INORGANIC
SYNTHESES

Volume X

Editor-in-Chief

EARL L. MUETTERTIES

E. I. du Pont de Nemours & Company

INORGANIC SYNTHESES

Volume X

McGRAW-HILL BOOK COMPANY

New York   San Francisco   Toronto   London   Sydney

INORGANIC SYNTHESES, VOLUME X

PREFACE

In Volume X synthetic procedures are presented for fifty-eight compounds. This group of fifty-eight compounds covers three main areas of inorganic chemistry. One is the chemistry of metal compounds, particularly transition metals; the second covers some aspects of the rapidly growing field of boron chemistry; and the third deals with the chemistry of three elements from group V of the periodic table, namely, nitrogen, phosphorus, and arsenic. Previously, the syntheses in a volume of INORGANIC SYNTHESES were arranged on the basis of the Mendeleev periodic classification with subdivision into A and B groups. This practice is followed in the present volume in spirit but not in detail. Any arrangement will be in some cases somewhat arbitrary. Attention is called to the fact that a number of the boron compounds based on boron-nitrogen ring systems have not been placed in Chap. 2 dealing with boron chemistry but in Chap. 3 under the nitrogen subsection. This decision was made because in the nitrogen section a general exposition is given for the synthesis of amino and imino derivatives; and on this basis, the placement of the boron compounds was a logical one.

In the last two years, a number of administrative and procedural changes have been made within Inorganic Syntheses, Inc., which is a nonprofit organization. Of these changes, one of the most significant is the adoption of an annual publishing policy. Volume X of INORGANIC SYNTHESES is the second volume to come under this new publishing policy. There has been no change in the underlying philosophy behind the INORGANIC SYNTHESES series. The objective remains the same: to

provide well-characterized syntheses of compounds which are of general interest to chemists. We still consider reproducibility a critical element for all our syntheses; and for that reason, we are continuing to require experimental checks of all syntheses in independent laboratories. In consideration of the objectives and also the mechanism for achieving these objectives, INORGANIC SYNTHESES is the product of and for the general scientific community. For that reason, we heartily encourage a more widespread participation in this publishing endeavor by members of the scientific community. There are several areas of synthetic inorganic chemistry, for example, solid-state chemistry, which have not been adequately represented in past volumes of INORGANIC SYNTHESES, and we hope that this can be rectified in the future.

The following section entitled *Notice to Contributors* provides a detailed characterization of the present editorial policy. It should be noted that manuscripts are no longer submitted directly to the editor-in-chief but to the secretary to the Editorial Board, who is Dr. S. Kirschner, Department of Chemistry, Wayne State University, Detroit, Michigan 48202. Volume XI is being edited by Dr. W. L. Jolly, and he will be succeeded by Dr. R. W. Parry for Volume XII.

The individual contributions of those who submitted procedures for Volume X and the checkers of the procedures are specifically acknowledged in Chaps. 1 through 3. I am also deeply grateful for the assistance given me by members of INORGANIC SYNTHESES. In particular, I would like to thank Miss Janet D. Scott for handling all the problems on nomenclature and indexing and for assistance in the final editing of the manuscript. I would also like to thank my associates in Central Research Department for their help in many phases of the preparation of Volume X. I am greatly indebted to Miss Marjorie Ridsdale for the typing, proofreading, and assistance in editing the manuscript.

Earl L. Muetterties

NOTICE TO CONTRIBUTORS

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

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

The Editorial Board lists the following criteria of content for submitted manuscripts: Style should conform with that of previous volumes of INORGANIC SYNTHESES. The *Introduction* should include a concise and critical summary of the available procedures for synthesis of the product in question. It should also include an estimate of the time required for the synthesis, an indication of the importance and utility of the product, and

an admonition if any potential hazards are associated with the procedure. The *Procedure* should present detailed and unambiguous laboratory directions and be written so that it anticipates possible mistakes and misunderstandings on the part of the person who attempts to duplicate the procedure. Any unusual equipment or procedure should be clearly described. Line drawings should be included when they can be helpful. All safety measures should be clearly stated. Sources of unusual starting materials must be given, and, if possible, minimal standards of purity of reagents and solvents should be stated. The scale should be reasonable for normal laboratory operation, and any problems involved in scaling the procedure either up or down should be discussed. The criteria for judging the purity of the final product should be clearly delineated. The section on *Properties* should list and discuss those physical and chemical characteristics that are relevant to judging the purity of the product and to permitting its handling and use in an intelligent manner. Under *References,* all pertinent literature citations should be listed in order.

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

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

CONTENTS

3. W. JOLLY: "Synthetic Inorganic Chemistry," p. 161, Prentice-Hall, Inc., Englewood Cliffs, N.J., 1960.

CORRECTION

In the synthesis procedure for chlorine(IV) oxide in Volume IV, page 153, the required approximate amount of sodium chlorite should be 0.13 g. instead of 1.3 g.

Chapter One

METAL COMPOUNDS

1. TITANIUM(IV) IODIDE

$$Ti + 2I_2 \rightarrow TiI_4$$

Submitted by R. NEIL LOWRY* and ROBERT C. FAY*
Checked by B. L. CHAMBERLAND†

Titanium(IV) iodide may be prepared by a variety of methods. High-temperature methods include reaction of titanium metal with iodine vapor,[1-3] titanium carbide with iodine,[4] titanium(IV) oxide with aluminum(III) iodide,[5] and titanium(IV) chloride with a mixture of hydrogen and iodine.[6] At lower temperatures, titanium(IV) iodide has been obtained by the combination of titanium and iodine in refluxing carbon tetrachloride[7] and in hot benzene or carbon disulfide;[8] a titanium-aluminum alloy may be used in place of titanium metal.[9] It has been reported that iodine combines directly with titanium at room temperature if the metal is prepared by sodium reduction of titanium(IV) chloride and is heated to a high temperature before iodine is

admitted into the reaction chamber.[10]   Titanium(IV) iodide may also be prepared by passing dry hydrogen iodide into warm titanium(IV) chloride which is gradually raised to its boiling point.[6]   The same reaction takes place at 0° in benzene solution[11] and at −25° in carbon tetrachloride.[12]

The procedure described here involves direct combination of the elements at 400 to 425°. This procedure is preferred for several reasons: (1) It gives a product of high purity in excellent yield* at very low cost. (2) It is convenient. No drying of solvents is required, and the same apparatus can be used for both synthesis and purification. (3) The synthesis shows potential as a rather general route to pure anhydrous metal iodides. Iodides of the following elements have been prepared by direct combination of the elements: beryllium(II),[13] magnesium(II),[14] aluminum(III),[15] gallium(III),[16] indium(III),[17] silicon(IV),[18] germanium(IV),[19] tin(IV),[20] zirconium(IV),[21] hafnium(IV),[22] thorium(IV),[23] vanadium(III),[24] niobium(V),[25] tantalum(V),[26] chromium(III),[27] iron(II),[28] and platinum(IV).[29] It appears that the procedure which follows could be used, with only minor modifications, for the preparation of a large number of metal iodides.†

Procedure

The apparatus is shown in Fig. 1. All joints are standard-taper and are lubricated with Dow-Corning Silicone stopcock grease. Into tube *B*, 2.56 g. (0.0534 mol) 99+ % titanium sponge (City Chemical Corp.) is inserted between plugs of glass wool *ca.* 8 cm. in length. The glass wool serves to hold the titanium in place; it also slows the rate of diffusion of iodine over the titanium, allowing for more nearly complete reaction to occur. Tubes *A* and *B* are assembled, and with a slow stream of dry

---

* Reaction of titanium metal with a 3% excess of iodine in refluxing carbon tetrachloride (24 hours) gave titanium(IV) iodide in only 30 to 50% yield.

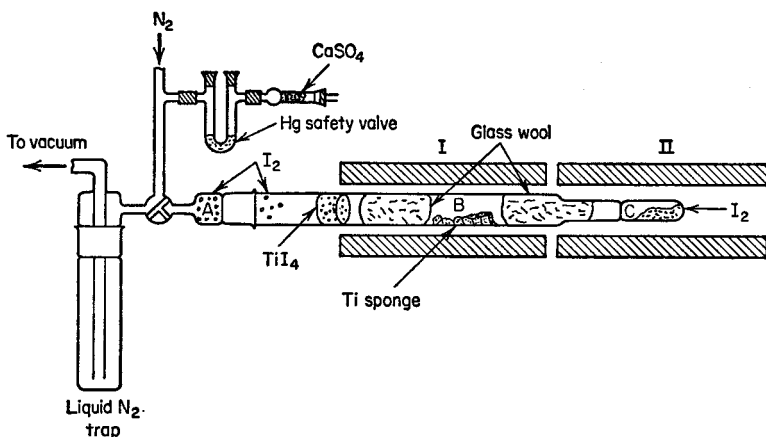† The procedure has been employed routinely in the authors' laboratories to prepare zirconium(IV) iodide in 80% yield.[30]

Fig. 1. *Apparatus for preparation of titanium(IV) iodide.*

nitrogen passing over the titanium, tube B is heated by furnace I to 400 to 425°. The nitrogen is dried by allowing the gas to bubble through concentrated sulfuric acid and then to pass through a drying tower (30 × 4.5 cm.) filled with Linde 4-A molecular sieve ($\frac{1}{16}$-in. diam.). When 400 to 425° has been attained, tube C which contains 27.10 g. (0.1068 mol) of iodine is assembled onto tube B. The nitrogen flow is cut off, and the entire assembly is evacuated with an oil pump which pulls a vacuum of at least 10 μ. After evacuation the three-way stopcock is turned to the position shown in Fig. 1, and furnace II is brought to 80° in order to sublime the iodine into reaction zone B at a slow, controlled rate.

When all the iodine has sublimed out of tube C (10 to 12 hours), nitrogen is admitted into the system, and the apparatus is allowed to cool to room temperature. Tube C is removed, and the glass-wool plugs and unreacted titanium (0.23 g.) are removed with a hooked copper wire while purging with nitrogen. ■ *Caution. Care should be exercised in removing the unreacted titanium from the tube; the titanium may be pyrophoric.* Then tube C is cleaned, dried, and reattached to tube B. Tube B is removed from attachment to A and, while holding tube B

vertically, the product, which has formed a dark reddish-brown ring as shown in Fig. 1, is quickly scraped with a spatula into tube C, which is then immediately stoppered.

For purification of the product, tubes A and B are cleaned, dried, and reassembled with a dry glass-wool insert in B. Tube C, containing the initially formed product, is attached to tube B as shown in Fig. 2. The system is evacuated and this time left open to the vacuum. The two furnaces are separated by *ca.* 1.5 cm. Furnace I is heated to 80° and furnace II to 130 to 140°. Sublimation is allowed to continue until all the titanium(IV) iodide has left tube C (12 to 16 hours). The purified product crystallizes in tube B at the separation of the two furnaces. The major impurity, iodine, crystallizes in tube A and in the liquid-nitrogen trap. A fluffy tan residue of negligible weight (0.04 to 0.06 g.) remains in tube C. If desired, further purification can be accomplished by moving tube B farther into furnace II, which results in a second sublimation of the product.

After cooling, nitrogen is admitted, tube C disassembled, and the glass-wool plug removed. A dry flask, equipped with a side-arm nitrogen inlet and stopcock, is attached to tube B, and the nitrogen which is passing through tube B is allowed to sweep through the flask. The side arm is then connected to a source of dry nitrogen, and the direction of nitrogen flow is reversed, i.e., from the side arm through the flask into tube B.
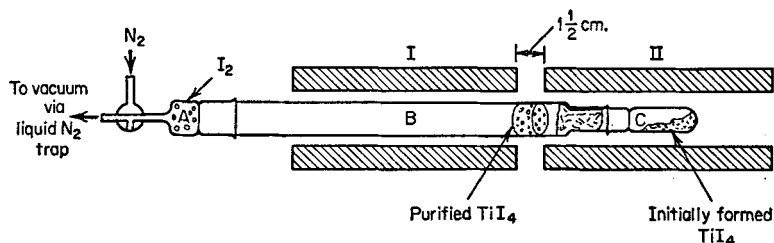

Fig. 2.   *Apparatus for purification of titanium(IV) iodide.*

After removing tube B from attachment A, the product is scraped, as before, into the flask. Tube B is removed, the flask is stoppered, and the stopcock closed. It is best to release any excess pressure in the flask before storage. The yield of titanium(IV) iodide is 25.0 g. (93% based on the titanium which reacted, 84% based on the total weight of titanium used). *Anal.* Calcd. for TiI_4: Ti, 8.62; I, 91.38. Found: Ti, 8.61; I, 91.28.

Properties

Titanium(IV) iodide is a lustrous, dark reddish-brown, crystalline solid. It melts at $150°$[6] and boils at atmospheric pressure without decomposition at $377.2°$.[3] Its vapor pressure in the range 160 to 370° is given by the relationship:

$$\log p(\text{mm.}) = -(3.054/T) + 7.577$$

The heat of vaporization is 13.98 kcal./mol.[3] The solid undergoes a phase transition between 100 and 125°. The high-temperature form is cubic and belongs to the space group $T_h^6\text{-}Pa3$ with eight molecules per unit cell; the lattice parameter a_0 is 12.21 A. at $125°$[31] and 12.00 A. at room temperature.[32] The low-temperature form is of lower symmetry.[31]

Titanium(IV) iodide is extremely hygroscopic. It dissolves in water with decomposition, and it fumes in air owing to hydrolysis. It forms 2:1 adducts with ammonia,[7] pyridine,[33] and ethyl acetate.[34] With excess ammonia it undergoes ammonolysis to give ammonobasic titanium(IV) iodides.[7] Analogous aminolysis reactions occur when titanium(IV) iodide is treated with an excess of primary or secondary amine.[35] Titanium(IV) iodide is sparingly soluble in petroleum ether, moderately soluble in benzene, and even more soluble in chlorinated hydrocarbons and carbon disulfide. At elevated temperatures it
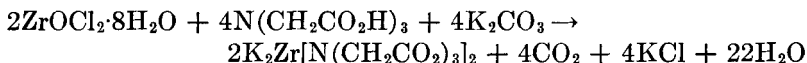
reacts reversibly with titanium metal to give titanium(II) iodide; upon reaction with titanium(II) iodide, it yields titanium(III) iodide.[10]

REFERENCES

1. R. WEBER: *Pogg. Ann.*, **120**, 291 (1863); cf. J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," vol. 7, p. 89, Longmans, Green and Co., Inc., New York, 1927.
2. H. MOISSAN: *Compt. Rend.*, **120**, 290 (1895).
3. J. M. BLOCHER, JR. and I. E. CAMPBELL: *J. Am. Chem. Soc.*, **69**, 2100 (1947).
4. A. C. LOONAM: U.S. patent 2,519,385 (Aug. 22, 1950); cf. *C.A.*, **45**, 316a (1951).
5. M. CHAIGNEAU: *Bull. Soc. Chim. France*, **1957**, 886.
6. P. HAUTEFEUILLE: *ibid.*, [2], **7**, 201 (1867).
7. G. W. A. FOWLES and D. NICHOLLS: *J. Chem. Soc.*, **1959**, 990.
8. G. VAUGHN and E. CATTERALL: British patent 945,766 (Jan. 8, 1964); cf. *C.A.*, **60**, 8932b (1964).
9. W. B. BLUMENTHAL and H. SMITH: *Ind. Eng. Chem.*, **42**, 249 (1950).
10. J. D. FAST: *Rec. Trav. Chim.*, **58**, 174 (1939).
11. K. H. GAYER and G. TENNENHOUSE: *Can. J. Chem.*, **37**, 1373 (1959).
12. M. L. NIELSEN: U.S. patent 2,904,397 (Sept. 15, 1959); cf. *C.A.*, **54**, 6062e (1960).
13. G. B. WOOD and A. BRENNER: *J. Electrochem. Soc.*, **104**, 29 (1957).
14. W. BILTZ and G. F. HÜTTIG: *Z. Anorg. Allgem. Chem.*, **119**, 115 (1921).
15. G. W. WATT and J. L. HALL: INORGANIC SYNTHESES, **4**, 117 (1953).
16. W. KLEMM and W. TILK: *Z. Anorg. Allgem. Chem.*, **207**, 161 (1932).
17. T. MOELLER: *J. Am. Chem. Soc.*, **64**, 953 (1942).
18. F. B. LITTON and H. C. ANDERSEN: *J. Electrochem. Soc.*, **101**, 287 (1954).
19. L. M. DENNIS and F. E. HANCE: *J. Am. Chem. Soc.*, **44**, 2854 (1922).
20. F. F. FITZGERALD: *ibid.*, **29**, 1693 (1907).
21. K. C. EBERLY: INORGANIC SYNTHESES, **7**, 52 (1963).
22. W. A. BAKER, JR. and A. R. JANUS: *J. Inorg. Nucl. Chem.*, **26**, 2087 (1964).
23. D. E. SCAIFE and A. W. WYLIE: *J. Chem. Soc.*, **1964**, 5450.
24. A. MORETTE: *Compt. Rend.*, **270**, 1218 (1938).
25. J. D. CORBETT and P. X. SEABAUGH: *J. Inorg. Nucl. Chem.*, **6**, 207 (1958).
26. R. F. ROLSTEN: *J. Am. Chem. Soc.*, **80**, 2952 (1958).
27. N. W. GREGORY and L. L. HANDY: INORGANIC SYNTHESES, **5**, 128 (1957).
28. M. GUICHARD: *Compt. Rend.*, **145**, 807 (1907).
29. G. R. ARGUE and J. J. BANEWICZ: *J. Inorg. Nucl. Chem.*, **25**, 923 (1963).
30. T. J. PINNAVAIA and R. C. FAY: unpublished results.
31. R. F. ROLSTEN and H. H. SISLER: *J. Am. Chem. Soc.*, **79**, 5891 (1957).
32. O. HASSEL and H. KRINGSTAD: *Z. Physik. Chem. (Leipzig)*, **B15**, 274 (1932).
33. H. J. EMELÉUS and G. S. RAO: *J. Chem. Soc.*, **1958**, 4245.
34. M. F. LAPPERT: *ibid.*, **1962**, 542.
35. R. T. COWDELL, G. W. A. FOWLES, and R. A. WALTON: *J. Less-Common Metals*, **5**, 386 (1963).

2. POTASSIUM BIS(NITRILOTRIACETATO)ZIRCONATE(IV)

$$2ZrOCl_2 \cdot 8H_2O + 4N(CH_2CO_2H)_3 + 4K_2CO_3 \rightarrow$$
$$2K_2Zr[N(CH_2CO_2)_3]_2 + 4CO_2 + 4KCl + 22H_2O$$

Submitted by E. M. LARSEN* and A. C. ADAMS*
Checked by JOHN P. FACKLER, JR.†

The bis(nitrilotriacetato)zirconium(IV) ion, first detected by Intorre and Martell,[1] has been obtained as a hydrated potassium salt by evaporation of a solution containing zirconium oxychloride and the potassium salt of nitrilotriacetic acid. On vacuum dehydration, the anhydrous complex is formed.

Procedure

To a slurry of 7.64 g. (0.04 mol) of nitrilotriacetic acid in 75 ml. of water, 8.30 g. (0.06 mol) of anhydrous potassium carbonate is slowly added. After the solids dissolve, the resulting solution is added to a solution of 6.44 g. (0.02 mol) of zirconium oxychloride 8-hydrate in 75 ml. of water. A white precipitate, which forms initially, completely redissolves after stirring the mixture for a few minutes. The solution is evaporated on the steam bath until crystals form. The final volume is about 15 ml. After cooling in an ice bath, the crystals are filtered and sucked dry. The product is recrystallized by dissolving the solid in 25 ml. of water and evaporating the solution on the steam bath until crystals again form. The crystals are filtered and dried *in vacuo* over calcium sulfate. Upon drying, the crystals tend to disintegrate. The product is checked for chloride ion by dissolving a small amount of the material in water and adding a drop of silver nitrate solution. If the test is positive, the recrystallization is repeated. The final yield is 2.3 to 4.3 g.

* The University of Wisconsin, Madison, Wis.
† Case Institute of Technology, Cleveland, Ohio.

(22 to 42%). *Anal.* Calcd. for $K_2Zr[N(CH_2CO_2)_3]_2$: K, 14.3; Zr, 16.7. Found: K, 14.3; Zr, 16.7.

Properties

This preparation gives the potassium bis(nitrilotriacetato)-zirconate(IV) as very small irregular crystals. However, if the solution is evaporated slowly during the recrystallization, large diamond-shaped crystals* are formed. In the rubidium[2] and the potassium[3] salts, the two nitrilotriacetate ligands are coordinated to the zirconium in a slightly distorted dodecahedral arrangement.

REFERENCES

1. B. I. INTORRE and A. E. MARTELL: *J. Am. Chem. Soc.*, **82**, 358 (1960).
2. J. L. HOARD and J. V. SILVERTON: *Inorg. Chem.*, **2**, 235 (1963).
3. J. L. HOARD, E. WILLSTADTER, and J. V. SILVERTON: *J. Am. Chem. Soc.*, **87**, 1610 (1965).

3. METAL COMPLEXES DERIVED FROM *cis*-1,2-DICYANO-1,2-ETHYLENEDITHIOLATE AND BIS(TRIFLUOROMETHYL)-1,2-DITHIETE

Submitted by A. DAVISON† and R. H. HOLM‡
Checked by R. E. BENSON§ and W. MAHLER§

Since the initial preparations[1, 2, 3] of several four- and six-coordinate complexes of the general formulations $[MS_4C_4R_4]^z$ and

---

* The checker reports these crystals are similar to the crystals of $K_2Zr[N(CH_2\text{-}CO_2)_3]_2 \cdot H_2O$ studied by Hoard et al.[3] Upon drying the crystals *in vacuo* at room temperature over P_4O_{10} for 24 hours, a white powdery material was obtained. *Anal.* Calcd. for $K_2ZrC_{12}H_{12}O_{12}N_2$: C, 26.40; H, 2.20. Found: C, 26.2; H, 2.6.

† Massachusetts Institute of Technology, Cambridge, Mass.

‡ Harvard University, Cambridge, Mass.; present address: Massachusetts Institute of Technology, Cambridge, Mass.

§ Central Research Department, E. I. du Pont de Nemours & Company, Wilmington, Del.

$[MS_6C_6R_6]^z$, much interest has been generated in these complexes, particularly with respect to attempts to elucidate their electronic structures.[4,5] The most noteworthy feature of the chemistry of these complexes is that many with the same M and R may be interrelated by relatively facile one-electron-transfer reactions which may be effected chemically or electrochemically. Complexes with varying over-all charges z may then be formed which constitute members of electron-transfer series.[5,8,9,16] Such series with two or three members have been obtained. Tables I and II list representative complexes or series of complexes which either have been isolated or whose existence has been demonstrated by electrochemical measurements.

The synthetic chemistry of these complexes and their stability to various redox reagents may be considerably systematized by the use of polarographic half-wave potentials for the one-electron

T A B L E I $[MS_4C_4R_4]^z$ **Complexes***

Fe	Co, Rh	Ni	Pd	Pt	Cu, Au
[Fe/CN]¹⁻	[Co/CN]²⁻,¹⁻	[Ni/CN]²⁻,¹⁻	[Pd/CN]²⁻,¹⁻	[Pt/CN]²⁻,¹⁻	[Cu/CN]²⁻,¹⁻
[Fe/CF₃]¹⁻,⁰	[Co/CF₃]²⁻,¹⁻,⁰	[Ni/CF₃]²⁻,¹⁻,⁰	[Pd/CF₃]²⁻,¹⁻,⁰	[Pt/CF₃]²⁻,¹⁻,⁰	[Au/CN]¹⁻
	[Rh/CN]²⁻	[Ni/C₆H₅]²⁻,¹⁻,⁰	[Pd/C₆H₅]²⁻,¹⁻,⁰	[Pt/C₆H₅]²⁻,¹⁻,⁰	
		[Ni/CH₃]²⁻,¹⁻,⁰		[Pt/CH₃]²⁻,¹⁻,⁰	
		[Ni/H]²⁻,¹⁻,⁰			
		[Ni/C₂H₅]⁰			
		[Ni/p-C₆H₄X]⁰,			
		(X = CH₃,			
		OCH₃, Cl)			

* For details of preparation or identification, see accompanying text and references, 2, 6–13; complexes abbreviated as [M/R]ᶻ.

T A B L E II $[MS_6C_6R_6]^z$ **Complexes***

V	Cr	Mo	W	Others
[V/CN]³⁻,²⁻,¹⁻	[Cr/CN]³⁻,²⁻,¹⁻	[Mo/CF₃]²⁻,¹⁻,⁰	[W/CF₃]²⁻,¹⁻,⁰	[Re/C₆H₅]⁰
[V/CF₃]²⁻,¹⁻	[Cr/CF₃]²⁻,¹⁻,⁰	[Mo/C₆H₅]²⁻,¹⁻,⁰	[W/C₆H₅]²⁻,¹⁻,⁰	[Ru/C₆H₅]⁰
[V/C₆H₅]²⁻,¹⁻,⁰	[Cr/C₆H₅]²⁻,¹⁻,⁰			[Os/C₆H₅]⁰

* For details of preparation or identification, see accompanying text and references 3, 5, 14–17; complexes abbreviated as [M/R]ᶻ.

reactions which many of these complexes undergo. For reversible reactions these potentials are closely related to standard electrode potentials and may be used in a similar fashion. Some potentials relevant to the syntheses which follow are set out in Table III. More extensive tabulations of potentials for most of the complexes in Tables I and II may be found elsewhere.[5,9,13,16,20] Reference to all available potentials shows that the ease of oxidation of a species with given M and z increases in the order R = H, alkyl > C_6H_5 > CF_3 > CN for the complexes $[MS_4C_4R_4]^z$, and R = C_6H_5 > CF_3 > CN for the complexes $[MS_6C_6R_6]^z$. Further, the following strictly empirical generalizations can be made: (1) All reduced species in couples less positive than $\sim$0 v. are readily oxidized in solution by air, whereas all reduced species in couples more positive than this value are stable to air oxidation; (2) oxidized species in couples more positive than $\sim$+0.20 v. are unstable to reduction by weakly basic solvents such as ketones and alcohols, while those in couples within the approximate range −0.12 to +0.20 v.

TABLE III   Polarographic Half-wave Potentials of Complexes in Acetonitrile Solution

R	Couple	$E_{\frac{1}{2}}$ v.*
H	$(Ni)^{2-} = (Ni)^{1-} + e^-$	−0.92
C_6H_5	$(Ni)^{2-} = (Ni)^{1-} + e^-$	−0.74
CF_3	$(Ni)^{2-} = (Ni)^{1-} + e^-$	−0.12
H	$(Ni)^{1-} = (Ni)^{0} + e^-$	0.09
C_6H_5	$(Ni)^{1-} = (Ni)^{0} + e^-$	0.22
CN	$(Ni)^{2-} = (Ni)^{1-} + e^-$	0.23
CF_3	$(Mo)^{2-} = (Mo)^{1-} + e^-$	0.36
CF_3	$(Mo)^{1-} = (Mo)^{0} + e^-$	0.95
CF_3	$(Ni)^{1-} = (Ni)^{0} + e^-$	1.00

* Potentials were measured at room temperature relative to an aqueous calomel electrode saturated with NaCl, using a rotating platinum electrode; data for R = H complexes from reference 13, all other data from references 5 and 9.

are reduced by stronger bases such as aromatic amines; (3) oxidized forms in couples more negative than $\sim$0.12 v. are reduced by stronger reducing agents such as hydrazine or sodium amalgam; (4) reduced forms in couples less positive than $\sim$0.40 v. can be oxidized by iodine.   Finally, it is evident that $[MoS_6C_6(CF_3)_6]$ and $[NiS_4C_4(CF_3)_4]$ are the most powerful one-electron oxidizing agents in each series of complexes and should in principle oxidize any reduced species in couples less positive than their own.   The use of some of these generalizations is exemplified in the following synthetic procedures.

