 3HNO_2$$

$$2HNO_2 + CO(NH_2)_2 \rightarrow CO_2 + 2N_2 + 3H_2O$$

SUBMITTED BY G. SCHLESSINGER*
CHECKED BY JOHN STUEHR† AND MARK M. CHAMBERLAIN†

"Dichrochloride" serves as intermediate for the preparation of most water-soluble triamminecobalt compounds, which usually cannot be made from the difficultly soluble trinitrotriamminecobalt. It was originally prepared by Rose[1] by adding hydrochloric acid to an oxidized ammoniacal cobalt(II) chloride solution and later by Jørgensen[2] by the reaction of trinitratotriamminecobalt or trinitrotriamminecobalt with the same acid.[3] Meyer et al. have also described the latter method.[4]

Since the nitro compound is more readily prepared than the corresponding trinitratotriammine complex, Meyer's procedure has been adopted with some changes in order to obtain a purer product more rapidly and without the noxious evolution of oxides of nitrogen generally associated with the preparation.

Procedure

Twenty grams of trinitrotriamminecobalt (0.86 mol) is well ground in a mortar. Meanwhile a cold mixture of 100 ml. of concentrated sulfuric acid and 200 ml. of concentrated hydrochloric acid is prepared by allowing the sulfuric

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acid to run slowly from a dropping funnel fitted into a 500-ml. suction flask (cooled in ice) containing the hydrochloric acid.* The acid vapor is led into the hood and the flask is swirled continuously during the addition. *Caution.* Use hood. The mixture is cautiously transferred into a 600-ml. beaker and 20 g. of urea is stirred in. The powdered trinitrotriamminocobalt is then added† in portions with good stirring. All subsequent operations except the filtration should be performed in a hood to avoid hydrogen chloride vapors. The mixture is allowed to warm to room temperature, and when it has acquired a greenish tint it is heated to 35 to 40° with frequent stirring. When the vigorous effervescence has abated, the temperature is slowly raised to 50 to 55° with continuous stirring and maintained in this range until the suspension is grass green in tint and gas evolution has almost ceased (about $\frac{3}{4}$ hour). After cooling in ice, 250 ml. of ethanol is added, the mixture is recooled and filtered by suction through paper or through a medium fritted-glass filter, the solids are washed with ethanol and acetone and air-dried. Crude yield is 14 to 17.5 g. (78 to 97%). This crude product is entirely satisfactory for further synthetic use but may be recrystallized if desired by the following method.[5]

Ten grams of the salt is dissolved in 150 g. of water, acidified with several drops of hydrochloric acid, filtered, and 50 ml. of 1:1 hydrochloric acid is added. After standing for 3 hours, 50 ml. more of the acid is added. The procedure is repeated after 3 hours. During the next 9 to 12 hours three 50-ml. portions of concentrated acid are added at equally spaced time intervals. All additions of acid are made without stirring or shaking. The mixture is placed in the ice box for 24 hours and is suction-filtered; the crystals are washed with 1:1 hydrochloric acid and absolute

* Gloves are strongly recommended during the handling of the acid mixture.

† The checkers found that keeping the temperature of the reaction vessel well below room temperature during the initial addition of trinitrotriamminecobalt(III) gave a crude yield of 17.8 g.

ethanol, and dried in a desiccator. The yield is 8.5 g. (85% recovery).

Ammonia is determined by the Kjeldahl method. Cobalt is determined by decomposing the salt with aqueous sodium hydroxide, dissolving the cobalt(III) oxide in acidified potassium iodide, and titrating the liberated iodine with thiosulfate. *Anal.* Calcd. for $Co(NH_3)_3H_2O(Cl)_2Cl$: Co, 25.0; NH_3, 21.6. Found: Co, 24.6; NH_3, 21.8.

Properties

The salt as prepared above appears as small, olive-green, hexagonal prisms; however, when pure the material consists of needles which exhibit a purple-green dichroism and appear quite black when viewed from a distance. The salt is slowly aquated in aqueous solution but may be reprecipitated with hydrochloric acid under special conditions (see method of recrystallization). The salt reacts with warm, dilute alcoholic oxalic acid to form chlorooxalatotriamminecobalt(III) and with concentrated ammonia and ammonium chloride giving chloropentamminecobalt(III) chloride. When heated at 150° for several hours, the salt turns bright green, losing approximately 1 mol of water to form trichlorotriamminecobalt(III). Prolonged heating causes decomposition.

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58. RESOLUTION OF THE TRIS(ETHYLENEDIAMINE)COBALT(III) ION

$$4CoSO_4 + 12en + 4HCl + O_2 \rightarrow 4[Co(en)_3]ClSO_4 + 2H_2O$$

$$[Co(en)_3]ClSO_4 + Ba\ d\text{-tart} \rightarrow \begin{cases} (+)\text{-}[Co(en)_3]Cl\ d\text{-tart} \\ \qquad\qquad + BaSO_4 \\ (-)\text{-}Co(en)_3Cl\ d\text{-tart} \end{cases}$$

en = ethylenediamine; *d*-tart = *dextro*-tartrate radical

SUBMITTED BY J. A. BROOMHEAD,* F. P. DWYER,* AND J. W. HOGARTH†
CHECKED BY ROBERT E. SIEVERS‡

Tris(ethylenediamine)cobalt(III) chloride was first prepared by Werner.[1] Resolution was effected through the chloride *d*-tartrate which was obtained by allowing the chloride (1 mol) to react with silver *d*-tartrate (1 mol). The correct ratio of chloride ion to tartrate ion is important and this has meant that it was necessary to isolate the pure solid chloride, the synthesis of which has been described by Work.[2] In the present method the less soluble diastereoisomer is isolated directly and the expensive and unstable silver *d*-tartrate is replaced by barium *d*-tartrate. The addition of activated carbon ensures rapid oxidation of the initial cobalt(II) complex and eliminates small amounts of by-products of the reaction.

Procedure

A 500-ml. filter flask is fitted with a rubber stopper carrying an open glass tube extending to the bottom of the flask, and 20.4 ml. of 88.6% w/v ethylenediamine (0.3 mol) is

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added.* This is diluted with water (50 ml.); the mixture is cooled in ice and 10 ml. of 10 *N* hydrochloric acid added.† Cobalt(II) sulfate 7-hydrate (28.1 g.; 0.1 mol), dissolved in cold water (50 ml.), is then added, and finally activated charcoal (4 g.). A rapid current of air is passed for 4 hours. At the end of this time the pH of the mixture is adjusted by the addition of a few drops of either dilute hydrochloric acid or ethylenediamine into the range 7.0 to 7.5. The mixture is heated in an evaporating dish on the steam bath for 10 to 15 minutes to complete the reaction, cooled, and the charcoal filtered off. The charcoal is washed with 20 ml. of water. Barium *d*-tartrate‡ (0.1 mol) is added and the mixture heated on the steam bath with good mechanical stirring for about $\frac{1}{2}$ hour. The barium sulfate is filtered off and washed with a little hot water§ and the orange-red filtrate is evaporated to a volume of 60 ml. Crystallization of (+)-tris(ethylenediamine)cobalt(III) chloride *d*-tartrate 5-hydrate ensues on cooling and is completed by allowing to stand overnight.¶ The crystals are filtered off and the filtrate reserved for the isolation of the *levo* isomer. The crystals are washed with 40% ethanol-water and recrystallized by dissolving in 30 to 32 ml. of hot water, followed by cooling to room temperature and then in ice. After filtration the crystals are washed with 40% ethanol-water, then with absolute ethanol, and air-dried. The yield of the optically pure isomer,‖ $[\alpha]_D = +102°$, is 21 g.

* The exact composition of the ethylenediamine should be determined by dilution of a known volume with water and titration with standard acid, using methyl orange as the indicator. It is not necessary to take the concentrations quoted.

† An equivalent amount of weaker or stronger acid can be used.

‡ Prepared by mixing solutions of barium chloride 2-hydrate (24.4 g.; 0.1 mol) and sodium potassium tartrate 4-hydrate (28.2 g.; 0.1 mol) at 90°, cooling, filtering, and washing with warm water. The precipitate and filter paper are added.

§ At equilibrium a small amount of sulfate ion remains in solution. This does not affect the composition of the diastereoisomer that crystallizes.

¶ The solution may be cooled in ice, whereupon very small crystals result.

‖ The values quoted for the specific rotation are +101° (Werner[1]) and +103° (Busch[3]).

Anal. Calcd. for $[Co(en)_3]ClC_4H_4O_6 \cdot 5H_2O$: C, 23.41; H, 7.47. Found: C, 23.30; H, 7.44.

***Dextro* iodide.** The chloride *d*-tartrate is dissolved in 30 ml. of hot water; concentrated ammonia solution (0.5 ml.) is then added, followed with stirring by 35 g. of sodium iodide dissolved in 15 ml. of hot water. The iodide crystallizes as reddish-orange needles on cooling. Complete crystallization is effected by cooling in ice for 15 minutes. After filtration the crystals are sucked very dry and washed with ice-cold 30% sodium iodide (20 ml.) to remove tartrate and then with ethanol and acetone. The yield of the air-dried product, $[\alpha]_D = +89°$, is 24 g. (35%). *Anal.* Calcd. for $[Co(en)_3]I_3 \cdot H_2O$: C, 11.26; H, 4.11. Found: C, 11.23; H, 4.17.