A. Sodium *cis*-1,2-dicyano-1,2-ethylenedithiolate

$$NaCN + CS_2 + 3HCON(CH_3)_2 \rightarrow NCCS_2Na\cdot3HCON(CH_3)_2$$
$$2NCCS_2Na\cdot3HCON(CH_3)_2 \rightarrow$$
$$Na_2S_2C_2(CN)_2 + 6HCON(CH_3)_2 + 2S$$
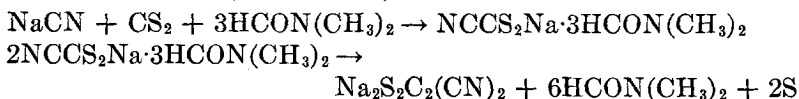
The following is an elaboration of the method given briefly by Bähr and Schleitzer[1] with some modification, notably a description of the isolation and purification of the anhydrous salt from aqueous solution.   This salt is used as a precursor for some elegant organic thiocyanocarbon chemistry[18] as well as the inorganic applications described in the subsequent sections for which, in some instances, the use of pure anhydrous material is mandatory.

Procedure

The following procedure is carried out in a ventilated hood. Finely powdered dry sodium cyanide (29.4 g., 0.60 mol) and 180 ml. of dimethylformamide (DMF) are placed into a 1-l., three-necked, standard-taper round-bottomed flask equipped with a reflux condenser, dropping funnel, and Hirshberg stirrer connected to a high-speed stirring motor.*   External cooling is provided by a cold-water or ice-water bath.   Carbon disulfide

---

* Fine particle size and efficient stirring increase the yield.

(36.2 ml.) is added dropwise over a 10-minute period. A yellow-green color develops initially which rapidly darkens to the characteristic red-brown color of the cyanodithioformate anion. When the addition is complete, the mixture is stirred vigorously for 30 minutes, during which time its color becomes intense and a red-brown solid mass is produced. At this stage the stirring is stopped, 500 ml. of reagent-grade isobutyl alcohol is added, and the mixture is heated to dissolve the product. The dark brown solution is filtered hot by suction using filter aid to remove any residual sodium cyanide. The filtrate is cooled in an ice-salt bath and agitated with a glass rod; the product crystallizes as a tan mass, which is collected by suction filtration and washed while still moist with anhydrous ethyl ether until the washings are pale yellow. Air-drying gives a yield of 160 g. (71%) of tan $NCCS_2Na\cdot3HCON(CH_3)_2$. This product is dissolved in 1300 ml. of distilled water. The dark brown solution rapidly lightens, and sulfur is precipitated. After 24 hours the dimerization is complete, and the supernatant solution is pale yellow. The sulfur is removed by filtration and the filtrate evaporated to dryness under reduced pressure by use of a rotary evaporator.

The yellow-brown solid is dissolved in a minimum volume (~600 ml.) of boiling absolute ethanol. The solution is filtered while hot to remove a small amount of insoluble material. Anhydrous ethyl ether (250 ml.) is added to the filtrate. The product separates on cooling in an ice bath as pale yellow crystals, which are collected by suction and washed with anhydrous ethyl ether until the washings are colorless. The product is then dissolved in 450 ml. of absolute ethanol and filtered. Addition of 200 ml. of ethyl ether causes the product to crystallize on cooling as a pale yellow microcrystalline solid. The last traces of solvent alcohol are almost completely removed by drying the product *in vacuo* (<0.1 mm.) at 80° for 24 hours. The yield is 27 g. (48% based on NaCN; 67% on $NCCS_2Na\cdot3DMF$). *Anal.* Calcd. for $Na_2C_4N_2S_2$: C, 25.80; H, 0.0; N, 15.05; S, 34.45. Found: C, 25.43; H, 0.20; N, 14.79; S, 34.75.

Notes

1. The preparation can be modified to use acetamide, dimethylacetamide, or N-methylpyrollidone as solvent.[18]

2. Potassium cyanide gives the cyanodithioformate anion in very low yields.[18]

3. Dimerization of the dimethylformamide-solvated sodium cyanodithioformate takes place in carbon tetrachloride and dichloromethane with elimination of sulfur[1,18] but at a much lower rate than in water.

4. The presence of solvated dimethylformamide is necessary for the dimerization to occur; the dimerization is stereospecific since no trans isomer is formed.[18]

5. The pure dry product is air-stable. Impure samples have poor storage properties and sometimes decompose.

B. Bis(*cis*-1,2-dicyano-1,2-ethylenedithiolato)metallate Complexes, [MS₄C₄(CN)₄]²⁻

B. Bis(cis-1,2-dicyano-1,2-ethylenedithiolato)metallate Complexes, $[MS_4C_4(CN)_4]^{2-}$

The method given is similar to those described elsewhere[6,7] but has the advantages that the solvent pair used for recrystallization enables large well-formed single crystals suitable for spectroscopic studies to be grown very easily, and that this method is generally applicable to the isolation of bis- or tris(*cis*-1,2-dicyano-1,2-ethylenedithiolato) complexes which are not subject to reduction by the solvent.

1. Tetra-*n*-butylammonium bis(*cis*-1,2-dicyano-1,2-ethylenedithiolato)-nickelate(2 −)

$$Ni^{2+} + 2S_2C_2(CN)_2^{2-} + 2(n\text{-}C_4H_9)_4N^+ \rightarrow$$
$$[(n\text{-}C_4H_9)_4N]_2[NiS_4C_4(CN)_4]$$
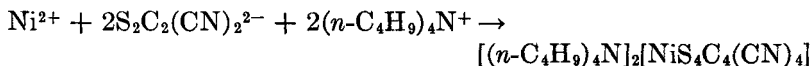
Procedure

A solution of 2.38 g. (0.01 mol) of nickel chloride hexahydrate in 15 ml. of water is added slowly, with stirring, to a solution of 4.10 g. (0.022 mol) of $S_2C_2(CN)_2Na_2$ (Sec. A) in 60 ml. of ethanol–water (1:1 v/v). The dark red solution is filtered, and

a solution of 7.4 g. (0.023 mol) of tetra-*n*-butylammonium bromide in 25 ml. of ethanol is added slowly with agitation. Small orange-red crystals separate immediately. These are collected by suction and washed with 20 ml. of water, followed by 20 ml. of ethanol–water (1:1 v/v), and sucked dry. The product is dissolved in 80 ml. of hot acetone and filtered. The filtrate is heated to boiling, and 35 ml. of isobutyl alcohol is added slowly. Most of the acetone is then evaporated by heating on a steam bath. When the volume is ~35 to 40 ml., the solution is set aside. Large deep red, well-formed crystals separate on cooling. These are collected and washed with 25 ml. of isobutyl alcohol, followed by three 50-ml. portions of *n*-pentane. A yield of 7.9 g. (96%) of air-dried product is obtained; m.p. 143 to 144°.

Notes

1. The procedure described above can be used to prepare complexes of the type $[MS_4C_4(CN)_4]^{2-}$ as suitable salts:

$[(n\text{-}C_4H_9)_4N]_2[CoS_4C_4(CN)_4]$: m.p. 141 to 143°, black, yield ~90% from cobalt chloride using degassed solvents and a nitrogen atmosphere to prevent oxidation to $[(n\text{-}C_4H_9)_4N][CoS_4C_4(CN)_4]$. Rapid cooling of the saturated isobutyl alcohol solution (ice-salt) causes immediate crystallization and essentially quantitative recovery of the complex as small well-formed crystals.

$[(n\text{-}C_4H_9)_4N]_2[CuS_4C_4(CN)_4]$: m.p. 123.5°, brown plates, yield ~85% based on $CuSO_4 \cdot 5H_2O$.

$[(n\text{-}C_4H_9)_4N]_2[PdS_4C_4(CN)_4]$: m.p. 157 to 158°, green platelets, yield 70% based on $PdCl_2$ (dissolved in water using a minimum of HCl). (Checkers report a 95% yield.)

$[(C_2H_5)_4N]_2[PtS_4C_4(CN)_4]$: m.p. 242 to 245° (decomp.), dark red crystals, yield 73% based on K_2PtCl_4.

$[(n\text{-}C_4H_9)_4N]_2[ZnS_4C_4(CN)_4]$: m.p. 156 to 158°, pale yellow needles, yield 93% based on $ZnCl_2$.

2. The complexes $[(n-C_4H_9)_4N]_2[MS_4C_4(CN)_4]$, where M = Co, Ni, Cu, and Rh are isomorphous, and mixed single crystals can be grown very easily using the acetone–isobutyl alcohol solvent pair and only slight modifications of the recrystallization procedure.

C. Bis(*cis*-1,2-dicyano-1,2-ethylenedithiolato)metallate Complexes, $[MS_4C_4(CN)_4]^{1-}$

Three procedures have been utilized to synthesize complexes of this type: (1) Direct reaction in aqueous media using trivalent metal ions, e.g., $[FeS_4C_4(CN)_4]^{1-}$ from hexaaquoiron(III) chloride,[7] $[AuS_4C_4(CN)_4]^{1-}$ from tetrachloroaurate(III),[8] which is basically the same as the procedure described in Sec. B for bivalent metal ions; (2) oxidation of $[MS_4C_4(CN)_4]^{2-}$ with iodine, a procedure generally applicable to those cases in which the product is not reduced by solvent; (3) oxidation of $[MS_4C_4(CN)_4]^{2-}$ with $[NiS_4C_4(CF_3)_4]$ in dichloromethane. The last method has the advantages that it is relatively easy to carry out and that insoluble cyano complexes crystallize directly and are not subject to solvent reduction. The two procedures described below are representative of methods (2) and (3) and have some general applicability to oxidation of disubstituted ethylenedithiolato complexes.

1. Tetra-*n*-butylammonium bis(*cis*-1,2-dicyano-1,2-ethylenedithiolato)-nickelate(1−)

$$[(n-C_4H_9)_4N]_2[NiS_4C_4(CN)_4] + \tfrac{1}{2}I_2 \rightarrow$$
$$(n-C_4H_9)_4NI + [(n-C_4H_9)_4N][NiS_4C_4(CN)_4]$$
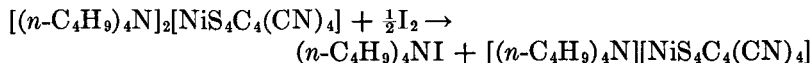
Procedure

A solution of 4.0 g. (0.016 mol) of iodine in 8 ml. of dimethyl sulfoxide is added in one portion to a solution of 8.24 g. (0.01 mol) of $[(n-C_4H_9)_4N]_2[NiS_4C_4(CN)_4]$ in 60 ml. of the same solvent. A slight darkening occurs on mixing, and after one minute the

mixture is poured into 210 ml. of 95% ethanol. The product separates during 20 minutes; periodic agitation aids the separation. It is collected by suction on a coarse-porosity sintered-glass funnel. The residue is transferred to the funnel with a 25-ml. ethanol wash and then washed repeatedly with 5- to 10-ml. portions of ethanol (~150 ml.). The shiny black crystals are then washed with three 25-ml. portions of anhydrous ether followed by three 25-ml. portions of *n*-pentane and air-dried. The yield is 3.73 g. (64%), m.p. 171 to 172°. The material analyzes satisfactorily at this point, but can be recrystallized from acetone–ethyl ether; e.g., the product is dissolved in 45 ml. of hot acetone, and 145 ml. of anhydrous ether is added to the hot solution; $[(n\text{-}C_4H_9)_4N][NiS_4C_4(CN)_4]$ separates on standing as small shiny black crystals, 3.22 g. (55%).

This procedure was repeated by checkers on one-half the scale and a yield of 1.40 g. (48%) was obtained.

Notes

1. This procedure works well for tetraalkylammonium salts of nickel and platinum complexes, e.g.,

$[(C_2H_5)_4N][NiS_4C_4(CN)_4]$: m.p. 288 to 290°, 83% yield.
$[(C_2H_5)_4N][PtS_4C_4(CN)_4]$: m.p. 288°, decomp.; 73% yield.

The palladium complex is extremely susceptible to reduction by solvent and for this reason is most conveniently prepared by the method which follows.

2. This procedure is generally unsatisfactory for tetraphenylarsonium salts because of coprecipitation of tetraphenylarsonium triiodide.

2. Tetra-*n*-butylammonium bis(*cis*-1,2-dicyano-1,2-ethylenedithiolato)-palladate(1−)

$[NiS_4C_4(CF_3)_4] + [(n\text{-}C_4H_9)_4N]_2[PdS_4C_4(CN)_4] \rightarrow$
$[(n\text{-}C_4H_9)_4N][PdS_4C_4(CN)_4] + [(n\text{-}C_4H_9)_4N][NiS_4C_4(CF_3)_4]$
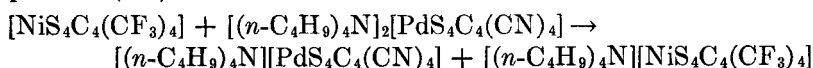
Procedure

A solution of 1.0 g. (0.0012 mol) of $[(n\text{-}C_4H_9)_4N]_2[PdS_4C_4\text{-}(CN)_4]$ (Sec. B) in 90 ml. of dichloromethane is heated to boiling and then treated with 0.59 g. (a slight excess over 0.0012 mol) of $NiS_4C_4(CF_3)_4$ (Sec. D). The solution changes rapidly from deep green to a dirty red-brown color. The solvent is evaporated very slowly using very slight heat until the solution volume reaches ~15 to 20 ml. The solution is cooled, and the product separates as shiny black crystals, which are collected by suction on a coarse-porosity sintered-glass funnel. The crystals are carefully washed with 2 ml. of dichloromethane using an eye dropper. The product is recrystallized from dichloromethane (in which it is moderately soluble and forms a violet solution), giving 0.43 g. (61%) of black crystals, which are collected and washed as above; m.p. 190 to 191°.

Note

The following compounds have also been prepared by analogous procedures:

$[(n\text{-}C_4H_9)_4N][CoS_4C_4(CN)_4]$: m.p. 198 to 199°, black crystals, 76% yield.

$[(n\text{-}C_4H_9)_4N][CuS_4C_4(CN)_4]$: m.p. 146.5 to 147°, dark red needles recrystallized from dichloromethane–ethanol, 78% yield.

D. Bis[cis-1,2-bis(trifluoromethyl)-1,2-ethylenedithiolato]metal Complexes

Complexes of this type cannot be prepared from the parent ligand, the bivalent anion, $[(CF_3)_2C_2S_2]^{2-}$, which has not yet been isolated as a simple salt. Attempts to prepare it from the novel heterocycle bis(trifluoromethyl)-1,2-dithiete[19] $(CF_3)_2C_2S_2$ cause dimerization or decomposition. The preparations are achieved by treating the heterocycle with a low-valent transition metal

complex, usually a carbonyl or phosphine complex.[3,5,9,16] The reaction is, in effect, an oxidation-reduction process in which the metal is oxidized and the heterocycle cleaved at the S—S bond and reduced. The general procedures are illustrated using the nickel complexes.

1. Bis[*cis*-1,2-bis(trifluoromethyl)-1,2-ethylenedithiolato]nickel

$$Ni(CO)_4 + 2(CF_3)_2C_2S_2 \rightarrow [NiS_4C_4(CF_3)_4] + 4CO$$
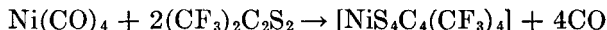
Procedure

A solution of 10.5 g. (0.046 mol) of freshly distilled bis(trifluoromethyl)-1,2-dithiete (Note 2) in 200 ml. of *n*-pentane is cooled to $-10°$ in a 1-l. round-bottomed flask equipped with an efficient reflux condenser and protected from moist air by a dry nitrogen blanket. A solution of 3.0 ml. (0.023 mol) of nickel carbonyl dissolved in 100 ml. of *n*-pentane is added down the condenser in one portion to this solution. The mixture is swirled to mix. An intense blue-violet color develops in about 15 to 20 seconds and after 1 to 2 minutes, vigorous evolution of carbon monoxide occurs. This evolution subsides in 10 minutes and the deep violet solution is allowed to warm to $0°$ during 2 hours to ensure complete reaction. Most of the pentane is removed by distillation at atmospheric pressure, the remaining $\sim$50 to 60 ml. is removed *in vacuo* (0.1 mm.), and the resultant crystalline mass is evacuated (0.1 mm.) at $50°$ for 4 hours. The crude product consists of shiny black-purple needles and weighs 11.8 g. (98%). Recrystallization from *dry* benzene (Note 3) gives shiny black crystals, m.p. 134 to 135° (sealed tube). The complex is air-stable but should be kept out of contact with moist air.

This procedure was repeated by checkers with a 400% increase in reagent scale and the yield of crude product was 43 g. (90%).

Notes

1. For optimum yields the stoichiometry must be strictly adhered to. Otherwise some purple, amorphous, benzene-insoluble material will be produced.

2. The $(CF_3)_2C_2S_2$[19] must be freshly fractionated before use. It dimerizes on standing, and in addition, some malodorous red material is produced. These by-products may be separated by careful fractionation. A 30-in. heated column packed with glass helices has proved suitable. The pure product is golden yellow and boils at 96°/760 mm.

3. [$NiS_4C_4(CF_3)_4$] is very readily reduced to the univalent anion, whose salts are insoluble in n-pentane but moderately to extremely soluble in most other organic solvents including aromatic hydrocarbons and carbon tetrachloride. To avoid reduction, all solvents and apparatus must be dry. Benzene and n-pentane stored over molecular sieves have been found to be adequately dry for use in the above procedure.

2. Tetra-n-butylammonium bis[*cis*-1,2-bis(trifluoromethyl)-1,2-ethylene-dithiolato]nickelate(1 −)

$$[NiS_4C_4(CF_3)_4] \xrightarrow[\text{(n-C}_4\text{H}_9)_4\text{NBr}]{\text{(CH}_3)_2\text{CO}} [(n\text{-}C_4H_9)_4N][NiS_4C_4(CF_3)_4]$$
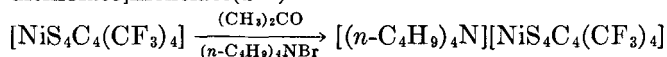
Procedure

The reduction is performed by treating 2.0 g. (0.0039 mol) of [$NiS_4C_4(CF_3)_4$] with 30 ml. of acetone. The mixture is initially violet but rapidly goes dark green (*ca.* 30 seconds). After 1 to 2 minutes the solution is diluted with 100 ml. of water and treated with 6 g. of filter aid (Note 1). To this mixture a solution of 2.0 g. of tetra-n-butylammonium bromide in 20 ml. of water is added slowly with stirring. The product separates and adheres to the filter aid. The mixture is agitated for 5 minutes and filtered by suction. The product is first washed with 200 ml. of water and sucked dry for $\sim$1 hour. At this

point *n*-pentane is passed through the filter bed until the washings are colorless (Note 2) (*ca.* 200 to 250 ml.). The pentane is removed by suction, and the product and filter aid are transferred to the original beaker where they are digested with 60 ml. of absolute ethanol and filtered hot by suction. The filter bed is washed with successive portions of hot absolute ethanol until the washings are colorless. The filtrate is evaporated until its volume is 50 ml. The filtrate is brought to a boil, and 20 ml. of water is added dropwise. The solution is covered and set aside to cool slowly. The green-brown needles of $[(n\text{-}C_4H_9)_4N][NiS_4C_4(CF_3)_4]$ are collected and washed with 25 ml. of ice-cold water–ethanol (70% v/v) mixture and dried *in vacuo*. The yield is 2.02 g. (69%); m.p. 107.5 to 109°.

Notes

1. The addition of filter aid enables the product to be easily separated by filtration. Its omission causes the separation of product as an emulsion.

2. Some decomposition occurs during the reduction; free nickel ion is present in the filtrate, and some free bis(trifluoromethyl)-1,2-dithiete is produced which is removed by the pentane washes.

3. Tetraphenylarsonium bis[*cis*-1,2-bis(trifluoromethyl)-1,2-ethylenedithiolato]nickelate(2−)

$$2[NiS_4C_4(CF_3)_4] + 4(C_6H_5)_4AsCl + N_2H_4 \rightarrow$$
$$2[(C_6H_5)_4As]_2[NiS_4C_4(CF_3)_4] + 4HCl + N_2$$
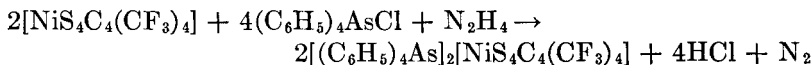
Procedure

A mixture of 50 ml. of 95% ethanol, 5 ml. of 95% hydrazine, and 5 ml. of water (or simply 10 ml. of hydrazine hydrate) is freshly prepared, and to this solution is added in one portion 1 g. (0.002 mol) of $[NiS_4C_4(CF_3)_4]$. The reduction is accompanied by vigorous evolution of nitrogen, which subsides

in ~30 seconds. A solution of 2.0 g. of tetraphenylarsonium chloride in 20 ml. of ethanol–water (70% v/v) is added to the orange solution, causing the product to separate as bright orange needles. These are collected by suction and washed successively with 25 ml. of ethanol–ether (1:1 v/v) followed by two 25-ml. portions of ethyl ether. Recrystallization can be effected as follows. The product is dissolved immediately in 50 ml. of acetone and heated to boiling, 50 ml. of isobutyl alcohol is added slowly to the boiling solution, and the solvent evaporated (Note) until incipient crystallization. The hot solution is allowed to cool with exclusion of air. The product crystallizes as shiny orange needles. It is collected by suction and washed with two 25-ml. portions of isobutyl alcohol and then by *n*-pentane and dried *in vacuo*. The yield is 2.07 g. (83%); m.p. 238 to 239° (checkers report m.p. 240 to 242°). The solid complex is moderately sensitive to oxidation and should be kept *in vacuo* or under nitrogen.

Note

Some oxidation to the univalent anion will occur in the recrystallization procedure, but the solvent vapor effectively excludes the air from the boiling solution, particularly if the recrystallization is done in a conical flask. The oxidized product is very soluble in acetone–isobutyl alcohol and does not contaminate the product. Prolonged exposure of the solutions to air is not recommended.

E. Tris[*cis*-1,2-bis(trifluoromethyl)-1,2-ethylenedithiolato]metal Complexes

Three preparations are described using the molybdenum complexes as representative examples. These can be modified as noted below to give the vanadium, chromium, and tungsten analogs.[5]

1. Tris[cis-1,2-bis(trifluoromethyl)-1,2-ethylenedithiolato]molybdenum

$$Mo(CO)_6 + 3(CF_3)_2C_2S_2 \rightarrow [MoS_6C_6(CF_3)_6] + 6CO$$
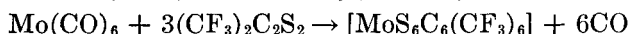
This procedure is a modification of that described by King[3] and considerably facilitates the isolation and purification of the product.

Procedure

A mixture of 6.79 g. (0.03 mol) of $(CF_3)_2C_2S_2$, 2.64 g. (0.01 mol) of $Mo(CO)_6$, and 100 ml. of dry methylcyclohexane (Note 1) is heated under reflux and protected from the air by a paraffin oil bubble trap. The mixture turns dark brown, and during 12 hours carbon monoxide gas is slowly evolved. After this time the violet-black reaction mixture is cooled to room temperature. The product is collected by suction on a coarse-porosity sintered-glass funnel. Repeated washings with small portions (*ca.* 25 ml.) of *n*-pentane remove all traces of a foul-smelling brown oil which is a by-product of the reaction. The crude product is a mass of glistening purple crystals sparingly soluble in *n*-pentane, giving a blue-violet solution. Purification is achieved by Soxhlet extraction* with *n*-pentane. The yield is 5.05 g. (65%) of well-developed shiny red-purple crystals which do not melt below 250° but can be sublimed slowly at ~185° (0.1 mm.).

Notes

1. The rate of reaction is markedly solvent-dependent. In the higher-boiling solvents *n*-octane, ethylcyclohexane, and *cis*-1,2-dimethylcyclohexane the reaction is much faster, but prolonged reflux in these solvents causes extensive decomposition. Some typical results are the following: *n*-octane, 1.75 hours, 64% yield; ethylcyclohexane, 2.0 hours, 60% yield.

---

* Extraction is slow, *ca.* 0.1 g./hour. Checkers report that direct sublimation of the crude product drastically lowers the yield.

2. The chromium and tungsten complexes can be prepared similarly: [CrS$_6$C$_6$(CF$_3$)$_6$], from Cr(CO)$_6$ in methylcyclohexane, 70 hours, 55% yield, well-developed crystals with pronounced golden-green reflex, m.p. 210 to 215° (decomp.); [WS$_6$C$_6$(CF$_3$)$_6$], from W(CO)$_6$ in ethylcyclohexane, 72 hours, 36% yield; in *n*-octane, 3 weeks, 36% yield; dark purple hexagonal prisms with green reflex; m.p. >250°, sublimation begins at ~235°.

3. [MS$_6$C$_6$(CF$_3$)$_6$] complexes are easily reduced to the univalent anion. Dry solvents and apparatus must be employed. Adequately dry solvents may be obtained by storage over molecular sieves.

2. Tetraphenylarsonium tris[*cis*-1,2-bis(trifluoromethyl)-1,2-ethylenedithiolato]molybdate(2 −)

2[MoS$_6$C$_6$(CF$_3$)$_6$] + 4(C$_6$H$_5$)$_4$AsCl + N$_2$H$_4$ →
2[(C$_6$H$_5$)$_4$As]$_2$[MoS$_6$C$_6$(CF$_3$)$_6$] + 4HCl + N$_2$
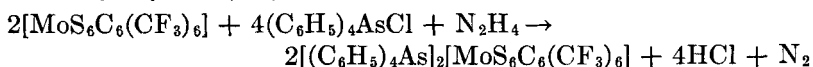
Procedure

A suspension of 3.87 g. (0.005 mol) of [MoS$_6$C$_6$(CF$_3$)$_6$] in 100 ml. of 95% ethanol is treated with a solution of 10 ml. of hydrazine–ethanol (1:1 v/v) or 10 ml. of hydrazine hydrate. Reduction occurs immediately with vigorous evolution of nitrogen to give a clear blue solution. A solution of 4.25 g. of tetraphenylarsonium chloride in 30 ml. of 95% ethanol causes the product to separate as bright blue needles. These are collected by suction and washed with two 25-ml. portions of cold 95% ethanol. A recrystallization procedure using acetone–isobutyl alcohol analogous to that for [(*n*-C$_4$H$_9$)$_4$N]$_2$[NiS$_4$C$_4$-(CN)$_4$] (Sec. B) gives a yield of 6.55 g. (85%) of shiny dark blue needles; m.p. >250°.

Note

The chromium, tungsten, and vanadium complexes can be prepared by an entirely analogous procedure.

$[(C_6H_5)_4As]_2[CrS_6C_6(CF_3)_6]$: shiny black needles, m.p. 193 to 194° (decomp.), from $CrS_6C_6(CF_3)_6$, 41% yield.

$[(C_6H_5)_4As]_2[WS_6C_6(CF_3)_6]$: red-purple needles, m.p. >250°, from $WS_6C_6(CF_3)_6$, 75% yield.

$[(C_6H_5)_4As]_2[VS_6C_6(CF_3)_6]$: purple plates, m.p. 205 to 206°, from sodium bis(diethylene glycol dimethyl ether)hexacarbonylvanadate and $(CF_3)_2C_2S_2$ in CH_2Cl_2; reduction in alcohol of the $VS_6C_6(CF_3)_6{}^{1-}$ species gives a 55% yield.