***Levo* iodide.** The *levo*-tris(ethylenediamine)cobalt(III) chloride *d*-tartrate remaining in the solution above is treated with concentrated ammonia solution (0.5 ml.) and the mixture is heated to about 80°. Solid sodium iodide (35 g.) is stirred in and the whole cooled in ice. The impure *levo* iodide is filtered off and washed with ice-cold 30% sodium iodide (25 ml.) and then with alcohol and air-dried, resulting in a yield of 27 g. Purification is effected by stirring the whole of the crude material into 65 ml. of water heated to 50°. The racemate remains undissolved and is filtered off. Sodium iodide (10 g.) is added to the warm filtrate (50°) and crystallization allowed to take place. After cooling in ice the solid is filtered, washed with ethanol and then acetone, and air-dried. The yield is 18 g. (26%), and $[\alpha]_D = -90°$. *Anal.* Calcd. for $[Co(en)_3]I_3 \cdot H_2O$: C, 11.26; H, 4.11. Found: C, 11.43; H, 4.01.

Properties

Both *dextro-* and *levo*-tris(ethylenediamine)cobalt(III) iodide monohydrate crystallize in deep orange needles or rhombs. The racemic phase which separates as the 1-hydrate is much less soluble in water. Racemization ensues

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when the substance is heated to 110° in the solid state in a sealed tube[4] or in aqueous solution in the presence of charcoal[5] and finely divided metals.[4] In the absence of these catalysts solutions in water or dilute acid are stable even at 100°. Alkali catalyzes racemization and decomposition in hot solution.

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59. *DEXTRO*-TRIS(ETHYLENEDIAMINE)COBALT(III) IODIDE BY A PARTIAL ASYMMETRIC SYNTHESIS

$$\mathrm{Co}(d\text{-tart}) + 3\mathrm{en} \rightarrow (+)\text{-}[\mathrm{Co(en)_3}](d\text{-tart}) \rightleftharpoons (-)\text{-}[\mathrm{Co(en)_3}](d\text{-tart})$$

$$4(+)\text{-}[\mathrm{Co(en)_3}](d\text{-tart}) + 4\mathrm{HCl} + \mathrm{O_2} \rightarrow 4(+)\text{-}[\mathrm{Co(en)_3}]\mathrm{Cl}(d\text{-tart})\downarrow + 2\mathrm{H_2O}$$

$$4(-)\text{-}[\mathrm{Co(en)_3}](d\text{-tart}) + 4\mathrm{HCl} + \mathrm{O_2} \rightarrow 4(-)\text{-}[\mathrm{Co(en)_3}]\mathrm{Cl}(d\text{-tart})(sol.) + 2\mathrm{H_2O}$$

$$(-)\text{-}[\mathrm{Co(en)_3}]^{3+} + (+)\text{-}[\mathrm{Co(en)_3}]^{++} + \mathrm{Cl^-} + d\text{-tart}^{=} \rightarrow (-)\text{-}[\mathrm{Co(en)_3}]^{++} + (+)\text{-}[\mathrm{Co(en)_3}]\mathrm{Cl}(d\text{-tart})\downarrow$$

en = ethylenediamine; *d*-tart = *dextro*-tartrate radical

Submitted by J. A. Broomhead,* F. P. Dwyer,* and J. W. Hogarth†
Checked by Ronald D. Archer‡

The procedure which is illustrated by the above series of reactions combines the stereospecific influence of *d*-tartrate

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ion with a second-order asymmetric synthesis in order to obtain almost exclusively the *dextro* isomer of the tris(ethylenediamine)cobalt(III) ion. Bailar and coworkers[1] have shown that the synthesis of *d*-tartrato-bis(ethylenediamine)cobalt(III) ion yields unequal amounts of the (+) and (−) isomers, and when allowed to react with ethylenediamine an excess of *dextro*-tris(ethylenediamine)cobalt(III) ion results. Busch[2] crystallized a mixture of (+) and (−) $[Co(en)_3]Cl(d\text{-tart})$ until much of the less soluble (+)-diastereoisomer had separated and then in the absence of oxygen introduced a little (±)-$[Co(en)_3]Cl_2$. Electron transfer racemization of the (−)-diastereoisomer occurred with further separation of the (+)-diastereoisomer. In this way more than a 70% yield of the (+)-$[Co(3en)_3]^{3+}$ was obtained.

In the present method until oxidation is complete some $[Co(en)_3]^{++}$ ion is present to bring about electron transfer racemization. The necessary condition of separation of a solid phase is achieved by performing the reaction in 25 to 30% ethanolic solution in which (+)-$[Co(en)_3]Cl(d\text{-tart})$ alone is sparingly soluble. Addition of a little activated carbon facilitates oxidation and, as well, ensures rapid equilibrium between the various products.

Procedure

Solutions of cobalt(II) sulfate heptahydrate (28.1 g.; 0.1 mol) and sodium *d*-tartrate (23.0 g.; 0.1 mol), each dissolved in 50 ml. of water at 65°, are mixed and stirred. After about a minute purple-red cobalt(II) *d*-tartrate separates and the mixture is maintained at 65° for 15 minutes, then cooled in ice, and filtered. The precipitate is washed with 50 ml. of ice water, then acetone, and air-dried. Ethylenediamine (20.4 ml. of 88.6% w/v; 0.3 mol)* is placed in a 500-ml. filter flask fitted with a rubber stopper and a

* The concentrations are not critical but must be known in order to preserve the correct ratio.

wide glass tube for the entry of air. After dilution with water (50 ml.) and ethanol (30 ml.)* the mixture is cooled in ice. Hydrochloric acid (10 ml. of 10 *N*; 0.1 mol)† is added gradually and the solution cooled to 4 to 8°. The cobalt tartrate is added slowly with stirring, whereupon a red color changing to orange is obtained. Animal charcoal (4 g.) is added and a stream of air‡ sucked through for 2 hours. The orange diastereoisomer commences to separate within 15 to 30 minutes.

The product, mixed with charcoal, is filtered off§ and washed with 40% ethanol (60 ml.), the washings being discarded. The diastereoisomer is then extracted from the charcoal with successive portions of hot water¶ (60°). The final wash portion should be colorless, and usually 300 ml. will suffice. The extract is evaporated to a volume of 50 ml., and on cooling in ice the pure diastereoisomer separates as orange-yellow crystals, $[\alpha]_D = +103°$; the yield is 40 to 41 g. or 78 to 82% on the assumption of complete conversion to one isomer. Conversion to the iodide $[\alpha]_D = +91°$ is effected as in the previous synthesis. The yield is 43 to 44 g. or 60 to 65%.

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* This amount is sufficient to make the final solution 25% (by volume) ethanol. It is important that the percentage not exceed 30%, for otherwise the (+) and (−) tartrates, not the chloride *d*-tartrate, separate with very poor resolution.

† The concentrations are not critical but must be known in order to preserve the correct ratio.

‡ The rate of air flow should be sufficient to keep the charcoal in suspension and prevent blocking of the tube.

§ Addition of sodium iodide to the filtrate yields only a little racemic $[Co(en)_3]I_3$.

¶ Care must be taken that the water is not hotter than 60° or the extraction prolonged, for otherwise racemization is brought about by the charcoal and the yield is lowered.

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60. TRINITROTRIAMMINECOBALT(III)

$$2Co(C_2H_3O_2)_2 + 6NaNO_2 + 2NH_4C_2H_3O_2 + 4NH_3(aq.) + H_2O_2 \rightarrow 2Co(NH_3)_3(NO_2)_3 + 6NaC_2H_3O_2 + 2H_2O$$

SUBMITTED BY G. SCHLESSINGER*
CHECKED BY WILMA FAYE BARKER† AND MARK M. CHAMBERLAIN†

Trinitrotriamminecobalt is by far the most important starting material in the triamminecobalt series. It was first prepared by Erdmann[1] and later by Jørgensen[2] by the air-oxidation of ammoniacal cobalt(II) salt solutions containing sodium nitrite and much ammonium chloride. It has also been prepared by heating *trans*-dinitrotetrammine salts with sodium nitrite[3] and from ammonium tetranitrodiamminecobaltate(III) and aqueous ammonia.[4]

The following method, which is an adaptation of that of Duval,[5] makes use of the catalytic effect of charcoal in forming cobalt-nitrogen bonds and avoids the unnecessary use of ammonium chloride. This procedure is much shorter than air-oxidation methods and yields a relatively pure product in acceptable yield.