3. Tetraphenylarsonium tris[*cis*-1,2-bis(trifluoromethyl)-1,2-ethylenedithiolato]molybdate(1−)

$$[(C_6H_5)_4As]_2[MoS_6C_6(CF_3)_6] + [MoS_6C_6(CF_3)_6] \rightarrow$$
$$2[(C_6H_5)_4As][MoS_6C_6(CF_3)_6]$$
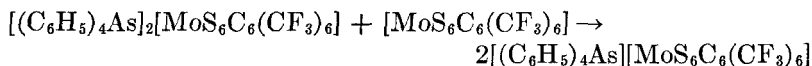
The univalent anions in this series, unlike those in the nickel group, cannot be prepared satisfactorily by solvent reduction because these anions are themselves reduced slowly by solvents.

Procedure

A mixture of 0.79 g. (a slight excess over 0.001 mol) of $[MoS_6C_6(CF_3)_6]$ and 1.54 g. (0.001 mol) of $[(C_6H_5)_4As]_2[MoS_6-C_6(CF_3)_6]$ in 100 ml. of *dry* dichloromethane is refluxed for 3 hours with careful exclusion of atmospheric moisture. The mixture becomes very dark blue, almost black. The solvent is removed *in vacuo* to leave a blue oil. This oil is dissolved in 30 ml. of *dry* dichloromethane and carefully triturated with dry *n*-pentane, which causes the product to crystallize. The product is collected on a sintered-glass funnel and washed with two 25-ml. portions of dry *n*-pentane. The product while still moist with *n*-pentane is dried over phosphorus(V) oxide in a vacuum desiccator. The yield is 2.1 g. (91%) of very dark crystals, m.p. 189 to 192.5° (checkers report m.p. 190 to 191°). The product is sensitive to reduction by atmospheric moisture.

An alternative procedure described by the checkers comprises reduction of the amount of dichloromethane to 30 ml. and

agitation of the reactants in a sealed bottle for 3 hours. The reaction slurry is filtered and the filtrate is triturated as above with dry *n*-pentane. The yield of product is 2.0 g. (87%).

Note

The analogous chromium and tungsten complexes can be prepared by the same procedure, and the vanadium complex from a carbonyl complex.

$[(C_6H_5)_4As][CrS_6C_6(CF_3)_6]$: m.p. 127.5 to 129°, black crystals, 90% yield.

$[(C_6H_5)_4As][WS_6C_6(CF_3)_6]$: m.p. 177.5 to 181°, blue-black crystals, 94% yield.

$[(C_6H_5)_4As][VS_6C_6(CF_3)_6]$: m.p. 175 to 177°, dark purple, from $[(C_6H_5)_4As]V(CO)_6$ and $(CF_3)_2C_2S_2$ in CH_2Cl_2; 50% yield.

REFERENCES

1. G. BÄHR and G. SCHLEITZER: *Chem. Ber.*, **90**, 438 (1957).
2. G. N. SCHRAUZER and V. MAYWEG: *J. Am. Chem. Soc.*, **84**, 3221 (1962).
3. R. B. KING: *Inorg. Chem.*, **2**, 641 (1963).
4. A. H. MAKI, N. EDELSTEIN, A. DAVISON, and R. H. HOLM: *J. Am. Chem. Soc.*, **86**, 4580 (1964); S. L. SHUPACK, E. BILLIG, R. J. H. CLARK, R. WILLIAMS, and H. B. GRAY: *ibid.*, 4594 (1964).
5. A. DAVISON, N. EDELSTEIN, R. H. HOLM, and A. H. MAKI: *ibid.*, 2799 (1964).
6. E. BILLIG, R. WILLIAMS, I. BERNAL, J. H. WATERS, and H. B. GRAY: *Inorg. Chem.*, **3**, 663 (1964).
7. J. F. WEIHER, L. R. MELBY, and R. E. BENSON: *J. Am. Chem. Soc.*, **86**, 4329 (1964).
8. A. DAVISON, N. EDELSTEIN, R. H. HOLM, and A. H. MAKI: *Inorg. Chem.*, **2**, 1227 (1963).
9. A. DAVISON, N. EDELSTEIN, R. H. HOLM, and A. H. MAKI: *ibid.*, **3**, 814 (1964).
10. E. BILLIG, S. I. SHUPACK, J. H. WATERS, R. WILLIAMS, and H. B. GRAY: *J. Am. Chem. Soc.*, **86**, 926 (1964).
11. G. N. SCHRAUZER and V. MAYWEG: *Z. Naturforsch.*, **19b**, 192 (1964).
12. G. N. SCHRAUZER and V. MAYWEG: *J. Am. Chem. Soc.*, **87**, 1483 (1965).
13. E. HOYER and W. SCHROTH: *Chem. Ind. (London)*, **1965**, 652.
14. G. N. SCHRAUZER, V. MAYWEG, H. W. FINCK, U. MÜLLER-WESTERHOFF, and W. HEINRICH: *Angew. Chem.*, **76**, 345 (1964).
15. J. H. WATERS, R. WILLIAMS, H. B. GRAY, G. N. SCHRAUZER, and H. W. FINCK: *J. Am. Chem. Soc.*, **86**, 4198 (1964).

16. A. DAVISON, N. EDELSTEIN, R. H. HOLM, and A. H. MAKI: *Inorg. Chem.*, **4,** 55 (1965).
17. R. EISENBERG and J. A. IBERS: *J. Am. Chem. Soc.*: in press.
18. H. E. SIMMONS, R. D. VEST, D. C. BLOMSTROM, J. R. ROLAND, and T. L. CAIRNS: *ibid.*, **84,** 4746 (1962); H. E. SIMMONS, D. C. BLOMSTROM, and R. D. VEST: *ibid.*, 4756, 4772, 4782 (1962).
19. C. G. KRESPAN: *ibid.*, **83,** 3434 (1961).
20. D. C. OLSON, V. P. MAYWEG, and G. N. SCHRAUZER: *ibid.*, **88,** 4876 (1966).

4. CHROMIUM(II) SALTS AND COMPLEXES

Submitted by DAVID G. HOLAH* and JOHN P. FACKLER, JR.*
Checked by CONSTANCE M. WRIGHT† and EARL L. MUETTERTIES†

Although it has been known since 1905[1] that very pure chromium metal reacts with acids, under oxygen-free conditions, to produce large quantities of chromium(II), this approach to the preparation of chromium(II) compounds has not been developed. Rather, syntheses generally involved (1) reduction of chromium(III), either by electrolytic means or by chemical agents (for example Zn/Hg), or (2) metathetical procedures. Both methods are inefficient and often lead to impure products. Recently[2-8] extensive use of reactions between electrolytic chromium and various acids has led to the synthesis of a wide variety of chromium(II) complexes which would be considerably more difficult to prepare by other methods.[9-11]

Because of the sensitivity of chromium(II) to air oxidation, synthetic work on these systems requires the use either of vacuum-line techniques[12] or of a nitrogen-filled box,[6] or both. This synthesis describes the preparation of chromium(II) complexes using a combination of a closed ground-glass "filter stick"[13] and a nitrogen-filled box.[6] The filter stick enables preparations, filtrations, and recrystallizations to be carried out

---

* Case Institute of Technology, Cleveland, Ohio.
† E. I. du Pont de Nemours & Company, Wilmington, Del.

in a flexible closed system inside a nitrogen-filled box, so that very oxygen-sensitive solutions are never exposed even to the atmosphere inside the box. This is desirable because atmospheres inside glove boxes are very difficult to maintain rigorously free from traces of oxygen. The filter stick therefore gives the complexes maximum protection when they are the most susceptible to oxidation, as when they are in solution or when crystals are still wet. Since many solid chromium(II) complexes are much less oxygen-sensitive when dry, even a moderately good nitrogen box is usually adequate for transferring samples from storage tubes into various cells for physical measurements and analyses.

A. Chromium(II) Salt Hydrates
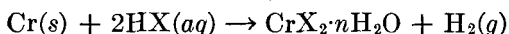
$$\text{Cr}(s) + 2\text{HX}(aq) \rightarrow \text{CrX}_2 \cdot n\text{H}_2\text{O} + \text{H}_2(g)$$
$$(X = \text{Cl}^-, n = 4; X = \text{Br}^-, \text{I}^-, \text{ClO}_4^-, n = 6; X = \text{SO}_4^{2-}, n = 5)$$

General Procedure[3,6]

Electrolytic chromium* and 40 to 50 ml. of the appropriate acid (see Table I) are mixed in the test tube A (Fig. 3). The adapter B is immediately lowered into place and nitrogen

---

* Obtained commercially from Schmeltztechnik G.m.b.H., Munich 42, Germany, through United Mineral and Chemical Corp., New York, N.Y.

TABLE I

Wt. of Cr for 40 to 50 ml. acid, g.	Acid	Approx. strength, %
8	HCl	20
8	HBr	40
8	HI	60
4	HClO₄*	20
5	H₂SO₄	20

* Necessary to activate Cr metal first by dipping in dilute HCl until a reaction starts, then washing with water.
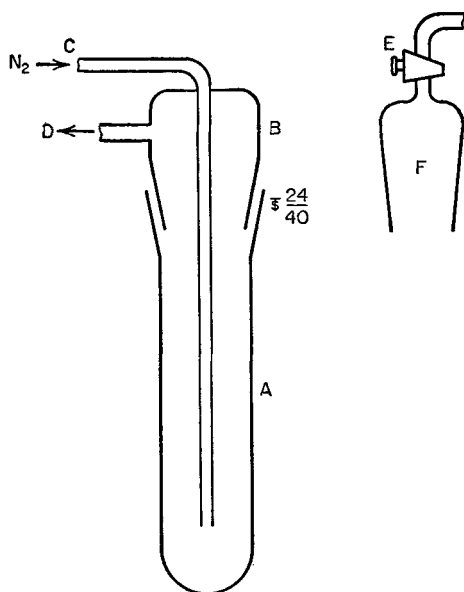
Fig. 3

passed slowly (3 to 5 bubbles per second) in through C and out
at D.   The reaction (depending on the acid) soon becomes
vigorous, and it may be necessary to cool the bright blue solution
to prevent its squirting out at D.   When the reaction subsides,
the tube is heated carefully on a water bath until the last traces
of chromium metal have dissolved.   The adapter B is slowly
raised while the nitrogen flow at tube C is increased so that when
the bottom of the tube C clears the surface of the solution, the
nitrogen is flowing at a high rate.   This prevents the entry
of air into the tube.   The adapter B is then completely removed,
and *as quickly as possible* the adapter F, previously attached to
a water pump, is connected to the tube and stopcock E opened.
If this operation is carried out quickly, no air reaches the
chromium(II) solution.   When cooled overnight in a refriger-
ator, this solution produces bright blue crystals.

The product and the filter stick (Fig. 4a), together with a
number of 24/40 S.T. test tubes and deoxygenated solvents, are
transferred into the nitrogen-filled glove box.[6]   The filter stick

Fig. 4

(a)

(b)
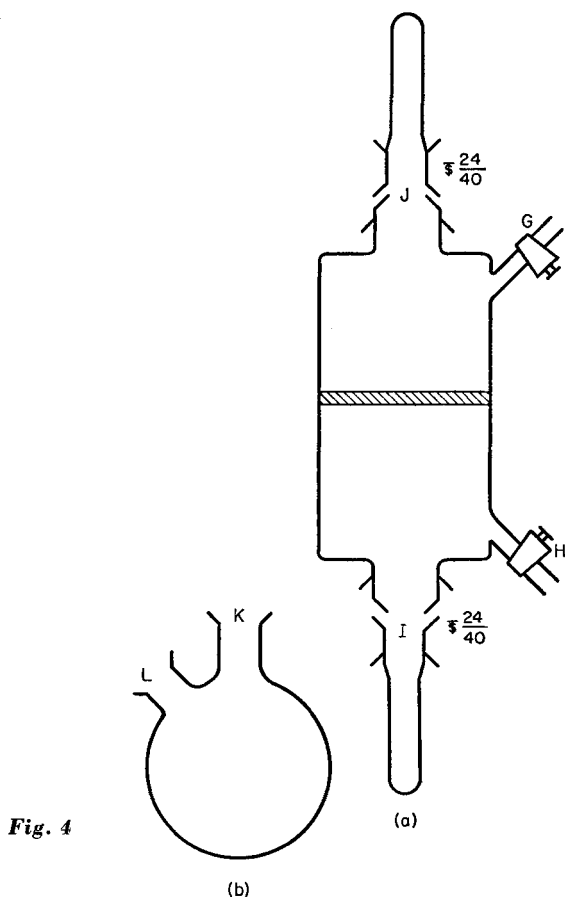
is evacuated and filled with pure nitrogen,* the tube containing the (still ice-cold) product then is attached at one end (e.g., at *I*, Fig. 4*a*), and the blue crystals are shaken down onto the frit by inverting the filter stick.   The ground-glass joints should be secured with spring clips.   With stopcock *H* closed, the crystals are filtered from the small quantity of mother liquor by evacuation at stopcock *G*.   Care should be taken that only pure nitrogen be admitted at stopcock *H* to release the vacuum.   The

* General Electric lamp-grade nitrogen, 2 p.p.m. oxygen, is passed through traps containing chromium(II) solutions.

tube at J containing the mother liquor is replaced by a clean one.   The crystals (*not of the iodide or perchlorate*) are washed with $\sim$20 ml. of oxygen-free acetone and dried by evacuating at stopcock G with stopcock H closed, for several minutes.   The tube containing the wash liquid is removed, and the crystals are shaken back into the tube at I and vacuum-dried further using an adapter F (Fig. 3).   The crystals are stored under pure nitrogen.   The yields can be increased (if necessary) to virtually 100% by evaporation of the small quantities of mother liquor. Or, the mother liquor may be used for the preparations in Sec. C. *Anal.*   Calcd.   for $CrBr_2\cdot6H_2O$:   Cr, 16.3.   Found: Cr, 16.1. *Anal.*   Calcd.   for $CrI_2\cdot6H_2O$:   Cr, 12.6.   Found: Cr, 12.5. *Anal.*   Calcd.   for $Cr(ClO_4)_2\cdot6H_2O$:   Cr, 14.5.   Found: Cr, 14.4.   *Anal.*   Calcd.   for $CrCl_2\cdot4H_2O$:   Cr, 26.7.   Found: Cr, 26.5.   *Anal.*   Calcd.   for $CrSO_4\cdot5H_2O$:   Cr, 21.9.   Found: Cr, 21.7.

Properties

Crystals of the chloride, bromide, and iodide hydrates are difficult to obtain free-flowing.   Prolonged evacuation results in gradual loss of water from the chloride and bromide and decomposition of the iodide.   The compound $Cr(ClO_4)_2\cdot6H_2O$ is rather unstable and slowly decomposes even when stored under nitrogen.[5,6]   All these solids, and their solutions, are extremely sensitive to traces of oxygen.   When $CrSO_4\cdot5H_2O$ is dry, however, the solid appears to be stable in air.[3]   When heated to 100° under vacuum, it changes to $CrSO_4\cdot H_2O$.[4]

The crystal structure of $CrCl_2\cdot4H_2O$ shows[14] the chromium(II) ion to be surrounded by a grossly distorted octahedron of four water and two chloride ligands.   The single-crystal[14] and reflectance spectra[6] of this complex have been measured, and the complex band system centered on 14,000 cm.$^{-1}$ has been interpreted[6] on the basis of these distortions.   Aqueous solution spectra between 8,000 and 20,000 cm.$^{-1}$ are identical for all

the above complexes and strongly suggest that the $[Cr(H_2O)_6]^{2+}$ ion, which is presumably present in all the solutions, is also distorted from O_h symmetry.[6] All the complexes have room-temperature magnetic moments within the expected range[5,6] (4.8 to 5.0 B.M.) for high-spin chromium(II).

B. Dichlorobis(acetonitrile)chromium(II)

$$CrCl_2 + 2CH_3CN \rightarrow CrCl_2 \cdot 2CH_3CN$$
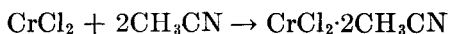
Procedure[15]

Approximately 3 g. of chromium(II) chloride tetrahydrate is heated to 140° under high vacuum for ~12 hours. The compound readily loses its water and changes to the off-white (slightly impure) anhydrous chromium(II) chloride. Absolute ethanol (the minimum quantity) is added slowly, with boiling, until all the solid is dissolved, forming a bright blue solution. Hot acetonitrile then is added until pale blue crystals just begin to form. The solution is cooled, removed from the glove box and stored overnight in a refrigerator. The tube is returned to the box and the pale blue crystals are filtered off (using the filter stick procedure described above), washed with acetonitrile and dried under vacuum at room temperature. *Anal.* Calcd. for $CrCl_2 \cdot 2CH_3CN$: Cr, 25.4; Cl, 34.6; C, 23.4; H, 3.0. Found: Cr, 25.4; Cl, 34.6; C, 23.2; H, 3.1.

Properties

Solutions of $CrCl_2 \cdot 2CH_3CN$ and the wet solid are extremely sensitive to oxygen. When dried, however, the complex remains unchanged in air for several minutes before oxidation becomes apparent. It is virtually insoluble in acetonitrile but quite soluble in ethanol. The room-temperature magnetic moment (4.8 B.M.) and electronic spectrum are consistent with a high-spin distorted octahedral Cr^{2+} ion.[15]

C. Chromium(II) Halide–Pyridine Complexes

$CrX_2 \cdot 2py$ (X = Cl, Br); $CrI_2 \cdot 4py$; $CrX_2 \cdot 6py$ (X = Br, I)
$CrX_2(aq) + xpy \rightarrow CrX_2 \cdot xpy$ (X = Cl, Br; x = 2; X = I, x = 4)
$CrBr_2 \cdot 2py + 4py \rightarrow CrBr_2 \cdot 6py$
$CrI_2 \cdot 4py + 2py \rightarrow CrI_2 \cdot 6py$
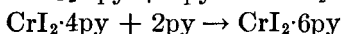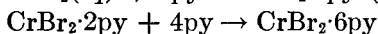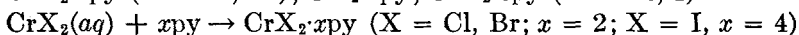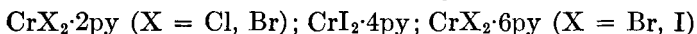
Procedure[7]

Chromium(II) halide hydrates ($\sim$2 g.) are dissolved* in $\sim$30 ml. of water and pyridine is added slowly with shaking. A green precipitate is immediately formed. Dropwise addition of pyridine is continued until no further precipitation occurs. The reactions are strongly exothermic. The green precipitate is filtered off (using the filter stick) and dried under vacuum at room temperature. The yield at this stage is almost quantitative. Round-bottomed flasks (100 ml.) are connected at *I* and *J* (Fig. 4a) and the filter stick purged of oxygen as previously indicated. The green chromium(II) chloride–pyridine complex is dissolved in the minimum quantity of hot dimethylformamide in one flask and filtered hot, and the solution is cooled in the second flask. This recrystallization produces light green needles which are filtered off, washed with ethanol, and dried under vacuum. As in Sec. A, care should be taken that the vacuum in the filter stick is released by admitting only pure nitrogen. Similarly, the bromide complex is recrystallized from 100% ethanol and washed with cold ethanol, and the green crystals are dried under vacuum. These complexes can be stored indefinitely under nitrogen. *Anal.* Calcd. for $CrCl_2 \cdot 2py$: Cr, 18.5; Cl, 25.3; C, 42.7; H, 3.6. Found: Cr, 18.6; Cl, 25.2; C, 42.5; H, 3.6. *Anal.* Calcd. for $CrBr_2 \cdot 2py$: Cr, 14.1; Br, 43.2; C, 32.5; H, 2.7. Found: Cr, 14.0; Br, 43.1; C, 32.3; H, 2.8.

---

* Alternatively, the mother liquors remaining after the original preparation of the hydrates (in Sec. A) can be used. Since these solutions are very concentrated, it is necessary to dilute them with deoxygenated water before addition of pyridine.

When the green iodide product is recrystallized (as above) from an ethanol-dimethylformamide mixture, brown crystals are obtained. These crystals, which analyze for $CrI_2 \cdot 4py$, are filtered off and dried under vacuum. *Anal.* Calcd. for $CrI_2 \cdot 4py$: Cr, 8.4; I, 40.8; C, 38.6; H, 3.2. Found: Cr, 8.3; I, 40.6; C, 38.6; H, 3.2.

The complexes $CrBr_2 \cdot 2py$ and $CrI_2 \cdot 4py$ react further with pyridine to give dark green products which are recrystallized (as above) from an ethanol-pyridine mixture. The compound $CrCl_2 \cdot 2py$ does not react further with pyridine. *Anal.* Calcd. for $CrBr_2 \cdot 6py$: Cr, 7.6; Br, 23.3; C, 52.6; H, 4.4. Found: Cr, 7.6; Br, 23.5; C, 52.3; H, 4.5. *Anal.* Calcd. for $CrI_2 \cdot 6py$: Cr, 6.7; I, 32.5; C, 46.2; H, 3.9. Found: Cr, 6.1; I, 31.7; C, 46.2; H, 3.9.

Properties

These pyridine complexes are considerably more stable than the hydrates. They remain unchanged in air for several minutes before slow oxidation begins. The hexapyridine complexes are surprisingly stable to loss of pyridine.[7,*] The $CrX_2 \cdot 2py$ (X = Cl, Br) complexes are isomorphous with the analogous distorted octahedral copper(II) complexes.[7] Reflectance spectra between 8,000 and 25,000 cm.$^{-1}$ are characteristic[7] of distorted octahedral chromium(II). The two hexapyridine–chromium(II) complexes are more stable[7] than $CuBr_2 \cdot 6py$, the latter complex losing pyridine rapidly in air to form $CuBr_2 \cdot 2py$.

D. Tris(bipyridine)chromium(II) Perchlorate

$$Cr(ClO_4)_2 \cdot xH_2O + 3C_{10}H_8N_2 \rightarrow Cr(C_{10}H_8N_2)_3(ClO_4)_2 + xH_2O$$

---
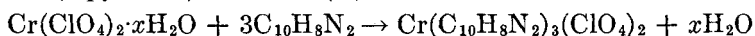
* Crystalline $CrBr_2 \cdot 6py$ slowly loses pyridine after a few days when confined in an x-ray capillary. The crystals are orthorhombic, space group *Pmma* or *Pmc2* or *Pma2*, with $a = 9.89$, $b = 15.4$, and $c = 18.8$. With $z = 4$, the calculated density is 1.6 g./cm.^{3}

■ *Caution should be observed in handling this compound, as with all perchlorate salts. The tris(bipyridine)chromium(II) perchlorate explodes violently on slow heating to 250° and can be set off by static electricity. It does not appear to be shock-sensitive on dropping an 8.3-g. steel ball from 4 ft., although the compound was tested only once. The explosive properties of related complexes have been described.*[16]

Procedure[17]

This reaction can be carried out in the filter stick without using a nitrogen box. The test tube at I (Fig. 4a) is replaced with a 100-ml. two-necked round-bottomed flask with two 24/40 S.T. ground-glass joints (Fig. 4b). One of these (K) is connected to the filter stick and the other (L) contains a stopper. The apparatus is completely purged of oxygen by repeated evacuation (at G) and filled with pure nitrogen at H. With G closed, a flow of nitrogen is maintained from H, through the flask and out at L. Reactants can be added through L without oxygen entering the flask.

Chromium metal (0.3 g.) is dissolved in ~4 ml. 1:1 hydrochloric acid in the flask and then diluted to approximately 30 ml. with deoxygenated water.* To this is added a solution of ~2.7 g. bipyridine in ~15 ml. deoxygenated methanol, producing a color change from bright blue to wine-red. Approximately 1 ml. of 70% perchloric acid in 40 ml. of water then is added, after deoxygenation. Precipitation of small black crystals is complete in 15 or 20 minutes. The stopcock at H is closed and at the same time the stopper is replaced at L. The crystals are then filtered, washed with deoxygenated methanol, and then ether, and dried in the way described in previous sections. Yields of the order of 80% are obtained. *Anal.* Calcd. for $Cr(C_{10}H_8N_2)_3(ClO_4)_2$: C, 50.1; H, 3.4. Found: C, 50.2; H, 3.4.

* The preparation was checked at two-thirds the scale described.

Properties

Tris(bipyridine)chromium(II) perchlorate is stable for long periods in dry air but slowly oxidizes when wet. It has a room-temperature magnetic moment of 3.0 B.M., typical of a low-spin chromium(II) compound.[18]

REFERENCES

1. J. Koppel: *Z. Anorg. Allgem. Chem.*, **45**, 359 (1905).
2. R. L. Pecsok and J. Bjerrum: *Acta Chem. Scand.*, **11**, 1418 (1957).
3. H. Lux and G. Illman: *Chem. Ber.*, **91**, 2143 (1958).
4. H. Lux, L. Eberle, and D. Sarre: *ibid.*, **97**, 503 (1964).
5. A. Earnshaw, L. F. Larkworthy, and K. S. Patel: *J. Chem. Soc.*, **1965**, 3267.
6. J. P. Fackler, Jr. and D. G. Holah: *Inorg. Chem.*, **4**, 954 (1965).
7. D. G. Holah and J. P. Fackler, Jr.: *ibid.*, 1112 (1965).
8. D. G. Holah and J. P. Fackler, Jr.: *ibid.*, 1721 (1965).
9. J. H. Balthis, Jr. and J. C. Bailar, Jr.: Inorganic Syntheses, **1**, 122 (1939).
10. M. R. Hatfield: *ibid.*, **3**, 148 (1950).
11. M. Kranz and A. Witkowska: *ibid.*, **6**, 144 (1960).
12. S. Herzog and J. Dehnert: *Z. Chem.*, **4**, 1 (1964).
13. D. G. Holah: *J. Chem. Educ.*, **42**, 561 (1965).
14. W. A. Runciman and R. W. G. Syme: *Phil. Mag.*, **8**, 605 (1963).
15. D. G. Holah and J. P. Fackler, Jr.: *Inorg. Chem.*, **5**, 479 (1966).
16. W. R. Tomlinson, K. G. Ottoson, and L. F. Audrieth: *J. Am. Chem. Soc.*, **71**, 375 (1949).
17. G. Brauer: "Handbuch der Präparativen Anorganischen Chemie," Vol. 2, p. 1192, Ferdin and Enke, Stuttgart, Germany, 1962.
18. J. P. Fackler, Jr., G. Kubas, and D. G. Holah: to be published.

5. CHROMIUM(III)–AMINE COMPLEXES

Submitted by DAVID BERMAN,* GARY BOKERMAN,* and R. W. PARRY*
Checked by WILLIAM C. SEIDEL,† JOHN A. FETCHIN,† DAVID G. HOLAH,† and JOHN P. FACKLER, JR.†

The synthesis of $[Cr(NH_3)_6]Cl_3$ from anhydrous chromium(III) chloride and liquid ammonia in the presence of catalytic quan-

* Department of Chemistry, University of Michigan, Ann Arbor, Mich.
† Department of Chemistry, Case Institute of Technology, Cleveland, Ohio.

tities of sodium amide has been described in an earlier volume of this series.[1]   A similar reaction involving anhydrous ethylenediamine with anhydrous chromium(III) salts to give salts of the $[Cr(en)_3]^{3+}$ cation has also been described in an earlier volume.[2]   The ethylenediamine complexes have also been prepared by the reaction of chromium(III) chloride hexahydrate with ethylenediamine[3] and by the reaction of aqueous chromium(III) chloride solution with aqueous ethylenediamine in the presence of activated charcoal.[4]   In general, the foregoing procedures start with materials of limited availability or produce, through side reactions, polymeric red oils.   Yields are frequently low.[5]

Balthis and Bailar[6] obtained tris(ethylenediamine)chromium-(III) complexes by the oxidation of chromium(II) solutions, using a procedure somewhat similar to that used for the synthesis of cobalt(III) complexes.   Mori[7] described the preparation of hexaamminechromium(III) salts from the oxidation of chromium(II) salts in the presence of ammonia.   The results obtained in both syntheses have been erratic.[8,9]   Berman noted that the foregoing syntheses are rendered dependable by the use of a catalyst of activated platinum on asbestos.   Schaeffer,[10a] in a subsequent study, independently used colloidal platinum as a catalyst but reported some difficulty in separating it from the product.[10b]   The procedures recommended and described here are based on the use of platinized asbestos as the catalyst.