Procedure

Fifty grams (0.42 mol) of pure cobalt(II) carbonate is prepared by slowly adding a saturated solution of an equivalent quantity of the chloride, nitrate, or sulfate to a hot solution of 60 g. (0.57 mol) of anhydrous sodium carbonate in 600 ml. of water. Some effervescence takes place. The mixture is next digested at the boiling point for 15 minutes with continuous stirring and then suction-filtered, the solids

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washed freely with water, and pressed as dry as possible on the filter.*

The cobalt(II) carbonate prepared as above is dissolved in a hot mixture of 70 ml. of glacial acetic acid and 140 ml. of water. This solution is then added to a cold solution of 105 g. of sodium nitrite (1.52 mols) in 500 ml. of concentrated ammonia contained in a 2-l. Erlenmeyer flask. The resulting mixture is well cooled in ice and 280 ml. of 3% H_2O_2 is slowly added with good swirling. The flask is then allowed to remain 20 minutes longer in the ice bath and 3.5 g. of activated charcoal is added. The mixture is next heated for 1 hour over a free flame (in the hood, as much ammonia escapes) and the volume is kept constant by the addition of water as necessary. The hot liquid is filtered rapidly by suction to remove the charcoal, and the filtrate is cooled in an ice-water mixture. The product that separates (crystallization is aided by scratching the walls of the container) is suction filtered, the filtrate reserved for further workup, and the solids washed with ethanol and ether and then air-dried.

To the above filtrate is added 3 g. of charcoal, and the mixture is then evaporated in a beaker over a free flame with continuous stirring to a volume of 650 to 700 ml. and filtered by suction while hot. More product is isolated from the solution as described above. The total yield is 55 g. (53%). The product may be recrystallized from a volume of water, faintly acidified with acetic acid, equal to thirty times the weight of the dry material. This gives an analytically pure sample, but the crude nonelectrolyte as obtained above is quite satisfactory for further synthetic use.

Analysis of the nitro group is performed by decomposing the complex with dilute sodium hydroxide, running the filtrate into an excess of cerium(IV) sulfate (which oxidizes the

* If desired, technical cobalt(II) carbonate (51 g.) may be dissolved in the minimum amount of 1:1 hydrochloric acid, filtered, and reprecipitated as above.

nitrite quantitatively to nitrate), adding potassium iodide, and back-titrating the iodine with thiosulfate. Cobalt is determined by dissolving the cobalt(III) oxide obtained in alkali, decomposing with acidified potassium iodide, and titrating the liberated iodine with thiosulfate. *Anal.* Calcd. for $Co(NH_3)_3(NO_2)_3$: Co, 23.8; NO_2^-, 55.6. Found: Co, 23.8; NO_2^-, 55.3.

Properties

The complex is brownish yellow or mustard-colored, consisting of thin plates and some orthorhombic prisms. The solubility in water at 16.5° is 0.177 g./100 g. and at 100° about 1 g./30 g. Aqueous solutions of the material have a negligibly small conductivity, thus indicating the formulation of the material as a nonelectrolyte. Concentrated nitric acid produces the highly hygroscopic triaquotriamminecobalt(III) nitrate. Cold dilute hydrochloric acid replaces one nitro group in the complex, and oxalic acid in hot aqueous solution two nitro groups. Warm, concentrated hydrochloric acid forms dichloroaquotriamminecobalt(III) chloride. A complete description of properties is available.[6]

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61. RESOLUTION OF THE ETHYLENEDIAMINE-TETRAACETATOCOBALTATE(III) ION

SUBMITTED BY F. P. DWYER* AND F. L. GARVAN*
CHECKED BY STANLEY KIRSCHNER†

Busch and Bailar[1] obtained optically active solutions of one of the enantiomers of the ethylenediaminetetraacetatocobaltate(III) ion by selective adsorption on optically active quartz and by fractional crystallization of the strychnine salt. More recently Dwyer, Gyarfas, and Mellor[2] reported the complete resolution using *d* and *l*-tris(ethylenediamine) cobalt(III) chloride. Precipitation of the diastereoisomers was effected by addition of ethanol to the aqueous solution. The volume of ethanol used was critical and often merely the potassium salt separated.

Schwarzenbach[3] prepared the sparingly soluble salt *dl-cis*-dinitrobis(ethylenediamine)cobalt(III)ethylenediaminetetraacetatocobaltate(III). The present rapid method of resolution utilizes *d*- or *l-cis*-dinitrobis(ethylenediamine)cobalt(III) chloride as the resolving agent.

Procedure

Two and four tenths grams of *d-cis*-dinitrobis(ethylenediamine)cobalt(III) bromide (3.4×10^{-3} mol) is suspended in 35 ml. of water in a 100-ml. conical flask. Freshly precipitated silver chloride (6 g.) is added, the mixture heated to 50 to 60°, and the flask stoppered and shaken vigorously for 4 to 5 minutes. The mixture is kept at about 50 to 60° during this time by warming periodically. The mixture is filtered and the silver halide precipitate washed with 5 ml. of warm water. Four grams of potassium ethylenedia-

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minetetraacetatocobaltate(III)[2,4] is added to the filtrate,* which is then cooled in ice. On scratching the sides of the vessel, the diastereoisomer $[d\text{-Co(en)}_2(NO_2)_2]\cdot[\text{Co(enta)}]\cdot 3H_2O$ crystallizes out between 10 and 0°. The mixture is maintained at 0 to 4° for a further 5 minutes before filtering. The filtrate (*A*) is reserved. The diastereoisomer is washed with cold 50% aqueous ethanol, followed by ethanol and acetone in that order, and air-dried at room temperature. The yield is 2.6 g. A 0.02% aqueous solution in a 1-dm. tube gives $[\alpha]_{5461} = -0.1°$.† The substances can be crystallized from warm water by the addition of alcohol but this does not raise the rotation. *Anal.* Calcd. for $[\text{Co(en)}_2(NO_2)_2]\cdot[\text{Co(enta)}]\cdot 3H_2O$: C, 25.01; H, 5.10; N, 16.68. Found: C, 25.10; H, 5.11; N, 16.47.

***l*-K[Co(enta)]·2H₂O.** The diastereoisomer (2.0 g.) is suspended in 15 ml. of water in a mortar. Four grams of potassium iodide is added and the mixture triturated for 4 to 5 minutes. The insoluble iodide $d\text{-[Co(en)}_2(NO_2)_2]I$ precipitates and is filtered. Eighteen milliliters of ethanol is added slowly to the filtrate with scratching of the sides of the vessel, and the *levo* salt separates as sparkling violet plates. This is allowed to stand for 3 or 4 minutes. Then more ethanol is gradually added until a total volume of 40 ml. has been added. The crystals are collected and washed with cold ethanol. Recrystallization is usually not necessary, but may be effected by dissolution in 15 ml. of warm water followed by the addition of 40 ml. of ethanol. The crystals obtained are washed with ethanol and acetone and air-dried. The yield is 1.2 g., or, if the whole of the diastereoisomer is used (2.6 g.), 1.5 g., representing a 75% yield.

A 0.01% aqueous solution in a 1-dm. tube gives

$$\alpha_{5461} = -0.1°$$

* The specific rotation is $[\alpha]_{5461} = -500°$.

† The high optical density of even a 0.01% solution makes observation of the field difficult. The zero of the polarimeter should be found with 0.01% solution of racemate.

The specific rotation is $[\alpha]_{5461} = -1000°$. *Anal.* Calcd. for K[Co(enta)]·2H$_2$O: C, 28.45; H, 3.82; N, 6.64. Found: C, 27.65; H, 3.82; N, 6.56.

***d*-K[Co(enta)]·2H$_2$O.** The *dextro* isomer is obtained either from filtrate (*A*) or by using *l*-[Co(en)$_2$(NO$_2$)$_2$]Br to prepare the diastereoisomer as before. To the filtrate (*A*) is added 8 g. of potassium iodide; the mixture is cooled to 0 to 4° in ice with scratching of the sides of the vessel to facilitate deposition of the excess resolving agent as the iodide. After 10 minutes this is filtered off and ethanol (90 ml.) added. On scratching the sides of the vessel, violet-pink micaceous plates of the dextro isomer separate. These are collected after remaining in the vessel for 5 minutes, washed with cold 50% ethanol, ethanol, and acetone in that order, and air-dried. This fraction is 1.2 g. A 0.01% aqueous solution in a 1-dm. tube gives $\alpha_{5461} = +0.1°$. Purification can be effected by dissolution in 15 ml. of warm water followed by the addition of 40 ml. of ethanol on cooling. A second fraction (0.4 g.), partly racemate, can be obtained by the addition of a further 50 ml. of ethanol.

Properties

Potassium ethylenediaminetetraacetatocobaltate(III) undergoes no loss in rotation in aqueous solution at 20 to 25° in a month but slowly racemizes at 100° with a half-life of 168 minutes.[2] The salt shows a large rotatory dispersion. Thus for the *levo* isomer: $[\alpha]_{5461} = -1000°$, $[\alpha]_D = +150°$, and $[\alpha]_{4100} = +950°$. The diamagnetism of the hydrated[4] and anhydrous[2] salts and the almost exclusive preference of trivalent cobalt for the 6-covalent state suggest strongly that it is a hexadentate chelate.