Procedure

Preparation of Catalyst

Approximately 2 g. of shredded asbestos slurried in 15 ml. of water is added to a solution containing 10 g. of sodium formate in about 30 ml. of water; the solution is boiled gently, then about 80 ml. of a 5% platinum(II) chloride solution is added. The solution is boiled until the platinum has been deposited.

The platinized asbestos is filtered, washed once with 10% sulfuric acid, once with hot water, once with hot 5% hydrochloric acid, and finally with hot water until no test for chloride or sulfate is found. The product is dried at 110° and stored until needed in a covered container. Each gram of asbestos contains about 0.5 g. of platinum.

A. Hexaamminechromium(III) Chloride

Chromium(II) chloride solutions can be prepared by any one of several different procedures. If pure electrolytic chromium is available, the procedure of Holah-Fackler (see synthesis 4) is recommended. Some modification as noted at the end of this procedure may be desirable. If metallic chromium is not available, commercial chromium(III) chloride may be reduced electrolytically (a suitable divided cell is needed), or the reduction may be effected by zinc and hydrochloric acid. The latter procedure, which starts with the most commonly available reagents and apparatus, is described here.

The apparatus required is indicated in Fig. 5. The supply of gaseous ammonia may be generated from ammonium sulfate by using the equipment in Fig. 5 which is enclosed by the dashed lines. Alternatively, a tank yielding gaseous ammonia may be used instead of the ammonia generator. All air is flushed from flask *B* (and *C* if used) and from the connecting lines using a stream of oxygen-free nitrogen. Valves 2 and 3 permit adjustment of nitrogen flow. If ammonia is to be generated from ammonium sulfate, 200 g. of potassium hydroxide or an equivalent amount of sodium hydroxide is added to flask *C*, and air is removed with a vigorous nitrogen stream. Ammonium sulfate (132 g.) is dissolved in a minimum amount of freshly boiled water and is added to the addition funnel on top of flask *C*. The nitrogen flow is continued to be sure that all oxygen is swept from flasks *B* and *C*. Alternatively, ammonia from a commercial cylinder can be employed.

To prepare the chromium(II) chloride solution, 25 g. of about
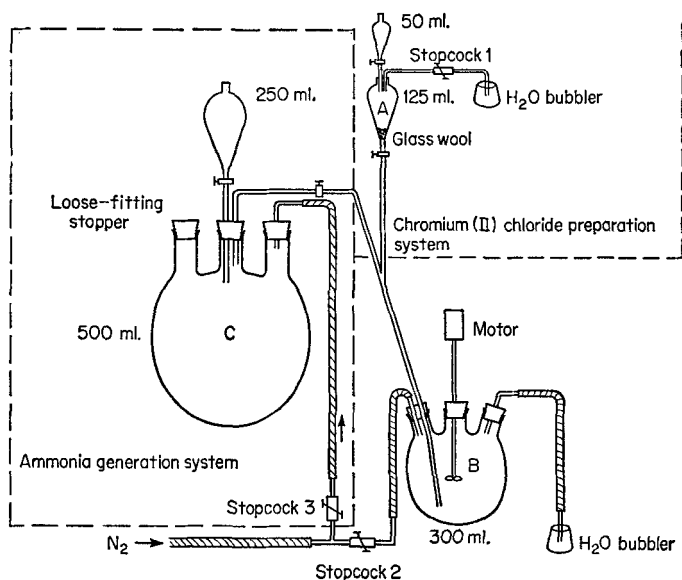
Fig. 5. Apparatus for preparation of hexaammines of chromium(III).

20-mesh metallic zinc is added to vessel *A*. Commercial chromium(III) chloride hexahydrate (15 g.) is thoroughly pulverized with a mortar and pestle, and the powder is added to vessel *A*. Then 30 ml. of concentrated hydrochloric acid is allowed to drip slowly from the addition funnel onto the reaction mixture in vessel *A*. When the chromium(II) chloride solution is bright blue in color (comparable to copper(II) sulfate solution) and the evolution of hydrogen has slowed, the blue liquid containing chromium(II) chloride is transferred to flask *B*. It is important that an oxygen-free atmosphere be maintained in flask *B* at all times. It is also desirable to proceed at once and add the ammonia and catalyst *immediately* to the freshly reduced solution. Yields are reduced if the chromium(II) chloride solution is allowed to stand. The transfer of the chromium(II) chloride solution to flask *B* may be accelerated by closing stopcock 1 of the water bubbler (Fig. 5).

After the chromium(II) chloride solution has been transferred to flask *B*, the flow of ammonia through the reaction vessel should be started. The ammonia delivery tube should approach but not dip below the liquid level in flask *B*. If tank ammonia is used, the tank should be opened carefully to avoid spattering of liquids by a sudden burst of gas. If ammonia is to be generated, the ammonium sulfate solution should be added *carefully* to the potassium hydroxide in flask *C*. It may be necessary to cool flask *C* with ice at first, then to warm the generator later in order to maintain a reasonably constant flow of ammonia. The use of tank ammonia avoids these problems. If zinc was used in the reduction, a precipitate of zinc hydroxide forms first and redissolves. The violet-blue solution stirred at 0° is saturated with ammonia, then a 2- to 3-g. sample of the platinum catalyst is added rapidly to flask *B*. A strong countercurrent of nitrogen is used to prevent entrance of air into the system when the catalyst is added. The reaction mixture is allowed to stir for one hour while the flask is cooled with ice.

The platinum asbestos is removed by filtration and the product which has deposited on this catalyst is dissolved in water. Alcohol is added to the combined filtered solution and washings, and the mixture is cooled with ice to precipitate the product. A second crop of crystals may be obtained by concentrating the solution under vacuum at room temperature, then cooling and adding hydrochloric acid until the pH is below 1. The crystals are thoroughly washed with ethanol.

The crude product may be recrystallized by dissolving it in a minimum amount of 1 N hydrochloric acid at room temperature and cooling in an ice bath to 0°. Concentrated hydrochloric acid is added slowly, 0.5 ml. at a time, until the initial volume is approximately doubled. Crystals are removed by filtration and washed with ethanol and diethyl ether. In a typical run the crude yield is 10.3 g. or 70%, and the recrystallized yield is 7.7 g. or about 53%.

B. Tris(ethylenediamine)chromium(III) Chloride

To the chromium(II) chloride solution prepared as described in the previous section, a 75-ml.* aliquot of a 65% ethylenediamine solution is added slowly with stirring.

A 2- to 3-g. sample of platinum catalyst is added to the reaction system. As before, a vigorous countercurrent of nitrogen is used to exclude air. The reaction mixture is stirred for half an hour while the flask is cooled with ice.

The platinum asbestos is filtered off. The product which has deposited on the catalyst is washed off with a minimum amount of water and the washings are combined with the filtrate. To avoid contamination of the final product with zinc, the zinc is removed from the solution by addition of about 55 ml. of a 20% ammonium sulfide solution (or ammonium sulfide is added until precipitation is complete). The zinc sulfide is removed by filtration, the solid is washed, and the washings are added to the solution. Alcohol is added to the filtrate and washings until some cloudiness appears, then the mixture is cooled to precipitate the product. Additional product may be obtained by concentrating the solution under vacuum, adding hydrochloric acid to obtain a pH below 1, and cooling. The crystals are washed with alcohol.

The crude product may be recrystallized by the same procedure as that used for $[Cr(NH_3)_6]Cl_3$ except that the cold acid solution is treated with about 4 volumes of cold alcohol to precipitate the product. The crystals are washed with alcohol and ether and allowed to dry. The crude yield is 15.3 g. of $[Cr(en)_3]Cl_3 \cdot 3H_2O$ or about 70% based on the original chromium(III) chloride used. The final recrystallized yield is 11.5 g. or 52%. Rapid work-up of the solution gives rise to less olation† and higher yields.

---

* Only 45 ml. of ethylenediamine is needed if the solution contains no zinc.
† Formation of polynuclear coordination complexes by means of hydroxyl groups as bridging ligands.

C. Tris(propylenediamine)chromium(III) Chloride

Substitution of propylenediamine (about 3 *M*) for ethylene-diamine in synthesis 5*B* gives [Cr(pn)₃]Cl₃ in good yield.

Comments on the Procedure if Other Methods for Preparation of Chromium(II) Chloride Are Used

If the chromium(II) chloride is prepared by the Holah-Fackler procedure from electrolytic chromium and hydrochloric acid, a three-necked round-bottomed flask may be used as a reaction vessel, and ammonia may be bubbled directly into the chromium(II) chloride solution using a T-joint in the nitrogen line. Bubbling of the ammonia through the liquid avoids the necessity for stirring. When the above procedure was used, it was necessary to centrifuge the final filtered solution at 2700 r.p.m. for 15 minutes in order to remove all the platinum catalyst.

Properties

The compounds [Cr(NH₃)₆]Cl₃, [Cr(en)₃]Cl₃·3H₂O, and [Cr(pn)₃]Cl₃ are all yellow crystalline solids. The color shade is dependent upon crystal size, larger crystals showing darker colors. On exposure of the crystals to bright light, their surface darkens, approaching purple in color. The replacement of NH₃ by Cl⁻ in the coordination sphere is indicated, giving products of composition [Cr(NH₃)₆₋ₓClₓ]Cl₃₋ₓ. Aqueous solutions become red on standing due to olation; the reaction is slow at 25° but rapid in hot solutions. The chelated ethylenediamine complex seems to be somewhat more stable than the ammonia complex. Approximate solubilities in water are: [Cr(NH₃)₆]Cl₃ about 18% by weight, [Cr(en)₃]Cl₃·3H₂O about 20% by weight.

REFERENCES

1. A. L. OPPEGARD and J. C. BAILAR, JR.: INORGANIC SYNTHESES, **3**, 153 (1950); C. L. ROLLINSON and J. C. BAILAR, JR.: *J. Am. Chem. Soc.*, **65**, 250 (1943).

2. C. L. ROLLINSON and J. C. BAILAR, JR.: INORGANIC SYNTHESES, **2**, 196 (1946).
3. L. E. MARCHI and J. P. MCREYNOLDS: *J. Am. Chem. Soc.*, **65**, 480 (1943).
4. J. C. BAILAR, JR., and J. B. WORK: *ibid.*, **67**, 176 (1945).
5. S. M. JÖRGENSEN: *J. Prakt. Chem.*, [2], **25**, 321 (1882); O. SCHMITZ-DUMONT: *Z. Elektrochem.*, **47**, 221 (1941).
6. J. H. BALTHIS and J. C. BAILAR, JR.: *J. Am. Chem. Soc.*, **58**, 1474 (1936).
7. M. MORI: *J. Chem. Soc. Japan, Pure Chem. Sect.*, **74**, 253 (1953); *C.A.*, 98429 (1953).
8. D. N. HUME and H. W. STONE: *J. Am. Chem. Soc.*, **63**, 1200 (1941).
9. D. A. BERMAN: Ph.D. dissertation, University of Michigan, 1956. "Some Amine and Phosphine Complexes of Chromium(II) and (III)."
10a. C. E. SCHÄFFER: "Chromium Ammines; Stability and Catalytic Phenomena," Advances in the Chemistry of the Coordination Compounds, S. Kirschner (ed.), p. 628, The Macmillan Company, New York, 1961.
10b. C. E. SCHÄFFER: private communication.

6. TRIS(*O*-ETHYL DITHIOCARBONATO) COMPLEXES OF TRIPOSITIVE CHROMIUM, INDIUM, AND COBALT

Submitted by F. GALSBØL* and C. E. SCHÄFFER*
Checked by PETER M. BARNA,† J. H. SHERMAN,‡ and E. L. MUETTERTIES‡

Methods for the preparation of tris(*O*-ethyl dithiocarbonato) complexes of chromium(III), indium(III), and cobalt(III) are presented and serve to illustrate procedures applicable to the preparation of *O*-alkyl dithiocarbonato, alkyl trithiocarbonato, *N,N*-dialkyldithiocarbamato, and *O,O'*-dialkyl dithiophosphato complexes of several metals.

A. Tris(*O*-ethyl dithiocarbonato)chromium(III)
[Tris(ethylxanthato)chromium(III)]

$$3C_2H_5OCSSK + CrCl_3 \rightarrow (C_2H_5OCSS)_3Cr + 3KCl$$
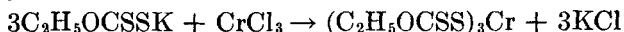
Tris(*O*-ethyl dithiocarbonato)chromium(III), first reported by Hlasiwetz,[1] was prepared by the reaction of anhydrous chromium

* Chemistry Department I, The H. C. Ørsted Institute, University of Copenhagen, Copenhagen, Denmark.
† Rocketdyne, Canoga Park, Calif.
‡ Central Research Department, Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, Del.

chloride with sodium ethylxanthate in carbon disulfide suspension. Dubsky[2] reported the preparation of the compound from reaction of chromium alum with potassium ethylxanthate in aqueous solution. This reaction proceeded slowly,[3] and yields were often low. The preparation reported here, carried out in a nonaqueous medium in which chromium chloride has high solubility, proceeds rapidly with good yields.

Procedure

Tetrahydrofuran, 200 ml., dried overnight with Linde 4A molecular sieve, is added to 17.4 g. (0.11 mol, 10% excess) of anhydrous chromium(III) chloride in a 1-l. conical flask. The flask is fitted with a condenser, calcium chloride drying tube, and a magnetic stirring bar. To remove air in the system, the suspension is stirred and heated for 15 minutes at the reflux temperature by use of a combination hot plate–magnetic stirring apparatus. A small amount of zinc dust is added* to the mixture, and stirring at the reflux temperature is continued for 30 minutes. The solution is cooled to room temperature, and 48.1 g. (0.30 mol) of pulverized potassium ethylxanthate is added with stirring. The reaction mixture warms and the solution color changes to the dark blue-violet characteristic of tris(O-ethyl dithiocarbonato)chromium(III). After stirring the solution for 30 minutes, the xanthate complex is precipitated by addition over a one-hour period of 700 ml. of water with continued stirring. More rapid addition of water to the solution results in precipitation of the complex as an oil, and more prolonged treatment of the product with water results in partial hydrolysis. The solid is collected on a Büchner funnel, washed thoroughly with water, and dried in air. The crude product (approximately 37 g.) is dissolved in chloroform and the solution is filtered. Ethanol is added dropwise to the

* The presence of zinc in catalytic proportions promotes formation of the soluble red-violet tetrahydrofuran (THF) complex, $Cr(THF)_3Cl_3$.[4]

stirred filtrate until the composition of the solvent is about 2:1 ethanol–chloroform. The resulting precipitate* is filtered, washed thoroughly first with a 1:2 mixture of chloroform and ethanol and then with ethanol, and dried in air. The yield is 28 g. (67%). *Anal.* Calcd. for $C_9H_{15}O_3S_6Cr$: C, 26.01; H, 3.64; S, 46.29. Found: C, 26.20; H, 3.88; S, 46.13.

Using this procedure, tris(alkyl trithiocarbonato)-, tris(N,N-dialkyldithiocarbamato)-, and tris(O,O'-dialkyl dithiophosphato)chromium(III), as well as other tris(O-alkyl dithiocarbonato)chromium(III) complexes, can be prepared from the appropriate potassium or sodium salts of the ligands, with the exception that some of the compounds are purified by other means. Examples of compounds which have been prepared by this method, with recrystallization procedures (in parentheses) are: $(CH_3OCSS)_3Cr$ (from chloroform by addition of petroleum ether), $[CH_3(CH_2)_3OCSS]_3Cr$ (isolated only as an oil), and $[(CH_3)_2CHCH_2OCSS]_3Cr$ (from diethyl ether by partial evaporation of the solvent), $(cyclo-C_6H_{11}OCSS)_3Cr$, $(CH_3SCSS)_3Cr$, $(C_2H_5SCSS)_3Cr$, and $[(C_2H_5)_2NCSS]_3Cr$ (each from chloroform by addition of petroleum ether).

B.   Tris(O-ethyl dithiocarbonato)indium(III)
   [Tris(ethylxanthato)indium(III)]

$$3C_2H_5OCSSK + InCl_3 \rightarrow (C_2H_5OCSS)_3In + 3KCl$$
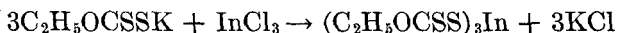
Procedure

For the preparation of tris(O-ethyl dithiocarbonato)indium-(III), reference may be made to the description of the apparatus,

---

* Because the product and also its solutions in chloroform are so highly colored, it is difficult to judge when complete solution has been achieved. The checker, operating on a scale one-third of that reported, dissolved 13.5 g. of crude product in 180 ml. of hot chloroform, filtered the solution, and added 360 ml. of ethanol. The product did not precipitate at room temperature, but 6.1 g. of material could be isolated after the solution had been chilled. An additional 3.1 g. of product was isolated after reduction of the volume of solvent to 70 ml. The combined crops constitute the yield claimed. It is recommended that the solubility characteristics of this complex which are given in Table I (p. 48) be used as a guide for dissolution of the crude product.

and solvent and product purification procedures employed in the preparation of tris(*O*-ethyl dithiocarbonato)chromium(III). Dried tetrahydrofuran, 200 ml., is placed in a 1-l. conical flask, and 22.1 g. (0.10 mol) of anhydrous indium(III) chloride is added while the mixture is stirred. This order of addition prevents caking. The flask is fitted with a condenser and calcium chloride drying tube, and the mixture is stirred at the reflux temperature until all the indium chloride has gone into solution. The solution is cooled to room temperature, 48.1 g. (0.30 mol) of pulverized potassium ethylxanthate is added, and the stirring is continued. The reaction mixture warms. The progress of the reaction may be monitored by observing the disappearance of the yellow potassium xanthate salt and the formation of color- less potassium chloride. After 3 to 4 hours, the product is isolated by the procedure described for the analogous chromium compound. The crude product weighs 46 g. After recrystal- lization, the yield is 41 g. (85%). *Anal.* Calcd. for $C_9H_{15}O_3S_6In$: C, 22.59; H, 3.16; S, 40.22. Found: C, 22.81; H, 3.22; S, 40.17.

The colorless tris(*O*-ethyl dithiocarbonato)arsenic(III) and yellow antimony(III) complexes have been prepared from the corresponding metal trichlorides using this procedure. Tris- (alkyl trithiocarbonato)-, tris(*O,O'*-dialkyl dithiophosphato)-, and other tris(*O*-alkyl dithiocarbonato)indium(III) complexes can undoubtedly be prepared from the potassium or sodium deriv- atives of the ligands using this procedure.

C. Tris(*O*-ethyl dithiocarbonato)cobalt(III)
[Tris(ethylxanthato)cobalt(III)]

$$2CoCl_2 \cdot 6H_2O + H_2O_2 + 10KHCO_3 \rightarrow$$
$$2K_3Co(CO_3)_3 + 18H_2O + 4CO_2 + 4KCl$$
$$K_3Co(CO_3)_3 + 3C_2H_5OCSSK \rightarrow (C_2H_5OCSS)_3Co + 3K_2CO_3$$
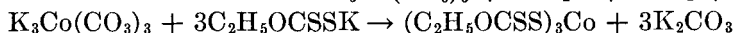
Tris(*O*-ethyl dithiocarbonato)cobalt(III) was apparently first prepared by Hlasiwetz[1,5] although some doubt about the com- position of his complex exists.[5] This and other reported synthe- ses[2,6] involve the reaction of cobalt(II) chloride with the xanthate

ion and are unsatisfactory in that a cobalt(II) complex and by-products of xanthate ion reduction are also formed.   In the synthesis reported here, prior to addition of the xanthate ion, cobalt(II) chloride is oxidized in solution to a cobalt(III) carbonate using an adaptation of procedures previously described for oxidation of cobalt(II) in solution[7,8] and for preparation of other cobalt(III) complexes.[9-15a]

Procedure

Cobalt(II) chloride hexahydrate, 23.8 g. (0.10 mol), is dissolved in 450 ml. of water, and 50 ml. of 30% hydrogen peroxide is added.   While being vigorously shaken, the solution is poured slowly onto 100 g. (1.0 mol) of potassium hydrogen carbonate contained in a 2-l. conical flask.*   The resulting dark green to black solution containing (probably among other ions) the tris(carbonato)cobalt(III) ion[24] is allowed to stand for 5 minutes, during which time the excess peroxide decomposes.   The xanthate complex is formed by the addition of small portions of a solution of 48.1 g. (0.30 mol) of potassium ethylxanthate dissolved in 150 ml. of water to the agitated solution of the cobalt(III) ion.   The product precipitates as a tough, sticky, noncrystalline mass.   After about 30 minutes, the mass hardens and is broken with a spatula.   After the mixture has been allowed to stand an additional 30 minutes, the solid is isolated on a Büchner funnel, washed thoroughly with water, and dried in air.   The crude product (approximately 41 g.) is dissolved in chloroform, and the solution is filtered.   Ethanol is added dropwise to the stirred filtrate until the composition of the solvent is approximately 2:1 ethanol-chloroform.   The resulting pre-

---

* The order of addition is important.   This procedure affords a solution of high cobalt concentration (approximately 0.2 M) which promotes decomposition of the excess hydrogen peroxide at a desirable rate.   Substitution of sodium for potassium hydrogen carbonate makes it impossible to obtain such a high concentration of cobalt in solution.

cipitate is filtered, washed thoroughly first with a 1:2 mixture of chloroform and ethanol and then with ethanol alone, and dried in air. The yield is 35 g. (83%). *Anal.* Calcd. for $C_9H_{15}O_3S_6Co$: C, 25.58; H, 3.58; S, 45.53. Found: C, 25.85; H, 3.82; S, 45.69.

Tris(alkyl trithiocarbonato)-, tris(N,N-dialkyldithiocarbamato)-, and tris(O,O'-dialkyl dithiophosphato)cobalt(III), as well as other tris(O-alkyl dithiocarbonato)cobalt(III) complexes, can be prepared by this procedure from the potassium or sodium salt[15b] of the appropriate ligand, except that some of these compounds have to be purified by other methods. Examples of compounds which have been prepared (with the method of recrystallization in parentheses) are: $(CH_3OCSS)_3Co$ (from chloroform by addition of petroleum ether), $[CH_3(CH_2)_3-OCSS]_3Co$ (isolated only as a syrup which in spite of several attempts could not be made crystalline), $[(CH_3)_2CHCH_2-OCSS]_3Co$ (from diethyl ether by partial evaporation of the solvent), $(cyclo-C_6H_{11}OCSS)_3Co$, $(CH_3SCSS)_3Co$, and $(C_2H_5-SCSS)_3Co$ (each from chloroform by addition of petroleum ether), and $[(C_2H_5)_2NCSS]_3Co$ (from chloroform by addition of diethyl ether).

Properties

Tris(O-ethyl dithiocarbonato)chromium(III) is obtained as a dark blue crystalline powder which decomposes at 100 to 140°. The indium(III) ethylxanthate complex forms small colorless crystals which decompose at 130 to 150°.[16,17] The cobalt(III) ethylxanthate complex is isolated as a dark green crystalline powder whose decomposition temperature determined by use of a thermal balance is 135 to 137° (lit. value, 117°;[2] 118 to 119°[6]). These compounds decompose slowly in air and more rapidly when heated in solution. The tripositive chromium, indium, and cobalt complexes are insoluble in water but are soluble in many organic solvents (Table I).

TABLE I   Solubilities of Tris(*O*-ethyl dithiocarbonato)
Complexes of Chromium(III), Indium(III), and
Cobalt(III) in Organic Solvents at 25°

Solvent	g./100 ml. solvent		
	Cr(exan)₃	In(exan)₃	Co(exan)₃
Chloroform	32	31	53
Tetrahydrofuran	24	20	41
Carbon disulfide	17	14	36*
Dioxane	8.3	7.5	16*
Carbon tetrachloride	3.3	3.0	6.6*
Acetone	3.4	2.0	5.1*
Diethyl ether	1.1	0.82	1.9
Cyclohexane	0.3	0.3	0.51
Ethanol	0.1	0.1	0.3*
Petroleum ether	0.1	0.08	0.2

* There is disagreement between these and previously reported
values.[23]

X-ray powder diagrams obtained by the Guinier method
show the tris(*O*-ethyl dithiocarbonato) complexes of chro-
mium(III), indium(III), cobalt(III), iron(III), arsenic(III),
and antimony(III) to be isomorphous. Carrai and Gottardi
have determined the structure of the arsenic(III)[18] and anti-
mony(III)[19] complexes. Crystallographic data for the
cobalt(III) and chromium(III) ethylxanthate complexes are
given by Derenzini[20] and Franzini and Schiaffino,[21] respectively.
The absorption spectrum of the tris(ethylxanthato)chro-
mium(III) complex in chloroform solution contains maxima at
624 mμ (ϵ = 289 l./mol-cm., half width $\Delta\nu$ = 2900 cm.$^{-1}$) and
492 mμ (ϵ = 300, $\Delta\nu$ = 3100 cm.$^{-1}$), in good agreement with
the previously reported spectrum.[22]   The absorption spectrum
of tris(ethylxanthato)cobalt(III) in chloroform solution contains
maxima at 625 mμ (ϵ = 338, $\Delta\nu$ = 2900 cm.$^{-1}$) and 482 mμ
(ϵ = 472).   The presence of bis(ethylxanthato)cobalt(II) in the
material used for the previously reported spectrum[22] [maxima at
618 mμ (ϵ = 269) and 480 mμ (ϵ = 363)] may account for the
differences in the results.

REFERENCES

1. H. HLASIWETZ: *Ann. Chem.*, **122**, 87 (1862).
2. J. V. DUBSKY: *J. Prakt. Chem.*, [2], **90**, 61 (1914).
3. J. V. DUBSKY: *ibid.*, [2], **93**, 42 (1916).
4. W. HERWIG and H. H. ZEISS: *J. Org. Chem.*, **23**, 1404 (1958).
5. A. ROSENHEIM and I. DAVIDSOHN: *Z. Anorg. Allgem. Chem.*, **41**, 231 (1904).
6. M. DELÉPINE and L. COMPIN: *Bull. Soc. Chim. France*, [4], **27**, 469 (1920).
7. F. FIELD: *Quart. J. Chem. Soc.*, **14**, 48 (1862).
8. R. G. DURRANT: *J. Chem. Soc.*, **87**, 1781 (1905).
9. G. A. BARBIERI: *Atti Accad. Naz. Licei*, [6], **7**, 747 (1928).
10. M. MORI, M. SHIBATA, and E. KYUNO: *Bull. Chem. Soc. Japan*, **29**, 883 (1956).
11. M. MORI, M. SHIBATA, E. KYUNO, and K. HOSHIYAMA: *ibid.*, **31**, 291 (1958).
12. M. MORI, M. SHIBATA, E. KYUNO, and Y. OKUBO: *ibid.*, **31**, 940 (1958).
13. M. MORI, M. SHIBATA, E. KYUNO, and F. MARUYAMA: *ibid.*, **35**, 75 (1962).
14. M. SHIBATA, M. MORI, and E. KYUNO: *Inorg. Chem.*, **3**, 1573 (1964).
15a. H. F. BAUER and W. C. DRINKARD: *J. Am. Chem. Soc.*, **82**, 5031 (1960).
15b. D. E. COLDBERY, W. C. FERNELIUS, and M. SHAMMA, INORGANIC SYNTHESES, **6**, 142 (1960).
16. G. J. SUTTON: *Roy. Australian Chem. Inst. J. Proc.*, **17**, 249 (1950).
17. M. DELÉPINE: *Ann. Chim. (Paris)*, [12], **6**, 645 (1951).
18. G. CARRAI and G. GOTTARDI: *Z. Krist.*, **113**, 373 (1960).
19. G. GOTTARDI: *ibid.*, **115**, 451 (1961).
20. T. DERENZINI: *Atti Soc. Toscana Sci. Nat. Pisa Memo.*, **47**, 114 (1938).
21. M. FRANZINI and L. SCHIAFFINO: *Atti Soc. Toscana Sci. Nat. (Pisa), Proc. Verbali Mem.*, Ser. A, **69**, 342 (1962).
22. S. KIDA and H. YONEDA: *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **76**, 1059 (1955).
23. A. KUTZELNIGG: *Z. Anorg. Chem.*, **256**, 46 (1948).
24. L. HUMMELSTEDT, M. EPSTEIN, T.-L. HUGGARE, and F. RELANDER: *Acta Academ. Aboens, Seh. B.*, **25**, [6], 1 (1965).

7. MOLYBDENUM(IV) BROMIDE

Submitted by P. J. H. CARNELL,* R. E. McCARLEY,† and R. D. HOGUE†
Checked by FRED W. MOORE,‡ MELVIN L. LARSON,‡ and ALAN K. MALLOCK‡

Preparation of the anhydrous molybdenum(IV) halides is a difficult task because of the relative ease of disproportionation

* Present address: Imperial Chemical Industries, Durham, England.
† Department of Chemistry and Ames Laboratory of the USAEC, Iowa State University, Ames, Iowa.
‡ Climax Molybdenum Company of Michigan, Ann Arbor, Mich.

of the solids to lower and higher halides in the case of molybdenum(IV) chloride[1-3] and fluoride,[4] and of decomposition into molybdenum(III) bromide and bromine in the case of molybdenum(IV) bromide. The most easily accessible tetrahalide is the tetrabromide obtained by the procedure described below, where the tribromide is reacted with liquid bromine at *ca.* 55°. Molybdenum(IV) bromide has also been prepared by the reaction of molybdenum(III) bromide and bromine at 400°,[5] and by the reaction of molybdenum hexacarbonyl with liquid bromine.[6] The method described here has the advantage that it makes use of convenient starting materials and is conducive to the formation of a high-purity product. An interesting use of liquid bromine as both solvent and reactant is also illustrated by the method.

Procedure

Molybdenum(III) Bromide. This compound is conveniently prepared from the elements in an apparatus such as that illustrated in Fig. 6. Bulbs *A*, *B*, *E*, and *F* are sections of 25-mm.-o.d. Vycor tubing joined together by sections of 15-mm.-o.d. tubing. Bulb *B* should be 2 to 3 in. long, and bulbs *E* each about 6 in. long. In a typical preparation, 3 g. of molybdenum foil (cut into small strips) is placed in *B*, and the apparatus
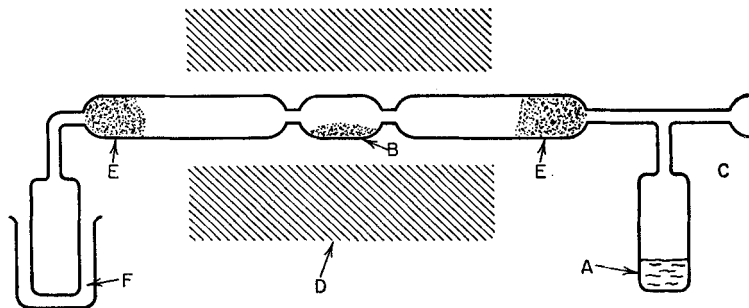
Fig. 6

is connected to a high-vacuum system and outgassed by brushing the tubing with a yellow flame from a hand torch. Bromine, previously dried over phosphorus(V) oxide and outgassed while maintained in the frozen state at $-78°$, is vacuum-distilled into *A* by keeping the bromine reservoir at room temperature and immersing *A* in an ice bath. After 5 to 10 ml. of bromine is condensed in *A*, the apparatus is sealed from the vacuum system at *C* by carefully collapsing the tubing with a hand torch and finally pulling it off at *C*.

The preparation of molybdenum(III) bromide is effected by transferring the reaction tube to a 12-in. split-winding furnace *D* with a heating zone of 10 to 12 in., so that *B* is located at the center of the furnace.* After the furnace has been heated to 600°, bromine is distilled from *A* to *F* simply by moving the ice bath to *F* and warming *A* to room temperature. A deposit of molybdenum(III) bromide is obtained at *E* as the reaction proceeds. When all bromine has been distilled into *F*, the ice bath is returned to *A* and the distillation repeated. Once the furnace temperature has been regulated, the reaction does not require further attention except to occasionally transfer the ice bath between *A* and *F*.

On completion of the reaction after 10 to 14 hours, the reaction tube is removed from the furnace. The bromine may be frozen at liquid-nitrogen temperature in either bulb *A* or *F*, and both *A* and *F* are removed by sealing with the hand torch near the bulb *E*. The remainder of the reaction tube is transferred to the dry-box under an inert atmosphere (helium, nitrogen, or argon) and opened by breaking at the constrictions between bulbs *B* and *E*.

In a typical preparation starting with 3.0 g. of molybdenum, 10.3 g. of molybdenum(III) bromide, or 98% yield, is obtained.

* For furnace tube lengths of less than about 10 in., as noted by the checkers, the constrictions at bulb *B* may become plugged with product and impede the reaction.

Anal.*,† Calcd. for MoBr₃: Mo, 28.57; Br, 71.42. Found: Mo, 28.55; Br, 71.13.

Molybdenum(IV) Bromide. The Pyrex reaction vessel used for this preparation is shown in Fig. 7. With a socket cap on *A*, the vessel is attached to the high-vacuum system via joint *B* and outgassed by opening the Teflon needle-valve stopcock. The stopcock is closed, the vessel removed to the dry-box, and 6 to 10 g. of molybdenum(III) bromide transferred to the top of the fine-porosity sintered-glass frit through side-arm *A*. Subsequently the vessel is again connected to the vacuum line at *B*, outgassed, and side-arm *A* sealed from the vessel with the torch. Bromine is vacuum-distilled into the vessel by immersing the lower tube in ice water until the vessel is filled to point *C*.

After the Teflon stopcock is closed, the reaction vessel is transferred to a water bath maintained at 60°. The lower end of the vessel should be immersed to within about 1 in. below the fritted-glass retainer. As refluxing of the bromine proceeds, a liquid layer should accumulate above the fritted-glass retainer. If this does not happen, some bromine should be poured through the bypass arm so that a liquid layer *ca.* 1 in. thick is maintained on the frit. It is essential that liquid bromine contact the tribromide in order to attain efficient conversion to tetrabromide. As the reaction proceeds, the product, dissolved in liquid bromine, extracts into the lower vessel and deposits there as fine black crystals.

Under the conditions described above, the formation and extraction of molybdenum(IV) bromide proceed at the rate of *ca.* 0.086 g. hour⁻¹ or 2.1 g. day⁻¹. For example, 6.85 g. of the tribromide afforded 7.53 g. of tetrabromide after an extraction

---

* Because of its resistance to attack by most reagents in solution, MoBr₃ is best analyzed by hydrogen reduction at 650°, whereby molybdenum is determined as the metal and bromine as hydrogen bromide.

† For this analysis the checkers recommend that the sample be dissolved in a solution of sodium hydroxide–hydrogen peroxide. The molybdenum is then determined by the benzoin oxime method and the bromine by potentiometric titration with silver nitrate.

**4-mm. Teflon®
needle valve**

B

A

35-mm. o.d.

8-mm. o.d.

Fine-porosity
sintered glass

14 in.

C

4.5 in.

18-mm. o.d.
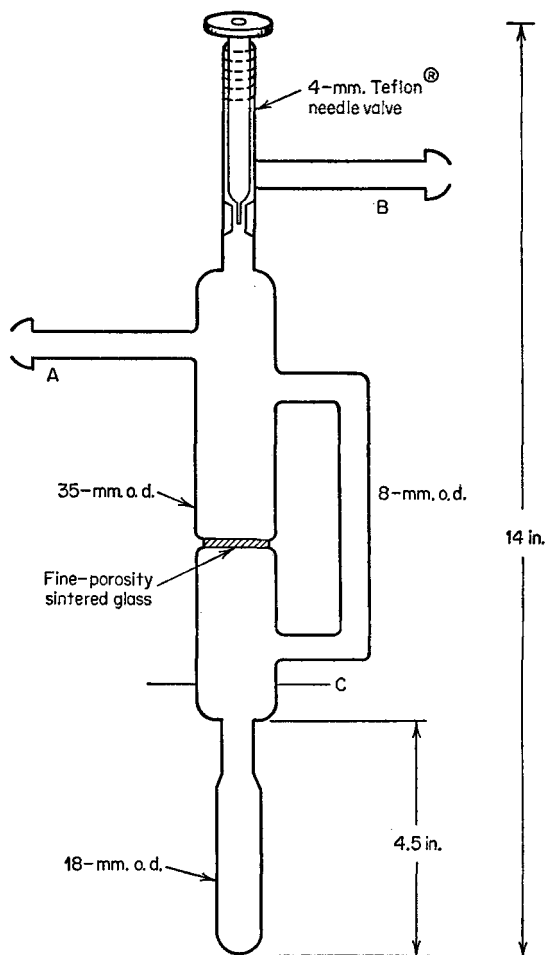
Fig. 7

time of 87 hours.*   When the reaction is complete, the bromine is removed by vacuum distillation through the stopcock and the product degassed of adsorbed bromine by warming to 50° under high vacuum.   The reaction vessel is then transferred to the dry-box and the product removed by breaking the tubing at the lower constriction.

Anal. Calcd. for MoBr₄: Mo, 23.08; Br, 76.91.   Found: Mo, 23.01; Br, 76.56.

* The checkers report a yield of only 66% after an extraction time of 7 days.

Properties

Molybdenum(IV) bromide is a black crystalline solid which is very sensitive to oxidation and hydrolysis; it should be handled only under a dry inert atmosphere. Its solubility in bromine at 51° is *ca.* 3.0 g./1000 g. of bromine, and bromine solutions were found to be nonconductors. For example, at 25° both the solvent bromine and a 0.96×10^{-3} *M* solution in molybdenum(IV) bromide exhibited a specific conductance of 1.3×10^{-10} ohm^{-1} cm.$^{-1}$ At 110 to 130° *in vacuo*, solid molybdenum(IV) bromide decomposes quantitatively into molybdenum(III) bromide and bromine, and because of this thermal instability it cannot be sublimed except under a bromine atmosphere.

REFERENCES

1. A. MICHAEL and A. MURPHY: *Am. Chem. J.*, **44**, 379 (1910).
2. D. E. COUCH and A. BRENNER: *J. Res. Nat. Bur. Std., A.,* Physics and Chemistry, **63A**, 185 (1959).
3. T. E. AUSTIN and S. Y. TYREE, JR.: *J. Inorg. Nucl. Chem.*, **14**, 141 (1960).
4. R. D. PEACOCK: *Proc. Chem. Soc.*, **1957**, 59.
5. W. KLEMM and H. STEINBERG: *Z. Anorg. Allgem. Chem.*, **227**, 193 (1936).
6. S. A. SHCHUKAREV, I. V. VASIL'KOVE, and N. D. ZATISEVA: *Vestn. Leningr. Univ.*, **16**, No. 22, Ser. Fiz. i Khim., No. 4, 127 (1961); *C.A.*, **56**, 9510 (1962).

8. MOLYBDENUM(VI) OXIDE CHLORIDE
(*Molybdenum Oxytetrachloride*)

$$MoCl_5 + O_2 \rightarrow MoOCl_4 + \tfrac{1}{2}O_2 + \tfrac{1}{2}Cl_2$$

Submitted by ALAN K. MALLOCK*
Checked by PETER B. FLEMING† and ROBERT E. McCARLEY†

Molybdenum oxytetrachloride has been prepared in limited quantities by several methods,[1,2] most of which give low yields

* Climax Molybdenum Company of Michigan, Ann Arbor, Mich.
† Department of Chemistry and Ames Laboratory of the USAEC, Iowa State University, Ames, Iowa.

and require several steps. The general approach has been to treat molybdenum-oxygen compounds with solvents containing chlorine or with molybdenum chlorides. These methods also involve a greater number of atmospherically unstable compounds, limiting the amount of material that can be prepared. The new procedure described for the preparation of molybdenum oxytetrachloride is a simple single-step reaction which involves no by-products. The synthesis is accomplished by the reaction of dry oxygen with molten molybdenum(V) chloride.

Procedure

The apparatus required for the preparation of molybdenum oxytetrachloride is illustrated in a schematic fashion in Fig. 8. The glass reaction vessel is described in detail in Fig. 9. This vessel is dried at elevated temperatures and then placed in a dry-box where bulb *B* is loaded with 100 g. of molybdenum(V) chloride through the opening in tube *C*. Rubber tubing is attached to the inlet and exhaust tubes *D* and the loading tube *C*, and the tubing ends are closed off with a clamp. The reaction vessel is removed from the dry-box and evacuated, and tube *C* is flame-sealed. Inlet *D* is attached through a T-joint to the helium and oxygen sources. The helium is purified by

Fig. 8

$$MoCl_5 + O_2 \longrightarrow MoOCl_4 + \tfrac{1}{2}Cl_2 + \tfrac{1}{2}O_2$$
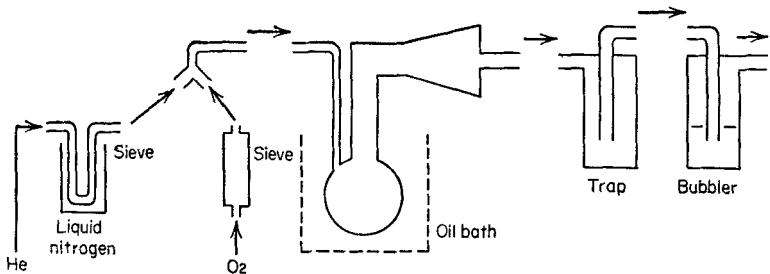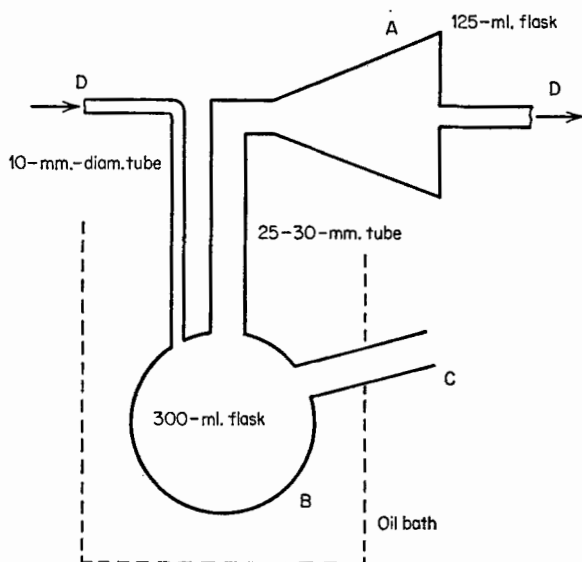
Fig. 9

passage through a bed of Linde 5-A molecular sieve cooled in liquid nitrogen, and the oxygen is dried by passage through a column of Linde 5-A molecular sieve at room temperature. Oxygen is passed through the apparatus at 256 ml./minute for 5 minutes, then reduced to a minimum flow as the apparatus is lowered into the preheated oil bath, 215 to 220°, to the upper level of the solid molybdenum(V) chloride contained in bulb *B*. The reduced flow of oxygen is maintained for 5 minutes to allow the pentachloride to melt without excessive sublimation. The temperature of the oil bath should be maintained at 215 to 220°. The apparatus is then lowered farther into the oil bath so that approximately 1 in. of the neck is immersed, and the oxygen flow is increased to 256 ml./minute for 55 minutes. After 55 minutes, the oxygen flow is discontinued and helium is then passed through the apparatus for 40 minutes. The apparatus is

removed from the bath immediately after the oxygen-to-helium change is made and allowed to cool to room temperature. The product is removed from the glass apparatus in the dry-box and then stored in evacuated ampules.

Analysis

	Mo	Cl	O by difference	Cl/Mo	O/Mo
Calculated	37.81	55.89	6.30	4.00	1.00
Found	37.64	56.30	6.06	4.04	0.97

Properties

Molybdenum oxytetrachloride is a dark green crystalline compound with a melting point of 100 to 101°. Infrared absorption (KBr disk) has been used to establish the absence of OH^- and H_2O in verification of the anhydrous state. A broad band appears in the 970-cm.$^{-1}$ region and reveals molybdenum-to-oxygen bonding. The oxychloride reacts with thoroughly dried Nujol so that satisfactory infrared spectra cannot be obtained with this as a dispersion medium. When exposed to light, molybdenum oxytetrachloride forms a brown film on the surface of the ampule. Since this film is not formed when the ampules are stored in the dark, molybdenum oxytetrachloride is concluded to be photosensitive.

REFERENCES

1. R. COLTON, I. B. TOMKINS, and R. W. WILSON: *Australian J. Chem.*, **17**, 496 (1964).
2. I. A. GLUKHOV and L. A. TIKHOMIROV: *Dok. Akad. Nauk Tadzh. SSR*, **3**, No. 2, 15 (1960).

9. RHENIUM(III) BROMIDE
(*Trirhenium Nonabromide*)

$$K_2ReBr_6 + 2AgNO_3 \rightarrow Ag_2ReBr_6 + 2KNO_3$$
$$3Ag_2ReBr_6 \rightarrow 6AgBr + \tfrac{3}{2}Br_2 + Re_3Br_9$$
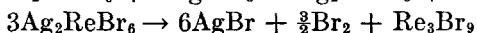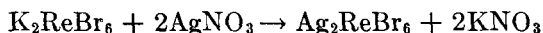
Submitted by RICHARD J. THOMPSON,* RONNIE E. FOSTER,* and JAMES L. BOOKER*
Checked by STEPHEN J. LIPPARD†

Trirhenium nonabromide has been made (1) by direct combination of the elements;[1] (2) by the thermal decomposition of rhenium(V) bromide, obtained by treating elemental rhenium with bromine at 650°;[2] or (3) by the thermal decomposition of silver hexabromorhenate(IV),[3-6] obtained from the metathesis of silver nitrate with potassium hexabromorhenate(IV).[5-8] Of these methods, (3) has proven to be the simplest and most efficient route to pure trirhenium nonabromide. The following procedure is superior to that previously given,[6] in that simpler equipment is used and larger quantities can be processed, with a resultant saving in time.

Procedure

Ten grams (0.0134 mol) of solid potassium hexabromorhenate(IV)[8] is added slowly to a vigorously stirred solution of 5.5 g. (0.032 mol) of silver nitrate in 50 ml. of concentrated nitric acid and 200 ml. of water. The slurry is stirred for 10 minutes after addition of the solid. After standing, the clear supernatant is decanted. The brown solid is transferred onto

* Texas Technological College, Lubbock, Tex.
† Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass.

the sintered-glass disk of a filter funnel and washed with dilute
(1:4) nitric acid until the filtrate gives no turbidity with 1%
hydrobromic acid. The funnel is fitted with a rubber stopper
and affixed to a dry filter flask, and the excess liquid is removed
at reduced pressure. The product is washed with three 50-ml.
portions of methanol and three 50-ml. portions of diethyl ether,
the rubber stopper is replaced, and the excess solvents are
removed at reduced pressure. The residual organic solvents
are removed *in vacuo* over phosphorus(V) oxide. The yield
of granular brown product is quantitative (11.8 g., 0.0134 mol).
Anal. Calcd. for Ag_2ReBr_6: Ag, 24.5. Found: Ag (as sulfate
residue), 24.3.

Into a size 6A porcelain boat (88 × 13 × 10 mm.) is placed
10.0 g. (0.0113 mol) of Ag_2ReBr_6 (as much as 15 g. may be
processed readily), and the boat is positioned near the sealed
end of a 25 × 300 mm. Pyrex tube fitted with an inner 29/44
S.T. sleeve joint. The tube is connected to a mechanical vacuum
pump (capable of reducing the pressure to *ca.* 50 μ) via either a
trap cooled by liquid nitrogen or a trap cooled by a Dry Ice–
isopropyl alcohol slush, which is in turn connected to an 11-mm.
Vycor combustion tube packed with copper gauze and main-
tained at 600° by means of a furnace. (Either protective
system between the tube and the pump will serve to remove
bromine, one of the reaction products.)

The tube is positioned in a tube furnace* so that the boat is
near the center of the furnace, a thermocouple is introduced in
the open end, and the open end of the furnace is plugged with
Pyrex wool. The tube is evacuated and the temperature raised
to 450° at about 3° per minute. A transitory blue deposit is
formed in the cool portion of the tube at 200°; at 300°, a green
ring forms in the tube just inside the furnace; at 300 to 350°, a
blue-black deposit, presumably a mixture of rhenium(V) bromide
and rhenium(VI) oxide tetrabromide,[2] forms in the portion of
the tube just outside the furnace; at 350 to 370°, a blue-black

* The authors used a Hevi-Duty Electric Co. Type 70-T furnace (13 in. long).

deposit forms within the tube 1 to $1\frac{1}{2}$ in. from the end of the furnace. At 430°, a pale yellow-green vapor appears and lustrous black crystals form in the tube 1 to 2 in. within the furnace. The evacuated tube is maintained at 450° for $1\frac{1}{2}$ hours, cooled, disconnected from the protective trap and tube, and the fine deposit of extraneous decomposition products removed from the mouth of the tube. The black lustrous crystals (4.0 g., 0.0094 mol, or 83% based on Ag_2ReBr_6), which are *ca.* 1 cm. inside the furnace, are transferred to a dark bottle and stored in a dry atmosphere. *Anal.* Calcd. for Re_3Br_9: Re, 43.7; Br, 56.3. Found: Re [as $(C_6H_5)_4AsReO_4$, average of four determinations], 43.3 ± 0.15; Br (as AgBr, average of six determinations), 56.1 ± 0.1.

Properties

The lustrous black crystals of trirhenium nonabromide are not rapidly degraded on exposure to the atmosphere; the crystals can be stored over desiccants for months without evidence of decomposition. The bromide dissolves fairly slowly and sparingly in ether and acetone. In methanol, the bromide gives yellow-orange solutions, but it is solvolyzed within minutes. Similarly, the bromide dissolves in water at room temperature to yield a violet solution which darkens rapidly, yielding a black precipitate, presumably the hydrated dioxide.[9] Contrary to published work,[10] the bromide does dissolve in ammonia with solvolysis, as is evidenced by lines attributable to ammonium bromide in x-ray diffraction data of the solid residue recovered from liquid ammonia solutions.[11] Trirhenium nonabromide reacts with Lewis bases such as phosphines and amines to form a series of complexes of the type $(base)_3Re_3Br_9$.[6]

The absorption spectra of trirhenium nonabromide in 48% hydrobromic acid and in acetone are essentially the same; in acetone the peaks are at 751, 535 (sh), 458, and 344 $m\mu$, and minima occur at 426 and 645 $m\mu$.

REFERENCES

1. H. HAGAN and A. SIEVERTS: *Z. Anorg. Allgem. Chem.*, **215**, 111 (1933).
2. R. COLTON: *J. Chem. Soc.*, **1962**, 2078.
3. F. KRAUS and H. STEINFELD: *Ber.*, **64**, 2552 (1931).
4. W. S. SHUTH and W. KLEMM: *Z. Anorg. Allgem. Chem.*, **220**, 193 (1934).
5. J. P. KING and J. W. COBBLE: *J. Am. Chem. Soc.*, **82**, 2111 (1960).
6. F. A. COTTON, S. J. LIPPARD, and J. T. MAGUE: *Inorg. Chem.*, **4**, 508 (1965).
7. G. BRAUER and H. D. ALLARDT: *Z. Anorg. Allgem. Chem.*, **316**, 134 (1962).
8. G. W. WATT and R. J. THOMPSON: INORGANIC SYNTHESES, **7**, 191 (1963).
9. H. V. A. BRISCOE, P. L. ROBINSON, and E. M. STODDARDT: *J. Chem. Soc.*, **1932**, 666.
10. W. KLEMM and G. FRISCHMUTH: *Z. Anorg. Allgem. Chem.*, **230**, 209 (1937).
11. JAMES L. BOOKER: M.S. thesis, Texas Technological College, Lubbock, Tex., 1965.

10. CESIUM COBALT(III) SULFATE 12-HYDRATE
(*Cesium Cobalt(III) Alum*)

$$Co^{2+} \xrightarrow{\text{anode}} Co^{3+} + e$$
$$Cs^+ + Co^{3+} + 2SO_4^{2-} + 12H_2O \rightarrow CsCo(SO_4)_2 \cdot 12H_2O$$
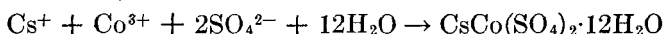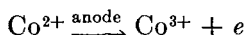
Submitted by D. A. JOHNSON* and A. G. SHARPE*
Checked by L. R. MORSS† and W. L. JOLLY†

The only known solid compounds containing the ion $Co(H_2O)_6^{3+}$ are the sulfate $Co_2(SO_4)_3 \cdot 18H_2O$ and its alums. Although the first synthesizer[1] of the sulfate reported he was able to store it in a stoppered tube for months without visible decomposition, later authors stated that this compound[2] and the ammonium alum[3] decompose at laboratory temperature within a few hours. By an improved drying procedure, the cesium alum is readily obtained in a form in which even the magnetic susceptibility (a very sensitive criterion for the presence of dipositive cobalt) shows that only very slow decomposition occurs.[4] Use of this

* University Chemical Laboratory, Cambridge, England.
† Department of Chemistry, University of California, Berkeley, Calif.

drying procedure also enhances the stability of hydrated cobalt(III) sulfate and the ammonium alum, but the cesium alum is the most stable substance available that contains the $Co(H_2O)_6^{3+}$ ion.

Procedure

The preparation is electrolytic. The anode consists of a few inches of thin platinum rod, to one end of which a $1 \times \frac{3}{4}$ in. piece of platinum foil is attached. This is surrounded by a hollow cylinder of platinum gauze of diameter 1 in. and length $1\frac{1}{2}$ in. The other end of the platinum rod is attached to an electric stirrer.*

The cathode is a rolled strip of copper gauze which fits snugly into a $3 \times \frac{3}{8}$ in. test tube and rests on a glass-wool plug which covers a hole of about $\frac{1}{4}$-in. diameter blown in the bottom of the test tube. During the preparation, the solution about half fills the tube, and the glass-wool plug protects the bulk of the oxidized solution from the cathode.

Seven grams (0.025 mol) of cobalt(II) sulfate heptahydrate and 4.55 g. (0.0125 mol) of cesium sulfate are dissolved in 75 ml. of 10 N sulfuric acid, and the solution is electrolyzed for $5\frac{1}{2}$ hours at a current of 1 amp. in a 150-ml. beaker, the temperature being kept below 5° by immersing the beaker in a wide-mouthed Dewar flask filled with an ice–sodium chloride mixture. At the end of this period, the current is stopped by rapid removal of the cathode compartment from the solution. The deep blue crystals of the alum are separated on a medium-grade sintered-glass funnel precooled with ice-cold 10 N sulfuric acid and are then washed well with portions totaling about 100 ml. of glacial acetic acid near its freezing point and 200 ml. of ice-cold diethyl ether previously dried over Linde 4-A molecular sieve. The yield is 11.2 g. (74%).

---

* The checkers found that a standard cylindrical platinum electrode (with or without a sheet of foil attached) of similar dimensions is suitable.

Cesium is determined as the tetraphenylborate, total cobalt as the anthranilate, sulfate as barium sulfate, and cobalt(III) by addition of the alum to excess of potassium iodide solution followed by titration with thiosulfate. *Anal.* Calcd. for $CsCo(SO_4)_2 \cdot 12H_2O$: Cs, 22.2; Co, 9.82; SO_4, 32.0. Found: Cs, 22.2; Co, 9.83; SO_4, 32.3; Co(III), 9.80.