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62. RESOLUTION OF *cis*-DINITROBIS(ETHYLENEDIAMINE)COBALT ION

SUBMITTED BY F. P. DWYER* AND F. L. GARVAN*
CHECKED BY STANLEY KIRSCHNER†

The *cis*-dinitrobis(ethylenediamine)cobalt(III) ion was first resolved by Werner[1,2,3] through the *d*-camphorsulfonate. However, that method, though it ultimately gives good yields of both optical antipodes, is laborious, and the resolving agent is comparatively expensive. Resolution is readily accomplished by the use of potassium *d*-antimony tartrate, and yields of each antipode of the order of 40 to 50% are obtained.

Procedure

It is necessary to adhere closely to the directions.

***Levo* Form.** Twelve grams of *dl-cis*-dinitrobis(ethylenediamine)cobalt(III) nitrite[4] (0.038 mol) is dissolved in 50 ml. of water at 60° by vigorous shaking. A solution of 7 g. of potassium *d*-antimony tartrate (0.02 mol) dissolved in 40 ml. of water at 75° by shaking is added rapidly. The mixture is immediately cooled under the tap to 25° and the sides of the flask scratched with a glass rod, whereupon the diastereoisomer $[l\text{-}\{Co(en)_2(NO_2)_2\}\cdot d\text{-}SbOC_4H_4O_6]$ separates in fine yellow crystals. The solution is kept for exactly 10 minutes at 25° with occasional shaking and then filtered. The filtrate *A* is reserved for extraction of the *dextro* form. The diastereoisomer is washed on the Büchner with 20 ml. of 50% aqueous ethanol, then ethanol, and finally acetone, and is air-dried. The yield is 5.5 to 6.0 g. *Anal.* Calcd. for $[Co(en)_2(NO_2)_2]\cdot SbO\cdot C_4H_4O_6$: C, 17.25; H, 3.62; N, 15.09. Found: C, 17.24; H, 3.68; N, 14.96. For a 0.171% solution

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of the diastereoisomer, $[\alpha]^{24°}_{obs.} = +0.081°$ in a 1-dm. tube; $[\alpha]^{24}_{D} = +47.4°$. The diastereoisomer (5.5 g.) is ground up in a mortar with 30 ml. of water. Seven grams of sodium iodide is added and the mixture triturated for 2 minutes. The sparingly soluble *l*-$[Co(en)_2(NO_2)_2]I$ separates, leaving sodium antimony tartrate in solution. The *levo* iodide is filtered through a Büchner and washed once with 15 ml. of ice water. The precipitate and filter paper* are transferred to a 100-ml. conical flask and shaken up vigorously with 30 ml. of water at 55°. Four grams of freshly precipitated silver chloride is added and the shaking continued for a further 3 minutes. The silver halide is filtered off and washed with 5 ml. of hot water. To the filtrate is added 3 g. of ammonium bromide.† The orange crystalline *levo* bromide separates on scratching and cooling in ice. After filtration through a Büchner funnel, the substance is washed with 10 ml. of 50% aqueous ethanol, then ethanol and acetone (in that order), and air-dried. The yield is 3.1 g. (47%). A 0.5% solution in water gives $[\alpha]_D = -0.44°$ in a 2-dm. tube, whence $[\alpha]_D = -44°$. *Anal.* Calcd. for $[Co(en)_2(NO_2)_2]Br$: C, 13.68; H, 4.59; N, 23.89; Br, 22.76. Found: C, 13.85; H, 4.62; N, 23.51; Br, 22.75.

***Dextro* Form.** To the filtrate *A* immediately after the removal of the *levo* diastereoisomer‡ is added 2 g. of ammonium bromide.† The sides of the flask are scratched with a glass rod and the mixture allowed to crystallize at 20 to 25° for 5 minutes. The impure *d*-bromide is collected and washed once on the Büchner with 10 ml. of ice water. From the filtrate *B* *dl*-$[Co(en)_2(NO_2)_2]I$ can be recovered by the addition of sodium or potassium iodide, 5 g. being a sufficient amount (yield approximately 40%). The impure

* The dispersed filter paper assists in the filtration of the silver halide.

† Equivalent amounts of sodium or potassium bromide may be substituted for ammonium bromide.

‡ The antimony tartrate of the *d*-form separates slowly on standing. The resolution depends on a difference not only in the solubilities of the diastereoisomers but in the rates of crystallization.

d-bromide and the filter paper* are transferred to a 100-ml., conical flask, shaken up vigorously with 35 ml. of water at 55°, and transformed to the chloride by the addition of 4 g. of freshly precipitated silver chloride with shaking for a further 3 minutes. After filtration of the silver halide, which is washed with 5 ml. of hot water, reprecipitation of the bromide is effected by the addition of 1.5 g. of ammonium bromide† and cooling at 20 to 25° for 10 minutes. The *d*-bromide is collected, washed, and dried as for the *l*-bromide above. The yield is 3.2 g., $[\alpha]_D = +0.44°$. *Anal.* Calcd. for *cis*-$[Co(en)_2(NO_2)_2]Br$: C, 13.68; H, 4.59; N, 23.89; Br, 22.76. Found: C, 13.70; H, 4.71; N, 24.01; Br, 22.71.

Properties

The optical antipodes of *cis*-$[Co(en)_2(NO_2)_2]Br$ are less soluble in water than the racemate. The solid may be heated at 130° for 60 minutes without loss of activity. At room temperature aqueous solutions show no rotational change in a month. Above 65° slow racemization occurs and this probably is accompanied by some isomerization.[4] At 78.5° the rate constant is 4.26×10^{-4} min.$^{-1}$, which corresponds to a half life of 27 hours.[5] Alkaline solutions are unstable, especially on warming.

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* The dispersed filter paper assists in the filtration of the silver halide.

† Equivalent amounts of sodium or potassium bromide may be substituted for ammonium bromide.

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63. BIS(ETHYLENEDIAMINE)NICKEL(II) CHLORIDE

$$2[Ni(en)_3]Cl_2{\cdot}2H_2O + NiCl_2{\cdot}6H_2O \rightarrow 3[Ni(en)_2]Cl_2{\cdot}xH_2O + aq.$$

SUBMITTED BY HAROLD M. STATE*
CHECKED BY F. P. DWYER,† I. K. REID,† AND J. W. HOGARTH†

Grossmann and Schück[1] obtained bis(ethylenediamine)-nickel(II) chloride (m.p. 157°) by concentrating and cooling a solution containing nickel(II) chloride and ethylenediamine in a 1:2 mol ratio, while Kurnakow[2] obtained only sticky, blue residues by a similar procedure. The latter result seems to be the more usual. The procedure described here is based upon a redistribution of ligands in methanol solution and precipitation of the complex by the addition of acetone.

Procedure

Five grams of nickel(II) chloride 6-hydrate and 12.1 g. of tris(ethylenediamine)nickel(II) chloride 2-hydrate‡ are gently refluxed for 5 minutes with a mixture of 47.5 ml. of methanol and 2.5 ml. of water, shaking at first until all the salts are dissolved. A beautiful deep blue solution results. This is filtered by gravity while still warm into a 400-ml. beaker, and the flask and paper are washed once with 5 ml. of hot methanol. Seed crystals are obtained by adding 3 to 4 ml. of acetone slowly to 2 to 3 ml. of the blue solution and scratching or shaking until crystals form; the separation of two liquid phases indicates the addition of too much acetone and makes the formation of crystals difficult.

Fifty milliliters of acetone is added from a dropping funnel in the course of 3 or 4 minutes to the bulk of the

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‡ The preparation of this compound is given in synthesis 64 in this volume.

well-stirred blue solution. A magnetic stirrer is most convenient. Fifty milliliters more of acetone is now added drop-wise while the stirring is continued; from time to time the solution is seeded with small quantities of the seed crystals previously prepared. When the crystals no longer dissolve, all the seed crystals may be added.

Stirring is continued for 10 minutes after the addition of the last of the acetone. The precipitated product is collected by suction on a coarse, sintered-glass crucible, washed twice with 15 to 20-ml. portions of acetone, and dried by placing in a 100 to 105° oven for ½ hour. The yield is 11 g. (84%). Equally satisfactory results are obtained if all quantities are doubled. *Anal.* Calcd. for $Ni(en)_2Cl_2$: Ni, 23.50; Cl, 28.39. Found: Ni, 23.54, 23.53; Cl, 28.45, 28.41.

Properties

Bis(ethylenediamine)nickel(II) chloride consists of pale blue prisms. It is very soluble in water, readily soluble in methanol, and only slightly soluble in acetone and absolute ethanol, but somewhat more soluble in 95% ethanol. In contrast to the 1-hydrate reported by Grossmann and Schück, the substance does not melt below 300° but appears to undergo a decomposition at about 290°, gradually changing to a white crystalline material.

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64. TRIS(ETHYLENEDIAMINE)NICKEL(II) CHLORIDE 2-HYDRATE TRIS(PROPYLENEDIAMINE)NICKEL(II) CHLORIDE 2-HYDRATE

$$NiCl_2 \cdot 6H_2O + 3C_2H_8N_2 \rightarrow [Ni(C_2H_8N_2)_3]Cl_2 \cdot 2H_2O + 4H_2O$$
$$NiCl_2 \cdot 6H_2O + 3C_3H_{10}N_2 \rightarrow [Ni(C_2H_8N_2)_3]Cl_2 \cdot 2H_2O + 4H_2O$$

SUBMITTED BY HAROLD M. STATE*
CHECKED BY I. K. REID† AND F. P. DWYER†

These two compounds are of use as starting materials in the preparation of bis(ethylenediamine)nickel(II) chloride and bis(propylenediamine)nickel(II) chloride 1-hydrate.