Properties

Cesium cobalt alum consists of granular cubic crystals unstable to excess of water or to powerful drying agents which appear to remove lattice water from the compound and promote decomposition. A suggestion made by Zernike[5] that acetone, the drying solvent used previously,[2,6] exercises this unfavorable dehydrating effect is believed to be correct, and this is the reason for the use of glacial acetic acid, a relatively mild dehydrating agent. The instability of the compound to dehydration can be shown by storing samples over various drying agents when the times taken for decomposition decrease with the accepted order[7] of increasing desiccant efficiency.

The uncorrected magnetic susceptibility of the cesium alum, determined by the Gouy method using the complex $HgCo(NCS)_4$ as standard, is -0.12 c.g.s. units per gram; this has been found to change to -0.03 c.g.s. units after 14 weeks.[4]

REFERENCES

1. H. MARSHALL: *J. Chem. Soc.*, **59**, 760 (1891).
2. S. SWANN, T. S. XANTHAKOS, and R. STREHLOW: INORGANIC SYNTHESES, **5**, 181 (1957).
3. W. G. PALMER: "Experimental Inorganic Chemistry," p. 529, Cambridge University Press, London, 1954.
4. D. A. JOHNSON and A. G. SHARPE: *J. Chem. Soc.*, A(**1966**), 798.
5. J. ZERNIKE: *Rec. Trav. Chim.*, **71**, 965 (1952).
6. H. BOMMER: *Z. Anorg. Allgem. Chem.*, **246**, 275 (1941).
7. F. TRUSELL and H. DIEHL: *Anal. Chem.*, **35**, 674 (1963).

11. *trans*-DICHLOROTETRA(PYRIDINE)RHODIUM(III) SALTS

$$RhCl_3 \cdot 3H_2O \xrightarrow[\text{NaH}_2\text{PO}_2,\text{cat.}]{\text{C}_5\text{H}_5\text{N}} RhCl_2(NC_5H_5)_4Cl$$
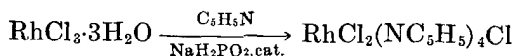
Submitted by R. D. GILLARD* and G. WILKINSON†
Checked by G. W. PARSHALL‡

The interesting complex chemistry of rhodium has been rather neglected; this is probably because most of the synthetic methods for obtaining complexes have been tedious.   In general, substitutions of chlorine atoms bonded to rhodium by other ligands are slow, and products have usually been mixtures.   The situation is now changing, since novel catalytic approaches to rhodium complexes have been developed.[1]   The catalysis in the present synthesis involves the rapid further reaction of the hydrido complex formed from 1,2,6-trichlorotri(pyridine)rhodium(III) in the presence of hypophosphite ion.

trans-Dichlorotetra(pyridine)rhodium(III) chloride pentahydrate was first prepared by Jorgensen[2] from the mixture obtained by heating rhodium trichloride with aqueous pyridine for several hours.   Delépine discovered[3] that the formation of the *trans*-dichloro compound was markedly catalyzed by the use of ethanol as a solvent.   In the course of studies[4] on the reduced states of rhodium, the very effective catalysis by hypophosphite was observed, though this was not recognized as such until much later.[5]

The procedure given here has been developed from the reaction with hypophosphite.   Other reducing agents such as ethanol, hydrazine, or even molecular hydrogen[6] are very effective catalysts and may be used instead of hypophosphite.

* The University, Sheffield 10, England.
† Imperial College, London, S.W. 7, England.
‡ Central Research Department, Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, Del.

Procedure

Rhodium(III) chloride trihydrate (0.27 g. from a sample containing 37.7% rhodium—alternatively sodium hexachlororhodate(III) may be used) is dissolved in water (5 ml.) in a beaker by warming on the steam bath, and a slight excess of pyridine (0.95 g.) is added. (A larger excess of pyridine should be avoided since this lowers the yield; although the product forms just as readily, it is very soluble in aqueous pyridine.) A pink-red precipitate of dipyridinium pentachloroaquorhodate(III) forms initially; this dissolves on warming over a free flame to give an orange solution (which contains mainly 1,2,6-trichlorotri(pyridine)rhodium(III)). To the hot orange solution, a few crystals of solid sodium hypophosphite are added, followed by water (5 ml.), and the solution is boiled over a free flame. After a few seconds, the orange solution suddenly becomes bright yellow.

At this stage, the reaction is complete. The solution is cooled, and crystals of *trans*-dichlorotetra(pyridine)rhodium(III) chloride pentahydrate appear as a shiny yellow mass. The mixture is cooled in ice for 10 minutes. Then the product (0.54 g., 88%) is collected and recrystallized from hot water (*ca.* 5 ml.). The solubility change is sudden, and the glittering spangles of the product are quite characteristic. After cooling in ice for half an hour, the solid compound is collected and washed with a little ice-cold water, in which it is almost insoluble. Yield 0.45 g., 73%, based on rhodium. *Anal.* Calcd. for $C_{20}H_{30}Cl_3N_4O_5Rh$: C, 38.9; H, 4.9; N, 9.1. Found: C, 38.8; H, 5.1; N, 9.0. The yield may be increased by evaporating the original filtrate, or by letting it stand for a few days, when a further crop (*ca.* 0.04 g.) is obtained.

Properties

The chloride salt forms bright yellow needles, which are readily soluble in hot water, ethanol, and such organic solvents

as dichloromethane. The chloride salt recovered from water air-dries to a pentahydrate composition; if dried at 100° in vacuum, a monohydrate is obtained. Like other compounds with the *trans*-[RhL₄Cl₂]⁺ structure, it has an electronic absorption band at 408 mμ, ϵ 75. The very sparingly water-soluble nitrate or perchlorate salt may be obtained by treating the saturated aqueous solution of the chloride with sodium nitrate or perchlorate.

When the chloride is allowed to stand under concentrated hydrochloric acid, it is slowly (*ca.* 14 days) transformed to the hydrochloric acid adduct,[7] *trans*-[Rhpy₄Cl₂](H₅O₂)Cl₂. On careful treatment with aqueous sodium tetrahydroborate, the cation forms[8] [Rhpy₄ClH]⁺, which is very pale brown and shows the characteristic high-field proton resonance signal of hydrogen bonded directly to a transition metal. The chloride reacts[1] with oxalate ion in aqueous solution, losing pyridine, and forming 1-chloro-2,6-oxalatotri(pyridine)rhodium(III), which is unstable to light.

Related Syntheses

Many compounds of rhodium(III) may readily be obtained by this general catalytic procedure. Rhodium(III) bromide may be substituted for the rhodium trichloride, and weakly basic nitrogenous ligands (2,2′-bipyridine, *o*- (or 1,10-)phenanthroline, or dioximes) for the pyridine. The products all have the halogen atom in *trans* positions.

REFERENCES

1. R. D. GILLARD, J. A. OSBORN, and G. WILKINSON: *J. Chem. Soc.*, **1965**, 1951.
2. S. M. JORGENSEN: *J. Prakt. Chem.*, **25**, 478 (1885).
3. M. DELÉPINE: *Compt. Rend.*, **236**, 559 (1953).
4. F P. DWYER and R. S. NYHOLM: *J. Proc. Roy. Soc. N. S. Wales*, **76**, 275 (1943).
5. B. N. FIGGIS, R. D. GILLARD, R. S. NYHOLM, and G. WILKINSON: *J. Chem. Soc.*, **1964**, 5189.

6. R. D. GILLARD, J. A. OSBORN, P. B. STOCKWELL, and G. WILKINSON: *Proc. Chem. Soc.*, **1964**, 284.
7. R. D. GILLARD and G. WILKINSON: *J. Chem. Soc.*, **1964**, 1640.
8. J. A. OSBORN, R. D. GILLARD, and G. WILKINSON: *ibid.*, **1964**, 3168.

12. TRIS(TRIPHENYLPHOSPHINE)HALORHODIUM(I)

Submitted by J. A. OSBORN* and G. WILKINSON*
Checked by J. J. MROWCA†

Although phosphite complexes of formula $[(RO)_3P]_3RhCl$ can be obtained[1] by direct interaction of the ligand with dichloro-tetracarbonyldirhodium (rhodium carbonyl chloride),[2] the reaction with triphenylphosphine gives only the carbonyl complex *trans*-$RhCl(CO)[P(C_6H_5)_3]_2$. A diphenylphosphine complex $[(C_6H_5)_2PH]_3RhCl$ can be obtained[3] by action of the ligand on the ethylene complex $[(C_2H_4)_2RhCl]_2$. The interaction of tertiary phosphines generally[4] and of stoichiometric amounts of triphenylphosphine in particular[5] with ethanolic solutions of rhodium chloride gives rise to rhodium(III) species such as $(R_3P)_3RhCl_3$ or to chlorine-bridged complexes. If a large excess of triphenylphosphine (6 M excess) is used, reduction occurs, leading to the rhodium(I) complex $RhCl[P(C_6H_5)_3]_3$.[6] This particular phosphine complex undergoes many unusual reactions and in particular is a very efficient catalyst for the homogeneous hydrogenation of olefins and acetylenes under subatmospheric pressure and at ambient temperatures.[6] These characteristics are, in part, associated with the fact that, of complexes of similar stoichiometry, only the triphenylphosphine complex (primarily due to steric factors) dissociates in solution to give a formally three-coordinate species which has three

* Chemistry Department, Imperial College, London, S.W. 7, England.
† Central Research Department, Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, Del.

solvent-occupied sites:

$$RhCl[P(C_6H_5)_3]_3 \rightleftarrows RhCl[P(C_6H_5)_3]_2 + P(C_6H_5)_3$$

A. Tris(triphenylphosphine)chlororhodium(I)

Procedure

$$RhCl_3 + 4P(C_6H_5)_3 \rightarrow RhCl[P(C_6H_5)_3]_3 + Cl_2P(C_6H_5)_3$$
$$Cl_2P(C_6H_5)_3 + H_2O \rightarrow OP(C_6H_5)_3 + 2HCl$$
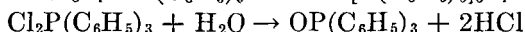
Rhodium(III) chloride trihydrate* (2 g.) is dissolved in 70 ml. of ethanol (95%) in a 500-ml. round-bottomed flask fitted with gas inlet tube, reflux condenser, and gas exit bubbler. A solution of 12 g. of triphenylphosphine (freshly crystallized from ethanol to remove triphenylphosphine oxide) in 350 ml. of hot ethanol is added and the flask purged with nitrogen. The solution is refluxed for about 2 hours, and the crystalline product which forms is collected from the hot solution on a Büchner funnel or sintered-glass filter. The product is washed with small portions of 50 ml. of anhydrous ether; yield 6.25 g. (88% based on Rh). This crystalline product is deep red in color.

An isomeric species which is orange is obtained if the total volume of ethanol used is 200 ml. or less and the solution is refluxed for a period of about 5 minutes. This substance often contains small amounts of the red product and, on continued refluxing, the orange crystals are slowly converted to the red form.

The excess triphenylphosphine used in the preparation can be recovered by addition of water to the ethanol filtrates until precipitation begins. After allowing the solutions to stand 2 to 3 days in a stoppered flask, the triphenylphosphine crystallizes out. Recrystallization from ethanol and ethanol–benzene (1:1) removes triphenylphosphine oxide contaminant.

* The commercial product usually corresponds closely to $RhCl_3 \cdot 3H_2O$ but small divergences from this stoichiometry are not significant in this preparation. The yield is calculated from the Rh content.

Properties

The red and orange forms of $RhCl[P(C_6H_5)_3]_3$ have apparently identical chemical properties; the difference is presumably due to different crystalline forms, and possibly bonding in the solid. The complex is soluble in chloroform and methylene chloride (dichloromethane) to about 20 g./l. at 25°. The solubility in benzene or toluene is about 2 g./l. at 25° but is very much lower in acetic acid, acetone, and other ketones, methanol, and lower aliphatic alcohols. In paraffins and cyclohexane, the complex is virtually insoluble. Donor solvents such as pyridine, dimethyl sulfoxide, or acetonitrile dissolve the complex with reaction, initially to give complexes of the type $RhCl[P(C_6H_5)_3]_2L$, but further reaction with displacement of phosphine may occur.

In solvents such as chloroform, methylene chloride, or benzene at 25° or below, the molecular weight is about half that expected, owing to essentially complete dissociation as noted above. Solutions of the complex quite rapidly absorb molecular oxygen to give the species $RhCl[P(C_6H_5)_3]_2O_2$, which is more soluble than the parent in the solvent; solutions must hence be protected from air. On heating benzene, toluene, or best, methyl ethyl ketone solutions (or suspensions) of $RhCl[P(C_6H_5)_3]_3$, salmon-pink crystals of the chlorine-bridged dimer $[(C_6H_5)_3P]_2RhCl_2Rh[P(C_6H_5)_3]_2$ are obtained essentially quantitatively. This dimer absorbs oxygen slowly even in the solid state. It may be reconverted to the trisphosphine complex by cleavage with triphenylphosphine in refluxing ethanol.

Solutions of $RhCl[P(C_6H_5)_3]_3$ absorb molecular hydrogen reversibly at 1 atmosphere and 25° to give the *cis*-dihydro complex $RhCl(H_2)[P(C_6H_5)_3]_2$; in solvents such as acetic acid, white crystalline solvates $RhCl(H_2)[P(C_6H_5)_3]_2 \cdot solv.$ may be obtained. The solutions are highly effective catalysts for the homogeneous hydrogenation of olefins and acetylenes.[6]

The solutions react rapidly with carbon monoxide at 25° and with aldehydes on warming to give *trans*-$RhCl(CO)[P(C_6H_5)_3]_2$;

with ethylene[6] and with tetrafluoroethylene or hexafluoro-2-butyne,[7] complexes are also obtained of stoichiometry $RhCl[P(C_6H_5)_3]_2$ (olefin or acetylene).

The complex also undergoes a variety of addition reactions with reagents such as methyl iodide, hydrochloric acid, benzoyl chloride, and allyl chloride.[8] In a reaction similar to that of the decarboxylation of aldehydes, the complex will abstract CS from carbon disulfide to give the *trans*-thiocarbonyl complex *trans*-$RhClCS[P(C_6H_5)_3]_2$.[9]

B. Tris(triphenylphosphine)bromorhodium(I)

Procedure

The method is similar to that for the chloride except that lithium bromide is added to the preparation.

To a solution of 2 g. of rhodium(III) chloride trihydrate in 70 ml. of ethanol is added 12 g. of triphenylphosphine in 250 ml. of hot ethanol. After refluxing until the red solution begins to lighten in color (about 5 minutes), 8 g. of lithium bromide dissolved in 50 ml. of hot ethanol is added and the mixture refluxed for an hour. The orange prisms of the complex are collected by filtration, washed with 50 ml. of anhydrous ether, and dried in vacuum; yield 5.1 g. (64% based on rhodium).

As with the chloride, a second form exists. This is obtained as follows. To a solution of 0.5 g. of rhodium(III) chloride trihydrate in 75 ml. of warm ethanol is added 2 g. of lithium bromide. After refluxing for 5 minutes, a solution of 3 g. of triphenylphosphine in 75 ml. of hot ethanol is added and the mixture refluxed for 30 minutes. After collection of the now deep brown crystals, the crystals are washed with 25 ml. of ether and dried as before; yield, 1.3 g. (69% based on rhodium).

Properties

The chemical properties of the bromide are similar to those of the chloride. The bromide is somewhat more soluble in organic

solvents. It is a more rapid hydrogenation catalyst than the chloride.[6]

Although the *iodide* can be prepared,[6] it is difficult to obtain in a pure state, free from admixed dimeric product $[(C_6H_5)_3P]_2$-$RhI_2Rh[P(C_6H_5)_3]_2$.

REFERENCES

1. L. VALLERINO: *J. Chem. Soc.*, **1957**, 2473.
2. For preparation see J. A. McCLEVERTY and G. WILKINSON: INORGANIC SYNTHESES, **8**, 211 (1966).
3. R. G. HAYTER: *Inorg. Chem.*, **3**, 301 (1964).
4. J. CHATT, N. P. JOHNSON, and B. L. SHAW: *J. Chem. Soc.*, **1964**, 2408.
5. R. J. MAWBY and L. M. VENANZI: *Experientia, Suppl.*, No. 9 (1964), "Essays in Coordination Chemistry," p. 240, Birkhauser Verlag, Basel.
6. J. A. OSBORN, F. H. JARDINE, F. H. YOUNG, and G. WILKINSON: *J. Chem. Soc.*, A, **1966**, 1711.
7. M. J. MAYS and G. WILKINSON: *ibid.*, **1965**, 6629.
8. D. N. LAWSON, J. A. OSBORN, and G. WILKINSON: *ibid.*, A., **1966**, 1733; M. C. BAIRD, D. N. LAWSON, J. T. MAGUE, J. A. OSBORN, and G. WILKINSON: *Chem. Commun.*, **1966**, 129.
9. M. C. BAIRD and G. WILKINSON: *ibid.*, **1966**, 267.

13. IODO(TRIMETHYL)PLATINUM(IV)

$$3CH_3MgI + K_2PtCl_6 \rightarrow PtI(CH_3)_3 + MgI_2 + 2MgCl_2 + 2KCl$$

Submitted by D. E. CLEGG* and J. R. HALL*
Checked by C. H. BRUBAKER, JR.,† G. L. GILBERT,† and M. DYKE†

The preparation of iodo(trimethyl)platinum(IV) of empirical formula $PtI(CH_3)_3$ was first reported by Pope and Peachey.[1] The substance was produced by the reaction between platinum(IV) chloride and methylmagnesium iodide. Gilman et al.[2] have repeated this method of preparation to give a 45% yield and have identified some of the side products of the reaction. Various starting materials and procedures have been used by

* Chemistry Department, University of Queensland, Brisbane, Australia.
† Department of Chemistry, Michigan State University, East Lansing, Mich.

other workers,[3,4,5] and yields up to 55% have been obtained. However, these methods suffer from the disadvantages of inconvenient starting materials, the number of intermediate steps, time involved, and relatively low yields. The procedure described below, carried out under anhydrous conditions, produces $PtI(CH_3)_3$ in 70 to 80% yield in a single step from the readily prepared potassium hexachloroplatinate(IV). Ivanova and Gel'man[4] have previously described the use of potassium hexachloroplatinate(IV) as a starting material. The present modification with excess Grignard reagent and methyl iodide gives superior yields.

Procedure

Solvents and reagents are dried in the following fashion: Benzene and ether are freshly distilled from sodium; methyl iodide is distilled over calcium chloride; and potassium hexachloroplatinate(IV) is dried at 110°.

In a three-necked 500-ml. flask fitted with a reflux condenser, stirrer, and dropping funnel are placed 10 g. (0.02 mol) potassium hexachloroplatinate(IV), 100 ml. benzene, and 50 ml. ether. The reflux condenser is capped with a calcium chloride drying tube. The Grignard reagent is prepared from 3.5 g. (0.14 mol) magnesium, 14.5 ml. (0.23 mol) methyl iodide, and 100 ml. ether by maintaining reflux conditions for 20 minutes. This reaction mixture is filtered through a sintered-glass disk, and the filtrate is placed in the dropping funnel of the three-necked reaction flask.

The reaction flask is cooled in an ice bath and the contents stirred while the Grignard reagent is added over a period of 10 minutes. The ice bath is removed and stirring is continued for 4 hours. The reaction mixture is allowed to stand for about 12 to 16 hours, during which time an off-white solid settles, leaving a clear orange-colored solution.

The reaction flask is placed in an ice bath and while the mixture is stirred, a slurry of 25 g. of ice and 100 ml. of ice-cold

10% hydrochloric acid is very slowly added. The aqueous layer becomes wine-red and the organic layer a deeper orange. The organic layer is decanted and the aqueous layer then extracted three times with 100-ml. aliquots of benzene. Each extraction is carried out under reflux conditions for a period of 20 minutes.

The original benzene–ether layer and the benzene extracts are dried with anhydrous sodium sulfate. After filtration, the organic solution is evaporated to dryness in a stream of air to leave a residue of orange-brown crystals contaminated with some dark-colored material. The latter is removed by washing once with 5 ml. of ethanol. The reaction product is then dissolved in a minimum of chloroform (about 120 ml.). The solution is filtered, the filtrate is evaporated to half its volume, and an equal volume of acetone is then added to give a yellow precipitate. This precipitate is collected, redissolved in chloroform, and precipitated again with acetone. The yie'd is 5.3 to 6.0 g. (70 to 80%). *Anal.* Calcd. for C_3H_9PtI: Pt, 53.1; C, 9.78; H, 2.47; I, 34.6. Found: Pt, 52.6; C, 9.95; H, 2.45; I, 34.5. A coarse crystalline orange product may be obtained by recrystallizing the material from hot chloroform.

Properties

Iodo(trimethyl)platinum(IV) is a yellow crystalline product which decomposes at 190 to 195°. It is soluble in most non-polar solvents and essentially insoluble in polar media such as water and acetone. In benzene solution, the iodo derivative is tetrameric.[6] X-ray investigations have shown that in chloro-(trimethyl)platinum four platinum atoms describe a tetrahedron as do the four chlorine atoms, and the two tetrahedra are interpenetrating so as to give a cubic array of platinum and chlorine atoms. Each platinum atom is bonded to three chlorine atoms and to three terminal methyl groups. Some of the trimethylplatinum derivatives of organic chelate ligands are dimeric and in these structures the platinum is again six-coordinate.[7]

Chemically, the platinum-carbon bond in iodo(trimethyl)-platinum(IV) is relatively nonreactive and is unaffected by water or oxygen. The iodine atoms may be replaced by other ions through simple metathetical reactions.

A white crystalline material of the composition $PtI(CH_3)_3$ has been obtained in the following fashion.[4] The yellow iodo derivative is converted to the sulfate by metathesis with silver sulfate. Addition of potassium iodide solution to an aqueous solution of trimethylplatinum(IV) sulfate yields a precipitate which, if recovered immediately by filtration, is white, analyzes precisely for $PtI(CH_3)_3$, is free of solvent, and decomposes at 190 to 200°.

REFERENCES

1. W. J. POPE and S. J. PEACHEY: *Proc. Chem. Soc.*, **23**, 86 (1907); *J. Chem. Soc.*, **95**, 571 (1909).
2. H. GILMAN, M. LICHTENWALTER, and R. A. BENKESER: *J. Am. Chem. Soc.*, **75**, 2063 (1953).
3. M. E. FOSS and C. S. GIBSON: *J. Chem. Soc.*, **1951**, 299.
4. O. M. IVANOVA and A. D. GEL'MAN: *Zh. Neorgan. Khim.*, **3**, 1334 (1958).
5. J. CHATT and L. A. DUNCANSON: *J. Chem. Soc.*, **1953**, 2939.
6. R. C. MENZIES and H. OVERTON: *ibid.*, **1933**, 1290.
7. J. E. LYDON, MARY R. TRUTER, and R. C. WATLING: *Proc. Chem. Soc.*, **1964**, 193.

14. BIS(2,4-PENTANEDIONATO)ZINC
(*Zinc Acetylacetonate*)

$$ZnSO_4 \cdot 7H_2O + 2C_5H_8O_2 + 2NaOH \rightarrow$$
$$Zn(C_5H_7O_2)_2 \cdot H_2O + Na_2SO_4 + 8H_2O$$
$$Zn(C_5H_7O_2)_2 \cdot H_2O + CH_3OH \rightarrow Zn(C_5H_7O_2)_2 \cdot CH_3OH + H_2O$$
$$Zn(C_5H_7O_2)_2 \cdot CH_3OH \rightarrow Zn(C_5H_7O_2)_2 + CH_3OH$$
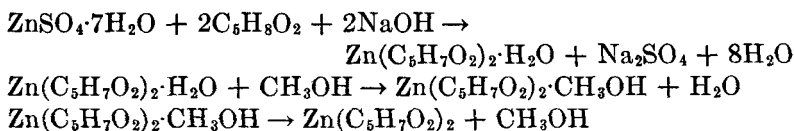
Submitted by GUNTER RUDOLPH* and MALCOLM C. HENRY*
Checked by EARL L. MUETTERTIES†

Bis(2,4-pentanedionato)zinc, obtained by the action of 2,4-pentanedione on zinc compounds, was long believed to be

* U.S. Army Natick Laboratories, Natick, Mass.
† E. I. du Pont de Nemours & Company, Wilmington, Del.

anhydrous. Graddon and Weeden[1] have surveyed the literature and established conclusively that the compound with m.p. 138° is, in fact, a monohydrate. Dehydration of this hydrate at 110° (0.1 mm.) is difficult due to its tendency to undergo conversion into $Zn_2(CH_3CO_2)(C_5H_7O_2)_3$, m.p. 198 to 200°.

A preferable, three-step, procedure for preparing anhydrous bis(2,4-pentanedionato)zinc, m.p. 127°, in good yields involves (1) the preparation of bis(2,4-pentanedionato)zinc hydrate from zinc sulfate heptahydrate and 2,4-pentanedione in aqueous solution in the absence of heat, (2) conversion of the bis(2,4-pentanedionato)zinc hydrate into a bis(2,4-pentanedionato)zinc-methanol adduct, and (3) decomposition of the methanol adduct.

Procedure

A. Bis(2,4-pentanedionato)zinc Hydrate

To a solution of 100 g. (1 mol) of 2,4-pentanedione and 40 g. (1 mol) of sodium hydroxide in 500 ml. of water is slowly added with stirring a solution of 144 g. (0.5 mol) of zinc sulfate hepta-hydrate in 500 ml. of water. After the suspension has stood for one hour, the white precipitate is filtered, washed with water, and dried, to give 122 g. (87%) of rather pure bis(2,4-pentanedionato)zinc hydrate with m.p. 138°. The crude product is dissolved in 1 l. of hot ethyl acetate, to which 50 ml. of 2,4-pentanedione has been added. The solution is filtered hot in order to remove a small amount of high-melting decomposition products. From the cooled solution, 90 g.* (64%) of bis(2,4-pentanedionato)zinc hydrate is obtained as needles, m.p. 138 to 140°.

B. Anhydrous Bis(2,4-pentanedionato)zinc

A filtered solution of 90 g. of bis(2,4-pentanedionato)zinc hydrate in 450 ml. of methanol is put into a 1-l. conical flask

* The yield obtained by the checker was 85 g.

surrounded by a packing of Dry Ice, and allowed to stand with occasional shaking until the contents have reached a temperature of −50°. The crystalline precipitate* is filtered rapidly through a Büchner funnel which has been precooled by storing it in Dry Ice for at least 10 minutes. The product, while still cold and wet with methanol, is transferred into a round-bottomed flask. Excessive exposure to moist air should be avoided, for the hydrate is re-formed readily. The methanol is removed by connecting the flask to a large, Dry Ice–cooled trap and evacuating the system with an oil pump. After 30 minutes of evacuation, the container is warmed to 80° with a water bath. Removal of the methanol will be complete in 8 hours. The yield of anhydrous bis(2,4-pentanedionato)zinc is 80 g.†

Properties

Bis(2,4-pentanedionato)zinc hydrate forms white crystals which melt at 138 to 140° to a milky liquid. It is rather unstable toward heat, decomposing into mesitylene and an acetate-containing compound of the formula $Zn_2(CH_3CO_2)(C_5H_7O_2)_3$.[2] The latter also tends to form on dissolution of the hydrate in cold organic solvents, but this can be prevented by adding 2,4-pentanedione to the solution. The crystal structure of bis-(2,4-pentanedionato)zinc hydrate has been determined recently.[3]

Anhydrous bis(2,4-pentanedionato)zinc melts at 127° to a clear liquid. A higher melting point and a slightly opaque melt indicate that hydrate is still present. The anhydrous product exhibits some significant differences from the hydrate, to which it is easily converted by moisture. It is recovered unchanged from toluene after refluxing for 24 hours, can be sublimed at

---

* The product crystallizing out of cooled methanol solutions appears to be an unstable methanol adduct of bis(2,4-pentanedionato)zinc. Recrystallization from hot alcohol yields the hydrate. Immediately after collection, this adduct melts at 80 to 90°; on standing in the open atmosphere, it is converted into the hydrate.