Procedure

For the preparation of tris(ethylenediamine)nickel(II) chloride 2-hydrate, 28 g. of 70% aqueous ethylenediamine is added to a solution of 23.8 g. (0.1 mol) of $NiCl_2 \cdot 6H_2O$ in 100 to 150 ml. of water. The purple solution is filtered to remove the small amount of hydrous iron oxide which precipitates and is then evaporated to a volume of 60 to 70 ml. on a steam bath. Two drops of ethylenediamine are added, and the solution is cooled in an ice bath. The orchid-colored crystals that form are collected by suction, washed twice with 95% ethanol, and air-dried. The yield is 28.6 g. (80%). Several more grams may be recovered from the mother liquor by adding ethanol and cooling. *Anal.* Calcd. for $[Ni(C_2H_8N_2)_3]Cl_2 \cdot 2H_2O$: Ni, 16.97%; Cl, 20.50%. Found: Ni, 16.87%; Cl, 20.48%.

For the preparation of tris(propylenediamine)nickel(II) chloride 2-hydrate, the above procedure is followed substituting 90% aqueous propylenediamine for the 70% ethyl-

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enediamine. The yield is 30.6 g. (84%). *Anal.* Calcd. for $[Ni(C_3H_{10}N_2)_3]Cl_2 \cdot 2H_2O$: Ni, 15.13%; Cl, 18.28%. Found: Ni, 15.12%; Cl, 18.22%.

65. TETRAKIS[PHOSPHORUS(III) CHLORIDE] NICKEL

$$Ni(CO)_4 + 4PCl_3 \rightarrow Ni(PCl_3)_4 + 4CO$$

SUBMITTED BY W. C. SMITH*
CHECKED BY E. O. BRIMM†

Tetrakis[phosphorus(III) chloride] nickel has been prepared by the reaction of nickel carbonyl with phosphorus(III) chloride at room temperature.[1] The synthesis of this compound as described below is based on this method.

Procedure

A three-necked, 500-ml. flask fitted with a thermometer, condenser, dropping funnel, and magnetic stirrer is flushed with dry carbon dioxide and charged with 68 g. (0.40 mol) of cooled nickel carbonyl under a carbon dioxide blanket.‡ A calcium chloride drying tube is attached to the outlet of the condenser to prevent moisture from entering the reaction vessel during later stages of manipulation. The dropping funnel is immediately charged with 438 g. (3.20 mols; 100% excess) of phosphorus(III) chloride and this is added dropwise to the nickel carbonyl in the reaction flask at room

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‡ Extreme caution must be exercised in handling nickel carbonyl. The properties of this material and the precautions to be taken in handling it have been described.[2] If the reaction is begun promptly, the carbon monoxide evolved will prevent oxygen from entering the reaction flask.

temperature with vigorous stirring over a 1-hour period. An instantaneous reaction occurs on the initial addition of the phosphorus(III) chloride, and carbon monoxide is evolved. There is no rise in temperature, and as the addition of the phosphorus(III) chloride is continued the carbon monoxide is evolved at a continuously decreasing rate.

When the addition of the phosphorus(III) chloride is complete, the reaction mixture is stirred for at least 16 hours at room temperature and then heated at reflux on a steam bath for about 2 hours or until black particles of nickel begin to appear in the clear, yellow solution. The resulting solution is handled under a blanket of dry carbon dioxide in all subsequent operations to prevent contact with atmospheric moisture. At this point the hot solution is filtered through a sintered-glass funnel of medium porosity and the negligible amount of residue is discarded. The filtrate is cooled to room temperature, allowed to stand for 48 hours, and the yellow crystalline product collected by filtration.* A second crop of crystals is precipitated by cooling the mother liquor in a solid carbon dioxide–acetone bath; this solid is separated by filtration as before and added to the first crop of crystalline product. The crude, moist product can be freed from most of the adhering phosphorus(III) chloride by passing nitrogen into a bottle containing the solid for a period of 1 to 2 hours; after such treatment the solid is essentially dry and may be pulverized without difficulty. The yield of this product is about 208 g. (86%).

The crude product may be purified,† if desired, by recrystallization either from *n*-pentane at −50° or from anhydrous diethyl ether that is chilled by the addition of solid carbon dioxide. This latter procedure is preferred since the presence of solid carbon dioxide during the process keeps

* Phosphorus(III) chloride may be used to aid in transfer of the product.

† While the product can be purified, it is more stable in the presence of small amounts of phosphorus(III) chloride, suggesting that an equilibrium is involved. The unpurified product has been stored for several months with little or no change, and although a slight pressure did build up in the storage container it did not become unduly high.

the solution cold and eliminates the need for jacketed filtration equipment. When the latter purification method is employed, a portion of the solid is dissolved in the minimum amount of anhydrous diethyl ether and the solution filtered to remove any particles of nickel present. Solid carbon dioxide is then added to the ethereal filtrate under nitrogen and in an amount such that solid carbon dioxide is present when the solution is cold. The product which precipitates, together with any solid carbon dioxide present, is then separated by filtration through a sintered-glass funnel under a nitrogen blanket. The solid product is stored in a container connected to a bubbler until the solid carbon dioxide present in the bottle has vaporized completely and the solid is at room temperature.

Properties

Tetrakis[phosphorus(III) chloride] nickel is a pale yellow crystalline solid at room temperature and becomes colorless on cooling to about $-30°$. This compound is stable in air when dry and unreactive with water at room temperature for a period of several days. It reacts slowly in the cold with dilute acids and with concentrated sulfuric or hydrochloric acid, but reacts rapidly in hot acid solutions. The compound reacts rapidly with ammonium hydroxide but more slowly with sodium hydroxide.[1] It is reported that no decomposition occurs below 120° when the solid is heated, but that at higher temperatures the solid is decomposed and phosphorus(III) chloride is liberated;[1] however, decomposition at 80° has been observed. Tetrakis[phosphorus(III) chloride] nickel appears to be nonvolatile.

The compound is readily soluble in organic solvents, *e.g.*, air-free benzene, carbon tetrachloride, pentane, and cyclohexane; the compound when dissolved in these solvents decomposes slowly at room temperature.[1] When the solutions are heated, decomposition is rapid and black precipitates of nickel are formed. The solution in pentane at

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$-50°$ is reported to contain 0.9 g./100 g. of pentane.[1] The product dissolves in alcohols and ketones but decomposition with the formation of green and brown solutions, respectively, is quite rapid. The solid dissolves in carbon disulfide but the solution darkens rapidly. The molecular weight of this compound determined by the freezing point depression method in benzene showed that the product was monomeric. Single crystals of tetrakis[phosphorus(III) chloride] nickel, several millimeters long, have been grown by cooling benzene solutions slowly from 25° to 10°. The density of the compound, as determined by the standard pycnometer method of weighing in water, is reported to be 2.10 ± 0.01 at 25°.[1]

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66. NITRIDO OSMIUM COMPOUNDS

Submitted by A. F. Clifford* and C. S. Kobayashi†
Checked by J. Wuller‡ and Therald Moeller‡

A. POTASSIUM NITRIDOOSMATE(VIII)

(Potassium Osmiamate)

$$OsO_4 + KOH + NH_3 \rightarrow KOsO_3N + 2H_2O$$

The salt potassium nitridoosmate(VIII) was first prepared by Fritsche and Struve[1] in 1847. Its preparation was further described by Joly[2] in 1891. The OsO_3N^- ion is of par-

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ticular interest because it is one of the few cases, except for those involving the elements carbon, nitrogen, and oxygen, in which nitrogen is bonded to only one atom. Other such cases are $OsCl_5N^=$, $OsBr_5N^=$, $ReO_3N^=$, MoO_3N^{3-}, $ClO_3N^=$, and possibly certain sulfur-nitrogen ions. The nitridorhenate,[3] nitridomolybdate,[4] and nitridoperchlorate[5] have only recently been prepared.

Procedure

Ten grams of osmium(VIII) oxide (0.0394 mol) and 10 g. of potassium hydroxide (0.179 mol) are dissolved in 5 ml. of water and the solution heated to 40°. Four milliliters of 6 *N* ammonium hydroxide is added until the dark brown color of the original solution lightens and golden crystals of potassium nitridoosmate(VIII) precipitate. An excess of ammonium hydroxide, which would result in precipitation of ammonium nitridoosmate(VIII), must be avoided. The crystals are filtered or centrifuged, washed with a minimum of cold water (not more than 5 ml.), and then recrystallized from 60 ml. of boiling water. The yields average 80% of the recrystallized product. Additional product, which is usually darker in color then the first crop of crystals, can be obtained by chilling or evaporating the mother liquor.

Properties

Potassium nitridoosmate(VIII) forms orange-yellow tetragonal crystals of density[6] 4.2. It is slightly soluble in water, only very slightly soluble in ethanol, and insoluble in ether. It is slightly sensitive to light, darkening upon long exposure. Darkening at 180° is also observed, while at higher temperatures the compound explodes. Heating to above 200° *in vacuo* causes nitrogen to be evolved, leaving a residue of potassium osmate and osmium(IV) oxide. Concentrated, aqueous potassium hydroxide (even hot) does not liberate ammonia from the compound. It darkens

slightly on crystallization from hot water and is reduced by concentrated hydrochloric or hydrobromic acid to K_2OsX_5N.

Solid potassium nitridoosmate(VIII) has an infrared absorption peak[7,8] at 1023 cm.$^{-1}$, which is attributable to osmium-nitrogen stretching, and osmium-oxygen peaks at 858 and 890 cm.$^{-1}$ (cf. 953 cm.$^{-1}$ in OsO_4).[8,9]

B. POTASSIUM PENTACHLORONITRIDOOSMATE(VI)

$$KOsO_3N + KCl + 6HCl \rightarrow K_2OsCl_5N + Cl_2 + 3H_2O$$

Potassium pentachloronitridoosmate(VI) was reported in 1901 by Werner and Dinklage.[6] It also is of interest because the nitrogen atom is bonded to only one other atom (osmium), making it a true nitride.

Procedure

Five grams of potassium nitridoosmate(VIII) (0.0172 mol) and 1.28 g. of potassium chloride (0.0172 mol) are mixed with 20 ml. of concentrated hydrochloric acid and allowed to stand with occasional stirring for ½ hour. The red crystalline solid is collected on a medium-porosity, fritted-glass filter. The product may be purified by quickly dissolving it in cold water, filtering, and reprecipitating with concentrated hydrochloric acid. The yields average 55%.

Properties

Potassium pentachloronitridoosmate(VI) consists of red prismatic crystals or a reddish-brown powder, freely soluble in water. Its dilute aqueous solutions slowly decompose giving a brown precipitate. The salt is insoluble in organic solvents, but moderately soluble in concentrated hydrochloric acid, giving intensely red solutions. Aqueous alkalies cause decomposition but do not liberate ammonia. The

salt is oxidized by ozone[10] to potassium nitridoosmate(VIII) and reduced by tin(II) chloride and hydrochloric acid to $K_2OsCl_5NH_2$. The infrared spectrum of the solid shows an absorption peak at 1073 cm.$^{-1}$, attributable to osmium-nitrogen stretching,[7,8] and at 335 cm.$^{-1}$, attributable to osmium-chlorine[11] (cf. 350 cm.$^{-1}$ in K_2OsCl_6).[12]

C. TRIOXO(*t*-BUTYLNITRIDO) OSMIUM(VIII)[8]

(*N*-*t*-Butyl Osmiamate)

$$OsO_4 + (CH_3)_3CNH_2 \rightarrow (CH_3)_3CNOsO_3 + H_2O$$

Procedure

Five grams (0.0197 mol) of osmium(VIII) oxide, dissolved in 100 g. of purified pentane, is chilled in a salt-ice mixture.* Fifteen grams (0.205 mol) of *t*-butylamine is added rapidly with efficient stirring. Stirring is continued for 5 minutes, and then the solution is filtered through a fine-porosity, sintered-glass funnel to remove the small amount of light brown impurity which may have been formed. The filtrate will be purplish due to the presence of unidentified by-products resulting from the reduction of the osmium(VIII) oxide. The pentane solution is poured into 1 l. of distilled water.† The crude trioxo(*t*-butylnitrido) osmium(VIII) appears as a light yellow curdy precipitate. The mixture is filtered through a sintered-glass funnel and the product is recrystallized twice from diethyl ether. Additional purification can be accomplished by sublimation in an all-glass‡ apparatus at 10^{-3} mm. and 40 to 50°. Yields of crude product up to 60% are obtained.

* The purity of the pentane is very important. Use of ordinary pentane cuts the yield to less than half of what is obtained with purified pentane.

† The checkers have noted that if the pentane solution is stirred for several minutes in an open beaker before filtration to allow concentration of the solution, considerable improvement of yield results.

‡ The compound attacks mercury and stopcock grease.

Properties

As first obtained from pentane, trioxo(*t*-butylnitrido) osmium(VIII) is a light yellow, fibrous solid. Recrystallized from petroleum ether, it occurs as bright yellow needles, while the solid obtained by sublimation consists of large, orange-yellow needles. This compound possesses an obnoxious odor at room temperature, sublimes *in vacuo* at 40 to 50°, and decomposes at 112° giving a black liquid. It is soluble in diethyl ether, petroleum ether, and carbon tetrachloride but insoluble in and stable to water and dilute nitric acid. It reacts with concentrated hydrochloric acid to produce $OsCl_5N^-$ and chlorine. With aqueous potassium hydroxide it reacts slowly to give potassium osmate. In daylight it darkens over a period of days but is stable in the dark. The infrared spectrum[8] of a solution in carbon tetrachloride shows a peak at 1184 cm.$^{-1}$, attributable to osmium-nitrogen stretching, and peaks at 912 and 925 cm.$^{-1}$, attributable to osmium-oxygen (cf. 1023, 858, and 890 cm.$^{-1}$ in OsO_3N^-).[7,8]

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67. PLATINUM(II) CHLORIDE

$$H_2PtCl_6 \cdot 6H_2O \xrightarrow[115°]{Cl_2} PtCl_4 + 2HCl + 6H_2O$$

$$PtCl_4 \xrightarrow[450°]{Cl_2} PtCl_2 + Cl_2$$

SUBMITTED BY ALVIN J. COHEN*
CHECKED BY B. A. FERRONE†

Berzelius[1] prepared platinum(II) chloride by evaporation of a solution of hexachloroplatinic(IV) acid and heating of the residue to about 300 to 350° with constant stirring. This method has been more recently modified by Kharasch and Ashford.[2] Nilson[3] obtained a more pure product by evaporation of a solution of tetrachloroplatinic(II) acid. The preparation of pure platinum(II) chloride from readily obtainable hexachloroplatinic(IV) acid 6-hydrate is given here. This is an adaptation of the method of Wöhler and Streicher.[4]

Procedure

Six grams of crystalline hexachloroplatinic(IV) acid, $H_2PtCl_6 \cdot 6H_2O$, is used to prepare platinum(IV) chloride according to directions given in Synthesis 81 of Volume II of this series.‡ The pulverized material is again placed in the combustion tube and heated slowly to 450° in a steady stream of dry chlorine. Overheating should be avoided, for although platinum(II) chloride is stable between 435 and 581°, it sublimes completely above 560°. The material

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‡ The directions of pages 253 and 254 are followed to the next-to-last sentence "The pulverized material is again. . . ." Then the directions above are continued from that point.

should be kept at 450° for 2 hours. Some sublimation of the product may occur, deep red (almost black) needles forming on the cooler portions of the combustion tube. This sublimate may be added to the final product. The platinum(II) chloride is removed from the combustion tube while the temperature of the tube remains at 450° and is cooled in a desiccator.

A small portion of the product is tested for any unreacted platinum(IV) chloride by leaching with a few drops of hot water. An equal volume of a saturated solution of ammonium chloride is added to the leach water, and if there is no precipitate within 1 minute the product is pure. If a precipitate appears, the entire product should be leached with water until free of the soluble platinum(IV) chloride. The purified product is partially dried by suction filtration and finally completely dried by a drying agent in a desiccator. The yield is 2.8 g. (91% based on $H_2PtCl_6 \cdot 6H_2O$). *Anal.* Calcd. for $PtCl_2$: Pt, 73.3; Cl, 26.6. Found: Pt, 73.0; Cl, 26.8.*

Properties

Platinum(II) chloride prepared by this method is a brownish-green, nonhygroscopic powder, practically insoluble in water but soluble in hydrochloric acid to form tetrachloroplatinic(IV) acid by disproportionation.

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* A preparation of platinum(II) chloride by a different method appears in Vol. V of Inorganic Syntheses.

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68. *cis-* AND *trans*-DICHLOROBIS(DIETHYL SULFIDE)PLATINUM(II)

SUBMITTED BY GEORGE B. KAUFFMAN* AND DWAINE O. COWAN*
CHECKED BY F. P. DWYER,† J. W. HOGARTH,† AND A. M. SARGESON†

Although dipole moment measurements would seem to provide an effective tool for experimentally determining the configuration of coordination compounds, very few such stereochemical studies have been performed. Not only are most complexes ionic and therefore not amenable to dipole-moment measurements, but also the majority of otherwise suitable nonelectrolyte complexes are insoluble in nonpolar solvents.‡ Dipole-moment measurements of isomers of type $[Pt(R_2S)_2X_2]$, which are among the few complexes soluble in benzene, enabled Jensen[1] to refute the view[2] that these compounds were structural isomers containing tetrahedral platinum. Instead, he showed them to be true stereoisomers, the configuration of tetracovalent platinum being planar. Contrary to Werner's previous view,[3] Jensen proved that the α-compounds were the *trans* isomers, while the β-compounds were the *cis* isomers, in agreement with other evidence.[4,5]

The action of an equivalent amount of the alkyl sulfide on potassium tetrachloroplatinate(II) yields the bright yellow *trans* chloride, while excess sulfide gives the very weakly greenish-yellow *cis* chloride.[1,2,6,7] Since separation of the two isomers is a difficult and lengthy process, experimental conditions should be chosen so that only one isomer is formed. This is done, as far as possible, in the methods given below for the diethyl sulfide compounds.