† The yield obtained by the checker was 73 g.

110° (0.1 mm.), and dissolves easily in dry organic solvents, forming clear solutions. Bis(2,4-pentanedionato)zinc can be recrystallized from *n*-hexane.

REFERENCES

1. D. P. GRADDON and D. G. WEEDEN: *Australian J. Chem.*, **16**, 980 (1963).
2. G. RUDOLPH and M. C. HENRY: *Inorg. Chem.*, **3**, 1317 (1964).
3. H. MONTGOMERY and E. C. LINGAFELTER: *Acta Cryst.*, **16**, 748 (1963).

15. EUROPIUM(II) SULFIDE

$$Eu_2O_3 + 3H_2S \rightarrow 2EuS + 3H_2O + S$$
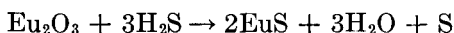
Submitted by R. D. ARCHER* and W. N. MITCHELL†
Checked by R. MAZELSKY‡

Although several methods of preparing europium(II) sulfide have been suggested,[1–4] contamination by the displaced anion is encountered if europium dichloride is used as the starting material;[2] and if europium metal is a reagent then the purity§ of the metal is a significant problem.[4]   In previous preparations of the sulfide from europium(III) oxide and hydrogen sulfide,[3] the possibility of oxygen contamination has not been considered. The necessity of considering oxygen contamination is evident from a study of manganese sulfide conducted in our laboratory[6] in which it has been found that 0.60% or more oxygen is not uncommon in the sulfide as normally prepared even though the

---

* University of Massachusetts, Amherst, Mass.
† Applied Physics Corporation, Monrovia, Calif.
‡ Research & Development Center, Westinghouse Electric Corporation, Pittsburgh, Pa.

§ The purest grade of europium metal available from the Lindsay Chemical Division of American Potash is 99.9% Eu in terms of rare earth content, but it may contain up to 1% of other metal impurities (mainly tantalum when prepared in tantalum vessels) and typically contains 2.8 mol % oxygen.[5]

elemental analyses for the anticipated elements are within experimental error.

Reaction between europium(III) oxide and hydrogen sulfide at 600° produces europium(III) sulfide predominately, but europium(II) sulfide is the product of reaction at higher temperatures.[3]   It has been found necessary to modify the previously published procedure[3] in order to remove the last traces of elemental sulfur which otherwise contaminate the product.

Procedure

A suitable induction-heater procedure involves placing a graphite sleeve (30 mm. i.d., 34 mm. o.d., and 100 mm. long) over the quartz tube and then using a water-cooled coil of copper tubing connected to a high-frequency induction source such as a Lepel T-5-3.   At the temperature used in this synthesis, the graphite is oxidized quite rapidly by air, but this can be avoided by enclosing the graphite sleeve with a larger quartz tube (*ca.* 50 mm. o.d.) held in place with rubber stoppers which are fitted with small tubes to allow a stream of nitrogen to flow over the graphite.   The protective atmosphere allows one graphite sleeve to be used for several preparations rather than several sleeves for one preparation.

Ten grams (0.03 mol) of powdered europium(III) oxide (Lindsay Chemical, 99.9% purity) is spread uniformly along 100 mm. of a 900- × 25-mm.-diam. quartz tube fitted with rubber stoppers and entry and exit tubes of at least 15 mm. to prevent free sulfur from clogging the system.   The tube is heated in a hydrogen sulfide atmosphere at 1150° for 2 hours.   The tube and its contents are preflushed, heated, and cooled in the hydrogen sulfide atmosphere.   After cooling, the hydrogen sulfide is flushed from the system with prepurified nitrogen. The product then is transferred in an inert atmosphere to another quartz tube connected to a high-vacuum system via a liquid-nitrogen trap and heated *in vacuo* at 900° for 2 hours to

remove the excess sulfur which contaminates the original product. The yield is almost quantitative.*

Properties

Europium(II) sulfide is a black powder possessing a sodium chloride lattice[7] and an unknown melting point. Crystals of the sulfide have a golden hue by reflected light. The compound exhibits ferromagnetism[8] with a Curie temperature of 17°K. Above this temperature, europium(II) sulfide behaves as a typical paramagnetic compound.[2]

REFERENCES

1. G. BECK and W. NOWACKI: *Naturwiss.*, **26**, 495 (1938).
2. W. KLEMM and H. SENFF: *Z. Anorg. Allgem. Chem.*, **241**, 233 (1939).
3. L. DOMONGE, J. FLAHOUST, and M. GUITTARD: *Compt. Rend.*, **429**, 697 (1959).
4. U. ENZ, J. F. FAST, S. VAN HOUTON, and J. SMIT: *Philips Res. Rept.*, **17**, 451 (1962).
5. Lindsay Chemical Division: private communication.
6. R. D. ARCHER and W. N. MITCHELL: *J. Chem. Phys.*, **39**, 250 (1963).
7. W. NOWACKI: *Z. Krist.*, **99**, 339 (1938).
8. R. L. WILD and R. D. ARCHER: *Bull. Am. Phys. Soc.*, **7**, 440 (1962).

* The oxygen analysis by high-energy-neutron activation indicated 0.06 ± 0.06% oxygen.

Chapter Two

BORON COMPOUNDS

16. BORANE ANIONS

Submitted by H. C. MILLER* and E. L. MUETTERTIES*
Checked by J. L. BOONE† ($B_3H_8^-$ and $B_{12}H_{12}^{2-}$), P. GARRETT,‡ and M. F.
HAWTHORNE‡ ($B_{11}H_{14}^-$)

A systematic study[1,2] has established that the reaction of
diborane with hydride ion or with a donor molecule, such as an
amine, can be employed to prepare a variety of complex borane
anions, including $B_3H_8^-$, $B_{10}H_{10}^{2-}$, $B_{11}H_{14}^-$, and $B_{12}H_{12}^{2-}$.
Control of this general reaction is primarily gained through
temperature, pressure, and solvent variation. A discussion
of borane anion synthesis is given by Miller, Miller, and Muet-
terties,[2] and explicit directions are given for good syntheses of
$B_3H_8^-$, $B_{11}H_{14}^-$, and $B_{12}H_{12}^{2-}$. However, most of these methods
prescribe diborane and pressure equipment. The procedures
detailed below require no pressure equipment and, with the
exception of the $B_3H_8^-$ synthesis, employ decaborane(14) instead
of the more reactive and hazardous diborane. Within the

* Central Research Department, Experimental Station, E. I. du Pont de
Nemours & Company, Wilmington, Del.
† U.S. Borax Research Corp., Anaheim, Calif.
‡ Department of Chemistry, University of California, Riverside, Calif.

experience of the submitters, these are the best synthetic procedures that do not require pressure equipment for $B_3H_8^-$, $B_{11}H_{14}^-$, and $B_{12}H_{12}^{2-}$ salts.

Safety considerations are paramount in any boron hydride synthesis. The energy yield from the oxidations of boron hydrides is too high for any cavalier treatment of boron hydrides. Exclusion of air is the critical consideration in diborane reactions. Decaborane(14) is less reactive, generally, in a kinetic sense, but the thermodynamic potential is comparable. In addition, all volatile boron hydrides are toxic. The procedures described in the latter two preparations are within our experience nonhazardous. These procedures should be followed in every detail; improvisation is not recommended.

A. $B_3H_8^-$

$$NaBH_4 + B_2H_6 \rightarrow NaB_3H_8 + H_2$$
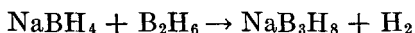
Procedure

■ *Caution. The handling of diborane presents very real and serious hazards. It is poisonous; it is spontaneously flammable in air; and it can explode with glass-shattering force when mixed with air in a confined space.* In the following procedure, it would be possible by improper operations to have diborane and liquid oxygen condensed together in the liquid-nitrogen cooled trap. Such a mixture would surely detonate with sufficient force to do damage to any ordinary protective shields and any adjacent personnel. The directions must be followed carefully. The operation is conducted in an efficient hood and should be shielded. The glassware must be sturdy, free of cracks, and assembled with tight joints and connections. The reaction should always be kept at a pressure slightly above atmospheric. To avoid condensation of oxygen from the air, the liquid-nitrogen cooled trap should at all times be under a slight positive pressure of nitrogen or of the off gases from the reaction.

A 300-ml. stainless-steel cylinder is fitted with a rupture disk assembly to which is fitted a Hoke valve (*A*). To this Hoke valve is fitted a T-connection, one arm of which is fitted with a 500-p.s.i. gage and the other arm of which carries a second Hoke valve (*B*) to which a hose connector is attached. The pipe fittings are all made up with pipe dope or pipe tape made of polytetrafluoroethylene resin. The pipe joints, as well as the valve stem packing on valve *A*, are checked for leaks at about 400 p.s.i.g. with nitrogen. The cylinder is then vented and finally dried by heating the assembly to 60 to 70° and evacuating with a mercury-vapor pump or an efficient oil pump. The tare weight of the empty evacuated cylinder assembly is recorded. The cylinder is connected to a diborane supply cylinder through a metal jumper. The jumper line has a T-connection with a Hoke valve on the side arm so that the jumper can be evacuated until free of air and then isolated from the vacuum system while diborane is transferred. The 300-ml. cylinder is filled at room temperature to about 350 p.s.i.g. with diborane (available in cylinders from Callery Chemical Co.) and valve *B* is closed. The diborane remaining in the jumper is pumped away, the 300-ml. cylinder disconnected from the jumper, and then cooled in liquid nitrogen. When the cylinder is thoroughly chilled, any residual pressure (hydrogen) is pumped away, the valves are closed, and the cylinder is allowed to warm to room temperature and weighed. A cylinder of this size will contain 13.9 g. (0.5 mol), of diborane at about 330 p.s.i.g., 8.3 g. (0.3 mol) at about 225 p.s.i.g., and 2.77 g. (0.1 mol) at about 75 p.s.i.g. As diborane is dispensed, the pressure drop in the cylinder can be used as a rough measure of the amount of diborane which has been used.

[An alternative diborane source was used by the checker. Diborane was generated by adding boron trifluoride–ethyl ether to sodium tetrahydroborate (sodium borohydride) in ether. The generator was charged to yield a maximum of 0.6 mol of

diborane, which was carried out of the generator with dry nitrogen through a Dry Ice–acetone trap to remove traces of boron trifluoride and ether, and then into the main reaction flask.]

A 500-ml. three-necked flask is equipped with a Glas-Col heating mantle and a magnetic stirrer.   One neck is fitted with a gas inlet tube which will not quite go below the surface of the 50 ml. of solvent to be added.   The inlet tube is connected with Tygon or rubber tubing to a mercury pressure-release bubbler and to a T-connection, which in turn is connected to a source of dry nitrogen and to the 300-ml. diborane cylinder or the diborane generator.   The second neck of the flask is fitted with a thermometer which will be below the surface of the charge. The final neck is fitted with a water-cooled reflux condenser connected in turn to a trap which can later be cooled with liquid nitrogen.   The exit of the trap is connected to a mercury bubbler through which the hydrogen generated is allowed to escape but which will prevent any reverse flow of air back to the reactor.   The mercury bubbler on the inlet side of the reactor must have a somewhat greater head of mercury than this exit bubbler.   The hydrogen generated can, if desired, be measured by joining this exit bubbler to a wet-test meter.

This apparatus is flushed with dry nitrogen.   The tubing from the diborane cylinder to the T-connection is disconnected at the cylinder end briefly to allow nitrogen to displace the air in the tubing.   The flask is charged with 11.3 g. (0.3 mol) of sodium borohydride powder and 50 ml. of anhydrous[3] diglyme (diethylene glycol dimethyl ether).   When the system has again been thoroughly flushed with nitrogen, the trap is cooled with liquid nitrogen.   The pressure within the system is then brought to just above 1 atmosphere with nitrogen as shown by the mercury bubbler, and a very slow stream of nitrogen is allowed to continue to escape through the mercury bubbler.   The flask contents are heated to 85° and stirred vigorously.   About 0.45

mol of diborane is now added over 4 hours. The nitrogen flow is discontinued, valve B is closed, and valve A is fully opened. Valve B is then adjusted so that the diborane pressure decreases at a rate of about 12 p.s.i.g. per 10 minutes. As the diborane is added, heat is evolved. The heating mantle is adjusted to maintain the internal temperature at 90 to 95°. Hydrogen will be evolved. Any ether carried over with the hydrogen and the excess diborane will collect in the liquid-nitrogen trap. When a little less than 0.4 mol diborane has been drawn from the cylinder, about 8.1 l. of hydrogen will have been evolved and the rate of hydrogen evolution will begin to slacken noticeably. When a total of 0.45 mol of diborane has been added, valves A and B are closed, heating is discontinued, and a gentle flow of nitrogen is used to flush all unused diborane into the liquid-nitrogen trap.

The liquid-nitrogen trap will contain about 0.15 mol of unused diborane, which is swept out into the hood by removing the trap from the liquid nitrogen while the nitrogen is still flowing. After the trap has warmed to room temperature and the reaction mixture has cooled to about 50 to 60°, the reaction mixture is clarified by filtration through a coarse sintered-glass funnel on which a $\frac{1}{4}$-in. pad of Celite filter aid, wet with diglyme,[3] has been placed. The filter cake is washed with diglyme,[3] and the combined filtrate is diluted to about 600 ml. with anhydrous[3] dioxane and chilled to about 5°. The white precipitate is collected, washed with a little dioxane, and dried *in vacuo* to constant weight at room temperature to give 60 to 65 g. (60 g. = 0.184 mol, 61% of theory) of $NaB_3H_8 \cdot 3C_4H_8O_2$. Recrystallization can be effected as follows: The crude material is dissolved in 200 ml. of anhydrous[3] glyme (1,2-dimethoxyethane) at 70 to 80° and then filtered through Celite. The Celite is washed with 25 ml. of hot glyme.[3] The combined filtrate is diluted to a total of about 500 ml. with dioxane. The recovery is about 90%. A minimum exposure to moisture during work-up is necessary and the dioxane complex must be

carefully protected from air and water to be stable upon long storage at room temperature. Storage under vacuum is recommended. Good analytical values will not be obtained unless the sample is adequately protected from moisture. *Anal.* Calcd. for $NaB_3H_8 \cdot 3C_4H_8O_2$: Na, 7.0; B, 9.9; H, 9.9; C, 44.0. Found: Na, 6.9; B, 10.0; H, 9.7; C, 43.5. The salt has the following characteristic infrared absorption bands (exclusive of those coincident with Nujol) when run as a Nujol mull: 2460/2390 doublet (s), 2120/2080 doublet (m), 1285 (s), 1245 (s), 1035 (s), 1110 (vs), 1075 (s), 1045 (s), 1010 (s), 895/890 doublet (s), 870 (vs), 770 (w), and 715 (m) cm.$^{-1}$

Properties

The $B_3H_8^-$ anion has been shown by x-ray analysis[4] to have the following structure:

$$
\begin{array}{c}
\text{H} \qquad \text{H} \\
\diagdown \quad \diagup \\
\text{B} \\
\diagup \quad \diagdown \\
\text{H} \qquad \text{H} \\
| \qquad\quad | \\
\text{B}\!-\!-\!-\!-\!\text{B} \\
\diagup | \qquad |\diagdown \\
\text{H} \quad \text{H} \qquad \text{H} \quad \text{H}
\end{array}
$$
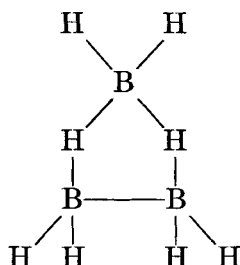
The hydrolytic stability of this anion is comparable to that of BH_4^-. Acid completely destroys the $B_3H_8^-$ ion to give hydrogen and boric acid:

$$H^+ + B_3H_8^- + 9H_2O \rightarrow 3H_3BO_3 + 9H_2$$

Nonsolvated salts such as CsB_3H_8 and $(CH_3)_4NB_3H_8$ are the most stable. Closely related to $B_3H_8^-$ are the neutral base derivatives of B_3H_7, e.g., $(CH_3)_3N \cdot B_3H_7$, which can be prepared from the $B_3H_8^-$ ion by displacement of the hydride ion:[5]

$$B_3H_8^- + (CH_3)_3NHCl \rightarrow Cl^- + H_2 + (CH_3)_3N \cdot B_3H_7$$

B. $B_{11}H_{14}^-$

$$NaBH_4 + B_{10}H_{14} \rightarrow NaB_{11}H_{14} + 2H_2$$
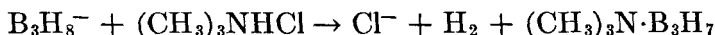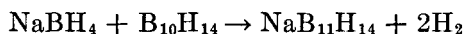
Procedure

Anhydrous[3] dioxane (100 ml.) and 0.95 g. (0.025 mol) of sodium borohydride are placed in a round-bottomed, three-necked flask fitted with a reflux condenser, a motor-driven stirring rod (or alternatively a magnetic stirrer), and a funnel for the addition of decaborane. The system is purged with nitrogen, and then 3.8 g. (0.031 mol) of decaborane is added. The flask is stoppered, and a T-tube through which a stream of nitrogen is flowing is attached to the exit of the reflux condenser. The reaction flask is slowly heated until mild reflux occurs. Stirring is maintained throughout the reaction period. After 20 hours, the evolution of hydrogen is complete. The product is then isolated while a strictly dry-nitrogen atmosphere is maintained. The reaction mixture is chilled to about 15° and filtered to give about 7.3 g. of crude $NaB_{11}H_{14}\cdot3C_4H_8O_2$. The crude product is dissolved in a minimum amount of warm glyme[3] (40 to 80 ml.). The solution is clarified by filtration and $NaB_{11}H_{14}$ is reprecipitated by at least a 400% dilution with dioxane. The complex tends to separate as an oil unless excess dioxane is added. Traces to small yields of $B_{12}H_{12}{}^{2-}$ can be present in the crude material. Since $Na_2B_{12}H_{12}$ is not soluble in glyme,[3] it is removed from the $NaB_{11}H_{14}$ by this recrystallization procedure. *Anal.* Calcd. for $NaB_{11}H_{14}\cdot3C_4$-H_8O_2: C, 34.3; H, 9.10; B, 28.3. Found: C, 33.9; H, 9.45; B, 27.5. The yield of recrystallized product* is about 6.8 g. (65%). [Checkers report a 7.5 g. (71%) yield.] Characteristic infrared absorptions (exclusive of those coincident with Nujol) are seen as follows in a Nujol mull: 2510 (vs), 1290 (w), 1280 (w), 1250 (s), 1110 (s), 1072 (m), 1040 (m), 1010 (w), 895 (m), 883 (w), 875 (m), 868 (s), and 720 (s) cm.$^{-1}$ This complex

---

* The dioxane content is variable. Generally the amount of dioxane will fall in the range of 2.5 to 3.0 mols per mol of $NaB_{11}H_{14}$, provided that the sample is vacuum-dried for ~24 hours at room temperature. Low carbon and high boron values will be obtained if the sample is not adequately protected from moisture.

slowly oxidizes in air and should be stored under dry nitrogen. Alternatively, the sodium salt may be converted to an unsolvated heavy-metal salt, e.g., cesium, by metathetical reaction in water.[6]

Properties

The structure of the $B_{11}H_{14}^-$ ion has not been established. A discussion of the spectral properties and the structural implications may be found in the original article by Aftandilian et al.[6] Hydrolytically, $B_{11}H_{14}^-$ is more stable than BH_4^-. Salts of $B_{11}H_{14}^-$ slowly oxidize in air, particularly if they are solvated (water or ether).

C. $B_{12}H_{12}^{2-}$

$$2(C_2H_5)_3N \cdot BH_3 + B_{10}H_{14} \xrightarrow[\text{Ultrasene}]{190°} [(C_2H_5)_3NH]_2B_{12}H_{12} + 3H_2$$
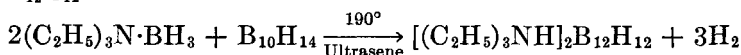
Procedure

A 500-ml. three-necked flask is fitted with a heated oil bath and a magnetic stirrer. A thermometer, adjusted to dip below the reaction mixture, and a nitrogen purge line are fitted in one neck. The second is equipped with a 100-ml. graduated dropping funnel positioned so that its discharge will not run down the wall of the flask. The third neck is fitted with a reflux condenser. The off gases from the reflux condenser are led to a mercury bubbler to prevent air from being drawn back into the reactor as it cools. If it is desired, the exit from the bubbler may be connected to a wet-test meter to measure the hydrogen generated.

The reactor is flushed thoroughly with nitrogen and then 240 ml. of Ultrasene* is added. A solution is prepared from

* Ultrasene is a highly purified grade of high-boiling kerosine offered by the Atlantic Refining Co. Its infrared spectrum is that of Nujol and is free of bands attributable to olefinic unsaturation or aromatic systems. Similar inert high-boiling hydrocarbons could be used.

30 g. (0.246 mol) of decaborane and 79 ml. (62.5 g., 0.54 mol, 10% excess) of triethylamine–borane. This solution must be prepared and handled under nitrogen to protect it from moisture and oxygen. Dissolution is endothermic. Stirring and gentle heat will hasten solution. Commercial grades of decaborane frequently contain insoluble impurities, but freshly purified decaborane will give a clear solution. The solution is clarified, if necessary, by filtration under nitrogen through a sintered-glass funnel and is added to the dropping funnel.

The Ultrasene is heated to 190°, and the contents of the dropping funnel are added over a period of 20 to 30 minutes. Effective mixing of the reactants should be maintained throughout the addition; magnetic stirring is adequate for this scale of reaction. The decaborane solution reacts almost instantly as it hits the hot liquid to precipitate the triethylammonium salt of $B_{12}H_{12}^{2-}$ with liberation of hydrogen. When addition is complete, nearly the theoretical 18 l. of hydrogen will have been evolved. After heating an additional 5 to 10 minutes, hydrogen evolution ceases, and the reactor is allowed to cool to at least 50 to 60°. There is obtained a slurry of nearly white solid $[(C_2H_5)_3NH]_2B_{12}H_{12}$ in Ultrasene containing a little excess triethylamine–borane. The solid is collected on a funnel and washed with ether (about 200 ml.) to remove the Ultrasene. After air drying, the crude product weighs about 77 g. (0.222 mol, 90% of theory). Upon boiling for about 10 minutes in 1.5 l. of water, the bulk of the crude material dissolves with some hydrogen liberation. The hot solution is acidified with about 4 ml. of 4 N hydrochloric acid and then filtered hot to remove 3 to 4 g. of insoluble gummy material. The filtrate is chilled. The crystalline product is collected by filtration and air-dried to give 67.3 g. (79% of theory) of pure $[(C_2H_5)_3NH]_2$-$B_{12}H_{12}$. *Anal.* Calcd. for $[(C_2H_5)_3NH]_2B_{12}H_{12}$: C, 41.6; H, 12.8; N, 8.10; B, 37.5. Found: C, 41.5; H, 12.9; N, 8.00; B, 37.3. As a Nujol mull, the salt has the following characteristic infrared absorption frequencies (exclusive of those coincident with

Nujol): 3150 (m), 2500 (s), 2040 (w), 2020 (w), 1850 (w), 1640 (w), 1275 (w), 1160 (m), 1065 (s), 1030 (s), 847 (m), 797 (w), 745 (w), and 720 (m) cm.$^{-1}$

The sparingly water-soluble triethylammonium salt of $B_{12}H_{12}{}^{2-}$ is readily converted to the highly water-soluble sodium salt. A carefully weighed sample of the triethylammonium salt is treated with an exactly equivalent amount of standardized aqueous sodium hydroxide. The mixture is heated to effect solution and then boiled to expel the free triethylamine until the vapors are no longer basic. Evaporation to dryness then leaves a crystalline hydrate of $Na_2B_{12}H_{12}$. The anhydrous salt is obtained by drying at 100°/1 μ for $\sim$24 hours and has characteristic infrared absorption frequencies as a Nujol mull (exclusive of any frequencies coincident with Nujol) at 2470 (s), 1010 (w), 1070 (m), 770 (w), 727 (m), 710 (m), and 700 (m) cm.$^{-1}$

Properties

The dodecahydrododecaborate anion, $B_{12}H_{12}{}^{2-}$, is termed unique with considerable justification. This ion and its perhalo derivatives, e.g., $B_{12}Cl_{12}{}^{2-}$, are the most symmetrical molecular aggregates known. The boron atoms occupy the vertices of a regular icosahedron and each is bonded terminally to a hydrogen atom; all boron atoms are environmentally equivalent.[7,8] This anion is the only known example of the I_h symmetry group.[8] General spectral, physical, and chemical properties of $B_{12}H_{12}{}^{2-}$ are detailed in a paper by Muetterties et al.[9]

The $B_{12}H_{12}{}^{2-}$ ion is the most stable boron hydride structure known. In aqueous media, it is degraded by neither strong acid nor strong base. In fact, salts of $B_{12}H_{12}{}^{2-}$ can be converted to the very strong acid $(H_3O^+)_2B_{12}H_{12}{}^{2-}$ by ion-exchange techniques. On oral ingestion, this anion appears to have very little, if any, physiological activity in contrast to the very toxic boron hydrides. The hydrogen atoms in $B_{12}H_{12}{}^{2-}$ can be replaced by other atoms or groups, and a vast derivative chemistry of $B_{12}H_{12}{}^{2-}$ has been described.[10-13]

REFERENCES

1. H. C. MILLER, N. E. MILLER, and E. L. MUETTERTIES: *J. Am. Chem. Soc.*, **85**, 3885 (1963).
2. H. C. MILLER, N. E. MILLER, and E. L. MUETTERTIES: *Inorg. Chem.*, **3**, 1456 (1964).
3. Commercially available anhydrous glyme (1,2-dimethoxyethane) and diglyme (diethylene glycol dimethyl ether) were passed through a column of molecular sieve 5A (under nitrogen) as needed. Matheson, Coleman and Bell Spectroquality® reagent-grade dioxane was used as received.
4. C. E. NORDMAN and C. R. PETERS: *J. Am. Chem. Soc.*, **82**, 5758 (1960).
5. C. E. NORDMAN and C. REIMAN: *ibid.*, **81**, 3538 (1959).
6. V. D. AFTANDILIAN, H. C. MILLER, G. W. PARSHALL, and E. L. MUETTERTIES: *Inorg. Chem.*, **1**, 734 (1962).
7. J. WUNDERLICH and W. N. LIPSCOMB: *J. Am. Chem. Soc.*, **82**, 4427 (1960).
8. E. L. MUETTERTIES, R. E. MERRIFIELD, H. C. MILLER, W. H. KNOTH, and J. R. DOWNING: *ibid.*, **84**, 2506 (1962).
9. E. L. MUETTERTIES, J. H. BALTHIS, Y. T. CHIA, W. H. KNOTH, and H. C. MILLER: *Inorg. Chem.*, **3**, 444 (1964).
10. W. H. KNOTH, H. C. MILLER, D. C. ENGLAND, G. W. PARSHALL, E. L. MUETTERTIES, and J. C. SAUER: *J. Am. Chem. Soc.*, **84**, 1056 (1962).
11. W. H. KNOTH, H. C. MILLER, J. C. SAUER, J. H. BALTHIS, Y. T. CHIA, and E. L. MUETTERTIES: *Inorg. Chem.*, **3**, 159 (1964).
12. W. H. KNOTH, J. C. SAUER, H. C. MILLER, and E. L. MUETTERTIES: *J. Am. Chem. Soc.*, **86**, 115 (1964).
13. W. R. HERTLER, W. H. KNOTH, and E. L. MUETTERTIES: *Inorg. Chem.*, **4**, 288 (1965).