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‡ This is seen in the syntheses of *cis-* and *trans*-dichlorodiammineplatinum(II) and *cis-* and *trans*-tetrachlorodiammineplatinum(IV).

Procedure

The melting points of these isomers are very sensitive to impurities (see properties). The diethyl sulfide used in these preparations is freed of mercaptan impurities by shaking with mercury(II) oxide, followed by filtration and distillation; only the fraction boiling at 92 to 93° is used.

A. *cis*-DICHLOROBIS(DIETHYL SULFIDE)PLATINUM(II)

$$K_2PtCl_4 + 2(C_2H_5)_2S \text{ (excess)} \rightarrow \textit{cis}\text{-}[Pt\{(C_2H_5)_2S\}_2Cl_2] + 2KCl^*$$

A solution of 4.15 g. (0.01 mol) of potassium tetrachloroplatinate(II) in 50 ml. of water is shaken vigorously in a 250-ml., glass-stoppered Erlenmeyer flask with 4.31 ml. (3.61 g. = 0.04 mol) of diethyl sulfide (density, 0.837) until the originally deep red supernatant liquid has become colorless (ca. 15 minutes). The mixture is allowed to remain in the stoppered flask for about 24 hours, whereupon the yellow precipitate of *trans* isomer initially formed above dissolves. The resulting clear yellow solution is filtered if necessary, transferred to an evaporating dish, and evaporated to dryness at room temperature.† *Caution.* A hood should be used. This evaporation can be accomplished in about 10 to 20 hours if a constant flow of air is maintained above the dish.

The isomer is extracted from the residue by treatment with a minimum amount (50 to 60 ml.) of hot benzene. The white residual potassium chloride is removed by filtration.‡ After filtration the benzene solution is evaporated to half volume and cooled in an ice bath (freezing point of benzene is 5.5°), whereupon fine, yellow crystals of the *cis* isomer form. The crystals are separated by suction filtra-

* The following steps have been suggested for the reaction by other workers:

(1) $K_2PtCl_4 + 2(C_2H_5)_2S \rightarrow \textit{trans}\text{-}[Pt\{(C_2H_5)_2S\}_2Cl_2] + 2KCl$

(2) $\textit{trans}\text{-}[Pt\{(C_2H_5)_2S\}_2Cl_2] + 2(C_2H_5)_2S \rightarrow [Pt\{(C_2H_5)_2S\}_4]Cl_2$

(3) $[Pt\{(C_2H_5)_2S\}_4]Cl_2 \rightarrow \textit{cis}\text{-}[Pt\{(C_2H_5)_2S\}_2Cl_2] + 2(C_2H_5)_2S$

† Heating may cause decomposition of the isomer.

‡ It is suggested by the checkers that the dry filter be heated.

tion and washed with several 5-ml. portions of petroleum ether to remove any *trans* isomer. The crystals are then dissolved in a minimum amount (ca. 5 ml.) of hot acetone. Cold petroleum ether (ca. 3 ml.) is added slowly to the hot acetone solution until the mixture just becomes cloudy, and the mixture is then cooled in an ice-salt bath until crystallization seems complete (ca. $\frac{1}{2}$ hour). The resulting greenish-yellow flakes are separated by suction filtration and air-dried. The yield is 3.14 g. (70.3%).* *Anal.* Calcd. for $Pt(C_2H_5)_2S_2Cl_2$: Pt, 43.73; C, 21.51; H, 4.52; S, 14.35; Cl, 15.88. Found: Pt, 43.46; C, 21.63; H, 4.58; S, 14.22; Cl, 16.01.

B. *trans*-DICHLOROBIS(DIETHYL SULFIDE)PLATINUM(II)

$$K_2PtCl_4 \text{ (excess)} + 2(C_2H_5)_2S \rightarrow \textit{trans}\text{-}[Pt\{(C_2H_5)_2S\}_2Cl_2] + 2KCl$$

A solution of 4.15 g. (0.01 mol) of potassium tetrachloroplatinate(II) in 50 ml. of water is placed in a 250-ml., glass-stoppered Erlenmeyer flask. Two and one-tenth milliliters (1.76 g. = slightly less than 0.02 mol) of diethyl sulfide (density, 0.837) is added† to this solution in small portions, the mixture being shaken vigorously after each addition to ensure complete reaction.‡ The bright yellow precipitate is immediately separated from the reddish solution by suction filtration, washed at once with several 5-ml. portions of ice-cold alcohol, and then washed with several 5-ml. portions of cold water to remove the potassium chloride. The crystals are dissolved in a minimum amount (ca. 6 ml.) of hot ethanol and the solution cooled in an ice-salt bath. The bright yellow needles are separated by suction filtration and air-dried. The yield is 2.3 g. (51.5%).§ *Anal.* Calcd.

* The checkers obtained a yield of 3.06 g. (m.p. 105 and 107.5°) after recrystallization from acetone and petroleum ether.

† The diethyl sulfide is best added from a microburet.

‡ Stepwise addition of less than the theoretical amount of diethyl sulfide prevents formation of the *cis* isomer.

§ The checkers obtained a yield of 2.4 g. (m.p. 105 and 105.5°) after recrystallization from alcohol.

for $Pt(C_2H_5)_2S_2Cl_2$: Pt, 43.73; C, 21.51; H, 4.52; S, 14.35; Cl, 15.88. Found: Pt, 43.72; C, 21.57; H, 4.50; S, 14.04; Cl, 16.09.

Properties[1]

Both the *cis* and *trans* compounds are yellow, the former possessing a greenish tinge. Both melt at 107 to 108°, but the melting point of either isomer is lowered tremendously by even traces of impurities such as the other isomer, diethyl sulfide, or mercaptans. Thus, "surplus" or "extra" isomers with lower melting points reported by some investigators[8,9] have been shown to be merely contaminated *cis* or *trans* isomers.

Both isomers are only slightly soluble in water, but are readily soluble in benzene, carbon tetrachloride, chloroform, methanol, and ethanol. However, only the *trans* isomer is soluble in petroleum ether. Both are nonelectrolytes, but the conductivities of both aqueous and alcoholic solutions of the *cis* isomer increase with time because of aquation and alcoholation, the latter taking place to the greater extent, *e.g.*,

$$[Pt\{(C_2H_5)_2S\}_2Cl_2] + 2CH_3OH \rightleftharpoons [Pt\{(C_2H_5)_2S\}_2(CH_3OH)_2]^{++} + 2Cl^-$$

The same reactions occur much more slowly with the *trans* isomer.

The possibility that the compounds might be "polymerization isomers" has been eliminated by cryoscopic determinations of molecular weights in benzene solution, which showed both isomers to be monomolecular. Dipole moments in such solutions were found to be 9.5 D. for the *cis* isomer and 2.41 D. for the *trans* isomer. The latter is not zero since the four ethyl groups lie on the same side of the plane containing the platinum, chlorine, and sulfur atoms. Interconversion of the isomers does not occur read-

ily in benzene solution, as shown by the constancy of dielectric constant measurements over a long period of time.

The chlorine atoms in these compounds are unusually labile, especially in the case of the *cis* isomer, which in aqueous and alcoholic solution yields an immediate precipitate with silver nitrate, while the *trans* isomer reacts more slowly. This lability also causes interconversion to occur readily, as during recrystallization from water or often in metatheses. The two isomers can readily be distinguished by treatment with silver(I) oxide.[2] The *cis* compound reacts immediately to give the soluble strong base $[Pt\{(C_2H_5)_2S\}_2(OH)_2]$, while the *trans* compound slowly decomposes to black platinum(II) oxide and diethyl sulfide, the solution remaining neutral.

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69. METAL-DIOLEFIN COORDINATION COMPOUNDS

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CHECKED BY RICHARD N. RHODA†

The unique bonding and the variety of structures presented by metal-olefin compounds have provided the stimulus for recent study of this class of compounds. Although many aspects of the bonding and structure of these compounds are still obscure, several general methods have been developed for their synthesis. The following series of preparations deals with the metal-olefin compounds containing more than one double bond in the hydrocarbon moiety. These preparations illustrate methods that may readily be adapted to the preparation of a number of metal-olefin compounds in which the hydrocarbon is a diolefin.

Procedure

A. POTASSIUM HEXACHLORO-μ-1,4-BUTADIENE-DIPLATINATE(II)

$$2K_2PtCl_4 + C_4H_6 \rightarrow K_2(Cl_3PtC_4H_6PtCl_3) + 2KCl$$

Chatt[1] has prepared and investigated this complex and presented evidence to show that the butadiene acts as a bridging group between two $PtCl_3^-$ units. The present preparation represents a slight modification of his procedure particularly with regard to the control of the acidity of the potassium tetrachloroplatinate(II) solution.

One gram of dry potassium tetrachloroplatinate(II)‡ is dissolved in 15 ml. of 5% hydrochloric acid. The container is thoroughly flushed with gaseous butadiene and then charged with butadiene to a pressure of 100 cm. The pres-

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† The International Nickel Company, Inc., Bayonne, N.J.
‡ This compound can be prepared according to R. N. Keller.[2]

sure gradually decreases and in a few hours additional amounts of butadiene must be added to maintain the pressure at 100 cm.

After $1\frac{1}{2}$ to 2 days the original red solution will turn to a light yellow color. Crystals of the compound may be obtained by either of the following techniques: The solution can be placed in a vacuum desiccator over potassium hydroxide and the solvent removed by evacuation of the desiccator with a water aspirator; or the solution can be slowly evaporated in a desiccator utilizing calcium chloride and potassium hydroxide as absorption agents.* By the latter method, orange needle-shaped crystals can be formed. It is essential that solutions of the complex have a pH of 1 or lower to prevent decomposition to metallic platinum. *Anal.* Calcd. for $K_2Pt_2Cl_6C_4H_6$: Pt, 53.1; Cl, 29.0. Found: Pt, 53.3; Cl, 30.2.†

The orange crystals decompose in vacuum at 265°, and the material is stable in dry air.

B. DICHLORO-μ-1,4-BUTADIENE-DICOPPER(I)

$$2CuCl + C_4H_6 \rightarrow ClCuC_4H_6CuCl$$

The method of preparation of the copper(I) chloride–1,4-butadiene complex has been described by Gilliland and coworkers.[3] The following procedure uses liquid 1,4-butadiene in contrast with the previous gas phase reactions.

Gaseous 1,4-butadiene is liquefied with a slush of Dry Ice in trichloroethylene, with provisions made to protect the liquid hydrocarbon from condensation of atmospheric moisture. Anhydrous copper(I) chloride is added to the liquid diolefin and the mixture allowed to stand at −10° for 1 hour. The excess butadiene is evaporated off at room temperature and the complex remains as a pale yellow solid.‡

* Drying time for the final product is from 2 to 3 weeks.

† The checker obtained an average yield of 83.6%.

‡ The checker reports decomposition of the yellow solid to be further prevented by evaporating the excess butadiene off at room temperature in a stream of dry argon. Without the use of this argon the complex seems to decompose readily.

The yields are quantitative.* *Anal.* Calcd. for $Cu_2Cl_2C_4H_6$: Cu, 50.8; Cl, 28.1. Found: Cu, 50.5; Cl, 28.7.

The pale yellow solid quickly decomposes when exposed to air; however, it may be stored in a closed container or desiccator. An analogous compound with similar stability characteristics may be prepared by the reaction of 1,4-butadiene and copper(I) bromide.

C. DICHLORO-(1,4-BUTADIENE)PALLADIUM(II)

$$PdCl_2 + 2C_6H_5C{\equiv}N \rightarrow PdCl_2(C_6H_5C{\equiv}N)_2$$
$$PdCl_2(C_6H_5C{\equiv}N)_2 + C_4H_6 \rightarrow PdCl_2C_4H_6 + 2C_6H_5C{\equiv}N$$

The procedure described by Kharasch[4] for the preparation of complexes of palladium and olefins containing a single double bond has been extended to the preparation of the 1,4-butadiene–palladium(II) chloride complex in the following procedure.

Two grams of anhydrous palladium(II) chloride is suspended in 50 ml. of benzonitrile and the mixture warmed to 100°. After 20 minutes the greater part of the palladium(II) chloride has dissolved to give a red solution. This solution is filtered while it is still warm and the filtrate is poured into 300 ml. of low-boiling petroleum ether. The product, light yellow in color, is removed by filtration and washed with additional quantities of petroleum ether. The yield is 4.0 g. or 93% of the theoretical yield.

The 1,4-butadiene complex is prepared by dissolving 1.5 g. of palladium(II) chloride–benzonitrile in the minimum amount of benzene and filtering the dark red solution to remove undissolved solids. A steady stream of 1,4-butadiene is passed through the solution, changing the color from red to yellow; after no further color change is observed, the reaction is stopped. Petroleum ether is added to the yellow solution, which causes the precipitation of a light yellow flocculent material. After filtering with suction and washing with further quantities of petroleum ether, the

* An average yield of 86.3% was obtained by the checker.

product is allowed to dry in air. *Anal.* Calcd. for $PdCl_2$-C_4H_6: Pd, 45.6; C, 20.8; H, 2.6. Found: Pd, 45.5; C, 21.5; H, 2.9.*

The compound is stable and may be heated in vacuum to 80° before extensive decomposition occurs.

D. FURTHER COMPOUNDS

It is to be noted that further compounds in this series can be readily prepared. These include dichloro(dicyclopentadiene)platinum(II), chloromethoxy(dichloropentadiene)platinum(II), and diiodo(dicyclopentadiene)platinum(II). Adequate syntheses of these compounds have been given.[5]

References

1. J. CHATT and L. A. DUNCANSON: *J. Chem. Soc.*, **1953**, 2939.
2. R. N. KELLER: INORGANIC SYNTHESES, **2**, 247–250 (1946).
3. E. R. GILLILAND, H. L. BLISS, and C. E. KIP: *J. Am. Chem. Soc.*, **63**, 2088 (1941).
4. M. S. KHARASCH, R. C. SEYLER, and F. R. MAYO: *ibid.*, **60**, 882 (1938).
5. J. R. DOYLE and H. B. JONASSEN: *ibid.*, **78**, 3965 (1956).

* The checker obtained a yield of 79%.

Inorganic Syntheses, Volume VI
Edited by Eugene G. Rochow

SUBJECT INDEX

Names employed in the cumulative subject index for Volumes I to VI are based upon those adopted in Volume II (Appendix, page 257) 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.

Some of the general principles that have been followed in setting up the index are: (1) The Stock system, based on the use of Roman numerals to designate oxidation state, has been generally preferred; for example, *Iron(III) chloride*, rather than ferric chloride; *Potassium hexachlororhenate-(IV)* rather than potassium chlororhenite. (2) In the case of heteropoly acids, the structure-determining element is named last, as for instance, *12-Tungstophosphoric acid* instead of phosphotungstic acid. (3) General headings such as *Chromium(III) complex compounds* and *Ammines* are employed for grouping coordination compounds of similar types. In addition, entries are made under the specific names for individual compounds. (Halogeno and cyano complexes, however, have been entered only under their specific names.) (4) Numerical prefixes and prefixes such as "ortho-" and "meta-" (but not "hypo-" and "per-") have been dropped at the beginning of many names to form general headings covering classes of compounds, such as *Silicon chlorides* and *Phosphoric acids*. (5) Formulas for specific compounds are used under general headings. The Formula Index should also prove particularly helpful in troublesome cases. (6) Because of changes in practice since the appearance of Volume I, it has been deemed advisable to make extra entries or cross references under names that have been changed and under many specific names for compounds entered also under general headings. (7) Two entries are made for compounds having two cations. (8) Unsatisfactory names that have been retained for want of better ones are placed in quotation marks.

Inverted names are used only for derivatives of silanes (as *Silane, dibromo-;* and *Disilane, hexachloro-*), germanes, phosphine, and the like, but not for the few organic compounds. For the nomenclature of some of these and other classes of compounds, see the heading *Nomenclature.*

Headings are alphabeted straight through, letter by letter, as in *Chemical Abstracts* indexes, not word by word. Roman numerals in Stock names are ignored in alphabeting unless two or more names are otherwise the same.

B

C

D

E

F

G

H

M

O

R

T

U

V

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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. To this end, formulas have been used wherever it seemed best in their usual form (*i.e.*, as used in the text) for easy recognition: PbO_2, $EuSO_4$, Si_2C_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): $PtCl_4K_2$; $[Al(C_2O_4)_3]K_3 \cdot 3H_2O$; $(IO_6)_2Ba_3H_4$. The guiding principle in these cases has been the chapter in the text in which the preparation of a compound 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 (simple halides other than fluorides are entered only under the other elements in most cases); $NaNH_2$ and NH_2Na; NH_2SO_3H and SO_3HNH_2.

Formulas for organic compounds are structural or semistructural so far as possible: $CH_3COCH_2COCH_3$. 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; $Zr(C_5H_7O_2)_4 \cdot 10H_2O$; $NaC{\equiv}CH$ and $CH{\equiv}CNa$.

The names used with the formulas are the preferred specific names.

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. 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 $C_2H_8N_2$)
NH_3

$Si(CH_3)Cl_3$
$Si(CH_3)_3Cl$
$Si(CH{=}CH_2)Cl_3$
$Si(C_2H_4Cl)Cl_6$

$Cr(CN)_6K_3$ (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" and a few similar abbreviations are retained for simplicity and are alphabeted as such rather than as $C_2H_4(NH_2)_2$ or $(NH_2)_2C_2H_4$, etc.)

C

G

H

I

K

O

P

R

S

T