17. ICOSAHEDRAL CARBORANES AND INTERMEDIATES LEADING TO THE PREPARATION OF CARBAMETALLIC BORON HYDRIDE DERIVATIVES
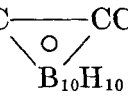
Submitted by M. FREDERICK HAWTHORNE,* TIMOTHY D. ANDREWS,* PHILIP M. GARRETT,* FRED P. OLSEN,* MARTEN REINTJES,* FRED N. TEBBE,* LES F. WARREN,* PATRICK A. WEGNER,* and DONALD C. YOUNG*
Checked by R. P. ALEXANDER,† R. W. BLUNDON,† H. A. SCHROEDER,† and T. L. HEYING†

The recent literature contains a number of references to the preparation and derivative chemistry of the icosahedral[1] carbo-

* Department of Chemistry, University of California, Riverside, Calif.
† Research Center, Chemicals Division, Olin Mathieson Chemical Corporation, New Haven, Conn.

rane $B_{10}C_2H_{12}$.[2a-l] Reactions of the versatile ion $B_9C_2H_{12}^-$ derived[3] from $B_{10}C_2H_{12}$ have produced two new chemistries, one leading to the formation of a series of new carboranes containing fewer than 10 boron atoms,[4a-c] and one leading to the preparation of the novel carbametallic boron hydride sandwich compounds.[5a-d]

Nomenclature for the carboranes is discussed by R. Adams, *Inorg. Chem.*, **2**, 1087 (1963). Briefly, the accepted name for the isomer of $B_{10}C_2H_{12}$ containing adjacent carbon atoms is 1,2-dicarbaclovododecaborane(12),* where the numbers prefixing the name indicate the relative positions of the carbon atoms in the framework and the number in parentheses indicates the number of hydrogens in the parent compound. If the formula and isomer are clearly understood, the common name *carborane* may be used. The term *carborane* has also been applied in a more general sense to other polyhedral species which contain fewer than 10 boron atoms. The position of substitution may be clearly stated by prefixing the substituent name with the number of the atom to which it is attached. Thus, 1,2-dimethyl-1,2-dicarboclovododecaborane(12) describes the molecule $B_{10}C_2$-$H_{10}(CH_3)_2$ containing adjacent framework carbons which are each substituted with a methyl group. This name will be abbreviated to dimethylcarborane in the text. A symbol for this species which will be used in an equation is CH_3C————CCH_3.

$$CH_3C \underset{\underset{B_{10}H_{10}}{\diagdown\;\diagup}}{\overline{O}} CCH_3$$

The nomenclature for 11-atom icosahedral fragment molecules has not yet been agreed upon formally. A numbering system for the icosahedral fragment B_9C_2 system has been proposed[5c] which designates in brackets the number of the position from which the boron atom has been removed. The carbon atom positions are also designated by number. The composi-

---

* It now appears that the official IUPAC recommendation for the designation of a closed polyhedron will be closo- rather clovo-.

tion of the molecule may be written to describe the number of carbon atoms present, the number of hydrogens, and the sum of the number of carbon and boron atoms. The charge on the species may be indicated in parentheses. For consistency with the method of assigning the smallest numbers to carbon atom positions in the $B_{10}C_2H_{12}$ series, the positions of adjacent carbon atoms will, in this article, be numbered 1 and 2. Thus, the $B_9C_2H_{12}^-$ ion with carbons adjacent in the open face of an assumed 11-particle icosahedral fragment may be named the [3]-1,2-dicarbadodecahydroundecaborate(1−) ion. It seems appropriate to designate this species in the text by its formula. The carbametallic boron hydride derivatives may also be assigned names based on this system. Thus, $(\pi\text{-}B_9C_2H_{11})_2Fe^-$ may be named the bis{[3]-1,2-dicarbaundecahydroundecaboranyl}iron(III)(1−) ion. This ion will also be designated by formula in the text.

The series of syntheses reported here presents (1) detailed procedures based on previously published work for the preparation of $B_{10}C_2H_{12}$ and some of its common *C*-substituted derivatives, (2) a procedure for conversion of a *C*-substituted derivative of the icosahedral carborane to the corresponding derivative of $B_9C_2H_{12}^-$, and (3) methods suitable for the preparation of $(\pi\text{-}B_9C_2H_{11})_2Fe^-$ and $(\pi\text{-}B_9C_2H_{11})_2Co^-$.

General Procedures

■ *Reactions of boron hydrides must be carried out with special care.* If properly conducted, the reactions reported here proceed without difficulty, but fires which do occur as the result of equipment failures or similar incidents are usually vigorous. It is recommended that all carborane preparations be carried out in areas designated for the use of hazardous materials.

■ *Caution. Solvents for decaborane must be chosen with some care. Halogenated solvents, such as carbon tetrachloride, and*
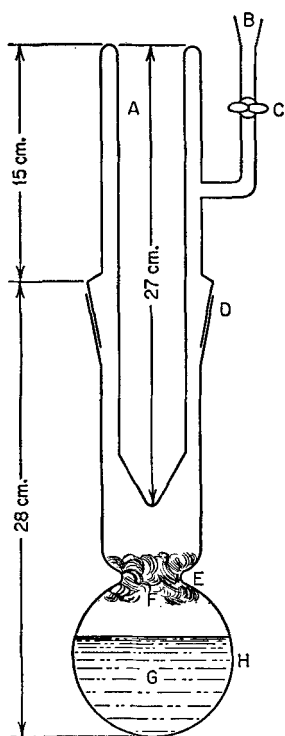
Fig. 10. *Apparatus for the sub-limation of decaborane. (A) cold finger; (B) ground-glass joint for connection to high-vacuum sys-tem; (C) high-vacuum stopcock; (D) 55/50 S.T. ground-glass joint; (E) neck constricted to about 3.5 cm. o.d.; (F) loose-fitting glass-wool plug; (G) sand and de-caborane mixture; (H) 500-ml. flask.*

some ethers, such as dioxane, form solutions which may be deto-nated by shock. Decaborane ($B_{10}H_{14}$) is a toxic material and care should be taken to avoid breathing the vapor or allowing the solid to contact the skin. Decaborane should be mechan-ically transferred in a well-ventilated hood. Towels used to wipe up inadvertent deca-borane spills should be disposed of out-of-doors.

The preparations of the un-substituted carborane ($B_{10}C_2H_{12}$) and   (bromomethyl)carborane have been carried out success-fully with unpurified decaborane (92 to 97% purity). Yields, however, are increased and the quantity of the unstable side-product   residues   is   reduced when the decaborane is of good purity. Decaborane has been purified   by   recrystallization from   heptane.[2f]   Purification by sublimation, described here, greatly reduces the exposure of personnel to the material. The sublimation apparatus (Fig. 10) is thoroughly dried before use. About 40 g. of decaborane is mixed with about 125 g. of dry Ottawa sand in the 500-ml. round-bottomed portion of the sublimation apparatus. The sand is not necessary; it has been used for more effective heat transfer. Glass wool, which serves to restrict the passage of fine dust impurities, is placed over the

mixture and a loose-fitting glass-wool plug is placed in the constricted neck of the flask. The joints are well lubricated with high-vacuum grease, and the apparatus is thoroughly evacuated in a system constructed with high-vacuum stopcocks, a liquid-nitrogen-cooled trap, a diffusion pump, and a good mechanical fore pump. (The checkers did not use a diffusion pump.) Ice is placed in the sublimator cold finger, and a silicone oil heating bath maintained at 80° is placed around the round-bottomed flask. ■ *Caution. Air must not be allowed to contact decaborane at this temperature.* The temperature should be well controlled, as *crude* decaborane near 100° becomes prone to violent decomposition with the evolution of large quantities of hydrogen. At 80°, small quantities of noncondensable gases are liberated, and pumping must be carried out continuously to prevent a pressure increase in the system and to allow the sublimation to proceed. The sand mixture must be thoroughly cooled to room temperature before the sublimation apparatus is opened to the air. With this procedure, about 20 g. of sublimed decaborane may be recovered per hour.

Several of the reactions reported in this series require only a standard three-necked flask and accessories as pictured in Fig. 11. A water-cooled stirring rod bearing reduces the quantity of solvent vapors entering the shaft and thus prolongs the effectiveness of the shaft lubricant. For carrying out reactions under a nitrogen atmosphere, it is convenient to sweep the flask with nitrogen at the outset and to maintain a slight positive pressure of nitrogen in the system during the reaction by introduction of the gas at the point indicated in Fig. 11. All the ground-glass joints should be lubricated and well secured in place.

A. 1,2-Dicarbaclovododecaborane(12)
(Carborane)

$$B_{10}H_{14} + 2(C_2H_5)_2S \xrightarrow{\text{n-propyl ether}} B_{10}H_{12}[(C_2H_5)_2S]_2 + H_2$$

$$B_{10}H_{12}[(C_2H_5)_2S]_2 + C_2H_2 \xrightarrow{\text{n-propyl ether}}$$
$$B_{10}C_2H_{12} + H_2 + 2(C_2H_5)_2S$$
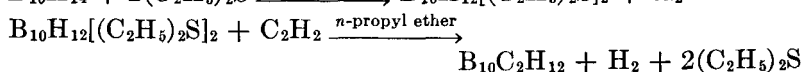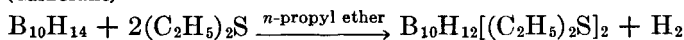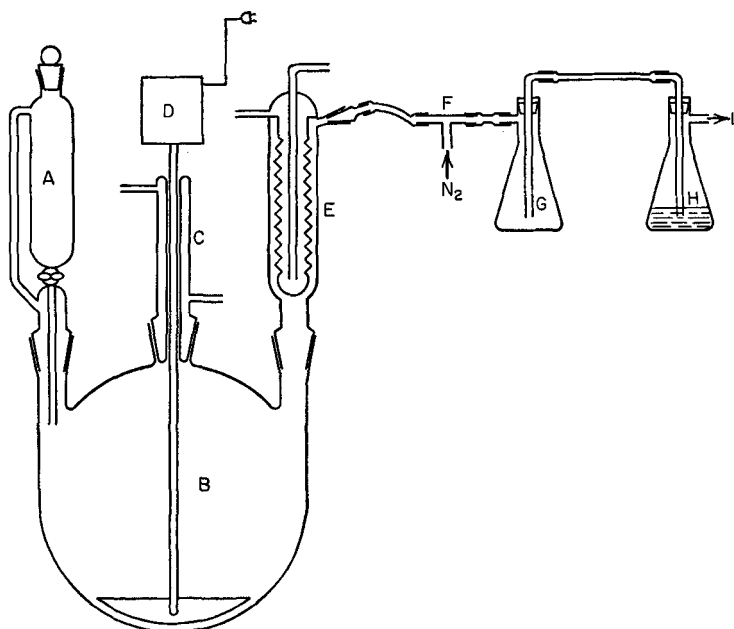
Fig. 11.   Standard equipment for reactions carried out under a nitrogen atmosphere.   (A) addition funnel; (B) standard three-necked   round-bottomed   flask;   (C)   water-cooled   bearing;   (D) spark-free stirring motor; (E) water-cooled Friederichs condenser; (F) nitrogen inlet tee; (G) trap for mineral oil inadvertently blown into   the   system;   (H)   125-ml.   mineral-oil-filled   bubbler;   (I) gas exit.

1,2-Dicarbaclovododecaborane(12) is best prepared by using a procedure based on that of Heying et al.[2a]   The two reactions are carried out consecutively without isolation of $B_{10}H_{12}[(C_2H_5)_2S]_2$.

■ *Caution.   Acetylene–air mixtures are explosive.*

Procedure

The apparatus is set up as illustrated in Fig. 12.   The use of a reaction flask and condensers fitted with ball-and-socket joints increases the flexibility of the apparatus and reduces the chance of air entering the system through improperly set joints.   The ground-glass joints are greased and held in place with well-tightened ball-and-socket–joint clamps.
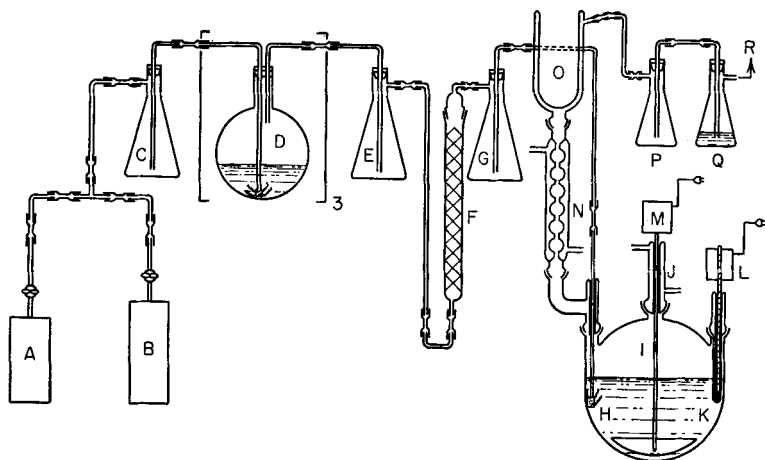
Fig. 12. Apparatus for the preparation of 1,2-dicarbaclovodo-decarborane(12) ($B_{10}C_2H_{12}$). *(A) acetylene cylinder; (B) nitrogen cylinder; (C) 1-l. trap; (D) three 500-ml. round-bottomed flasks in series, equipped with extra coarse gas dispersion tubes and filled no more than half full with concentrated sulfuric acid; (E) 1-l. trap; (F) column containing potassium hydroxide and anhydrous calcium sulfate; (G) 1-l. trap; (H) extra-coarse gas dispersion tube; (I) 1-l. round-bottomed flask fitted with 35/25 standard socket joints; (J) water-cooled stirrer bearing; (K) thermometer well; (L) automatic temperature-control device; (M) spark-free stirring motor; (N) water-cooled condenser; (O) Dry Ice–cooled condenser; (P) 125-ml. trap; (Q) 125-ml. mineral-oil-filled bubbler; (R) gas exit port.*

The acetylene purification train and exit gas train are interconnected with rubber or Tygon tubing. The greased ball-and-socket joints are tightly clamped together.

It is necessary that the acetylene entering the reaction flask be of high purity.* The acetylene purification train illustrated in Fig. 12 consists of three 500-ml. round-bottomed traps, each containing 250 ml. of concentrated sulfuric acid, followed by a 3-ft. column containing potassium hydroxide and a drying agent such as anhydrous calcium sulfate (Drierite). Empty flasks

---

* The acetylene used in this preparation was of 99.6% purity, obtained from the Matheson Company. The authors have encountered experimental difficulties with the use of a welding-grade acetylene, although the checkers have used this grade of acetylene routinely without incident. Since the specifications for the welding grade are not very restrictive, the high-purity grade is recommended.

are provided as indicated to serve as traps for liquids which may inadvertently back up through the system. An extra trap is included between the flasks containing sulfuric acid and the potassium hydroxide column. This serves to collect sulfuric acid if it should foam and be carried through the system during the passage of acetylene. The system is thoroughly dried and flushed with nitrogen before the reagents are introduced.

Sublimed decaborane, 100 g. (0.816 mol), is dissolved in 200 ml. of *n*-propyl ether freshly distilled from sodium benzophenone ketyl.*·† The solution is placed in the 1-l. three-necked flask illustrated in Fig. 12. Diethyl sulfide, 200 ml. (1.86 mol), dried over a molecular sieve 4A, is added in one portion. The solution is stirred for 3 hours at 40°. The temperature is then raised to 65 to 67°; it is important to keep the temperature below 70° at this stage in order to ensure high yields of carborane. The reaction is allowed to proceed at this temperature for 2 hours. The flask is then heated to a controlled temperature of 85 ± 2°, and about 7 mols of acetylene is passed through the purification train and reaction vessel over a period of 35 hours. On completion of the reaction, the solution should ideally be a pale yellow to light orange color. If it is deep orange or red, a low yield of product will generally result, and the fire hazard experienced during the hot-water treatment in the work-up is increased. Possible causes of an errant reaction are (1) overheating at any step of the reaction; (2) air leakage into the system; and (3) impure acetylene reaching the reaction mixture. If the solution is dark red or brown, as opposed to deep orange or red, it is best to discard the reaction mixture with minimum exposure to personnel.

After cooling, the reaction mixture is transferred to a 1-l.

---

* Sufficient sodium and benzophenone are used to produce a permanent deep blue color when the solution is refluxed under nitrogen; e.g., for 400 ml. of crude *n*-propyl ether, 10 g. of benzophenone and 15 g. of sodium are usually sufficient. The ether is then distilled under a nitrogen atmosphere.

† The checkers report that they normally use 34 ml. of *n*-propyl ether and 80 ml. of diethyl sulfide per 100 g. of decaborane.

round-bottomed single-necked flask, and the diethyl sulfide–*n*-propyl ether solvent mixture is removed and collected in a Dry Ice trap by using a rotary evaporator equipped with a mechanical vacuum pump and heat from a steam bath. The product (a light brown semisolid) is dissolved in 150 ml. of benzene and is added very slowly (2 hours) from an addition funnel to a solution of 150 ml. of acetone, 400 ml. of methanol, and 150 ml. of concentrated hydrochloric acid in a 3-l. three-necked flask fitted with a stirrer, addition funnel, condenser, and nitrogen inlet. The apparatus is set up as pictured in Fig. 11, except that nitrogen is introduced through the addition funnel so that it sweeps through the entire apparatus. This procedure converts reactive by-products to hydrogen and borates. The reaction is exothermic and the solution may reach the reflux temperature. There is an induction period for the decomposition reaction, and the initial rate of addition of impure carborane should not be too rapid. After stirring until no more gas is evolved (about 24 hours), the resulting solution is placed in a 1-l. addition funnel and added slowly (15 minutes) to 3 gallons of water maintained at a temperature of 95 to 100°. Additional decomposition of by-products occurs, hydrochloric acid and acetone are extracted into the water, and benzene is boiled off. Large quantities of unpleasant vapors are evolved and *this step should be performed in a well-ventilated area designed for the handling of hazardous materials, or out-of-doors. If the product contains an exceptional amount of impurities, the hot-water mixture may inflame.* After 10 minutes of additional stirring, the mixture is cooled and the crude carborane (whose texture and color resemble those of well-done scrambled eggs) is skimmed from the top.

The crude carborane is dissolved in 500 ml. of methanol in a 2-l. Erlenmeyer flask. A cold solution of 50 g. of potassium hydroxide in 75 ml. of water is added rapidly. The mixture is agitated for precisely 3 minutes. The reaction is exothermic and it may be necessary to cool the solution in ice water. The

solution then is poured into 11.4 l. of ice water, stirred for 10 minutes, and filtered. After drying in a vacuum over phosphorus(V) oxide, the crude product is mixed with 30 g. of anhydrous calcium chloride (4 to 40 mesh) and placed in a thimble of a Soxhlet extraction apparatus. The mixture is extracted with 500 ml. of heptane for 20 hours. Carborane separates as a white solid and is isolated by filtration (m.p. 320°). The volume of heptane is reduced to 50 ml. by using a rotary evaporator with gentle heat from a steam bath. On cooling, a second crop of carborane is obtained. The combined yield after drying is 85 g. (72%; checkers report 70%). An additional 3 or 4 g. of impure material may be obtained by evaporating the heptane solution to dryness. In multiple runs, this impure material may be added to the Soxhlet thimble along with the new preparation.

Properties

Carborane, $B_{10}C_2H_{12}$, is quite soluble in aromatic solvents and is sparingly soluble in aliphatic solvents. The infrared spectrum has been previously reported.[2b] The proton nuclear magnetic resonance spectrum of a chloroform-d_3 solution of carborane contains a broad CH resonance at 6.46 τ.

B. 1-Bromomethyl-1,2-dicarbaclovododecaborane(12)
[(Bromomethyl)carborane]

$$B_{10}H_{14} + 2CH_3CN \xrightarrow{C_6H_6} B_{10}H_{12}(CH_3CN)_2 + H_2$$

$$B_{10}H_{12}(CH_3CN)_2 + HC{\equiv}CCH_2Br \xrightarrow{C_6H_6}$$
$$HC{\underset{\underset{B_{10}H_{10}}{\diagdown\!\! O\!\!\diagup}}{\rule{2cm}{0.4pt}}}CCH_2Br + H_2 + 2CH_3CN$$
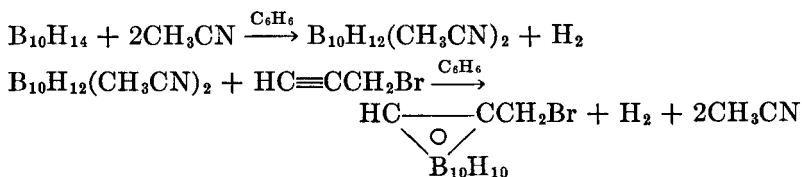
(Bromomethyl)carborane[2a,f] [1-bromomethyl-1,2-dicarbaclovododecaborane(12)] may be prepared in high yield with standard laboratory equipment. It is a convenient starting material

for the preparations of methylcarborane and dimethylcarborane, also reported in this series.

The $B_{10}H_{12}(CH_3CN)_2$[6] need not be isolated, and the two reactions may be carried out consecutively in one flask.[2a]

Procedure

The quantities used in this description are decaborane 49.9 g. (0.408 mol), acetonitrile 32 ml. (0.61 mol), propargyl bromide (3-bromopropyne) 33 ml. (0.42 mol), and benzene 350 ml. The decaborane is sublimed before use. Acetonitrile (Matheson, Coleman and Bell, industrial grade), and benzene* (reagent grade) are each refluxed for about one hour with calcium hydride and are then distilled from calcium hydride under an atmosphere of nitrogen. Propargyl bromide is used as supplied.† The equipment consists of a 1-l. three-necked flask fitted with a ground-glass stopper, mechanical stirrer, condenser, and a nitrogen inlet. The apparatus resembles that of Fig. 11, except that an addition funnel is not used during the initial part of the procedure. A steady flow of nitrogen into the apparatus at point F is maintained throughout the reaction.

The dry nitrogen-filled flask is charged with the decaborane, acetonitrile, and benzene. The spare flask neck is stoppered, and the stirred solution is heated at the reflux temperature for 2 hours before addition of the acetylene is started. The $B_{10}H_{12}(CH_3CN)_2$ formed during this step has limited solubility in benzene and a portion of it may precipitate. The propargyl bromide is added in three separate portions in the following way. A nitrogen-filled addition funnel containing one-third (11 ml.)

---

* The checkers did not employ benzene as a solvent. Acetonitrile was used in excess, 3 mols of acetonitrile per mol of decaborane.

† Farchan Research Laboratories. Propargyl bromide when pure is a colorless liquid. If it should turn brown during storage, the acetylene may be evaporated from the polymer by use of a rotary evaporator equipped with a Dry Ice–cooled trap and a mechanical vacuum pump. The acetylene is not heated during this distillation.

of the propargyl bromide is mounted in the spare neck of the flask, and the propargyl bromide is added to the refluxing solution dropwise over a one-hour period.   The reaction becomes noticeably exothermic on addition of propargyl bromide, and care must be taken to control the addition rate.   Only one-third of the full charge of acetylene is placed in the addition funnel at the outset so that the danger of an uncontrolled addition is reduced.   The funnel is removed, the flask restoppered, and the solution maintained at the reflux temperature for $1\frac{1}{2}$ hours before the next portion is added.   After all the acetylene has been added in this manner, the stirred solution is maintained at the reflux temperature for an additional 35 hours.

The solution is cooled to room temperature and is washed with a few milliliters of benzene into a single-necked flask.   The solvent is removed with a rotary evaporator connected to a water aspirator vacuum; gentle heat is supplied from a steam bath.   The residue is cooled to room temperature before air is admitted.   About 200 ml. of hexane is added and stirred with the residue to extract most of the carborane.   The brownish tar which remains undissolved is allowed to settle and the solution is decanted.   A second extraction of the tar with 40 ml. of hexane converts the residue to a solid which is removed by filtration.   The solid is washed on the filter with an additional 40 ml. of hexane.   The combined hexane extracts are filtered and then washed in a separatory funnel with four 100-ml. portions of a chilled aqueous 10% sodium hydroxide solution, followed by four 100-ml. portions of water.*   After the yellow hexane solution has been dried over anhydrous magnesium sulfate and filtered, the solvent is removed by use of a rotary evaporator connected to a water aspirator.   The carborane is washed with a small amount of pentane into a 300-ml. single-necked flask which is attached to an alembic column as pictured in Fig. 13.

---

* The aqueous extracts should be quickly flushed down the drain.   The solid residue must not come in contact with basic water, nor should it be left in the laboratory.   It is best disposed of out-of-doors.

Glass wool is placed in the solution, in the neck of the alembic distillation column, and at the top of the column to inhibit bumping during the distillation. The distilling flask, collection flask, and column are continuously evacuated with a high-vacuum system. When the bulk of the pentane and residual hexane have distilled away,* the temperature of a silicone oil bath surrounding the distillation flask is raised from room temperature to 125° over about a one-hour period. When the distillation rate diminishes appreciably, the temperature is slowly raised to 150° and maintained there until no more liquid is obtained.† The distillation flask is cooled to room temperature before air is admitted to the system. The distilled product weighs 86.5 g. (89% yield; checkers report 89%‡) and

Fig. 13. Water-cooled alembic column for distillation of (bromomethyl)carborane. (A) ground-glass joint for connection to high-vacuum system; (B) loose-fitting glass-wool plug; (C) water jacket; (D) loose-fitting glass-wool plug; (E) receiver; (F) distilling flask.

melts at 32 to 32.5°. In this state of purity, (bromomethyl)-carborane is suitable for most uses, but it may be further purified by crystallization from pentane or methanol. For example, crystals obtained by chilling a solution of 86.5 g. of the car-

---

* A clogged solvent trap resulting in loss of vacuum should be guarded against.

† Depending on the temperature of the tap water and the rate of flow, the product may tend to solidify in the distillation head.

‡ The checkers report that they have routinely run this reaction by a slightly different procedure, bypassed the chemical purification and directly distilled with a Claisen head and an air-cooled condenser.

borane dissolved in 50 ml. of pentane to −8° weighed 58.6 g. after distillation through the alembic column and melted at 33 to 33.5°. This corresponds to 59% recovery in the first crop.

Properties

(Bromomethyl)carborane is soluble in common organic solvents. It may be stored and handled in air without difficulty. The infrared spectrum (Nujol mull) contains major absorption bands at 3.28 (w), 3.87 (vₛ), 8.01 (s), 8.19 (w), 8.40 (w), 8.91 (m), 9.40 (m), 9.83 (m), 9.96 (w), 10.87 (w), 10.69 (w), 10.90 (w), 12.17 (w), 12.78 (w), 13.81 (s), 14.59 (w), and 14.97 (w) μ. The proton nuclear magnetic resonance spectrum of the carborane in carbon tetrachloride solution shows the methylene resonance at 6.10 τ.

C. 1-Methyl-1,2-dicarbaclovododecaborane(12)

(Methylcarborane)

$$HC\underset{\diagdown O \diagup}{\overline{\hspace{1.5em}}}CCH_2Br + Mg \xrightarrow[3\ hours]{(C_2H_5)_2O} HC\underset{\diagdown O \diagup}{\overline{\hspace{1.5em}}}CCH_2MgBr$$
$$\overset{B_{10}H_{10}}{} \qquad\qquad \overset{B_{10}H_{10}}{}$$

$$HC\underset{\diagdown O \diagup}{\overline{\hspace{1.5em}}}CCH_2MgBr + H_2O \xrightarrow{(C_2H_5)_2O} HC\underset{\diagdown O \diagup}{\overline{\hspace{1.5em}}}CCH_3 + MgBrOH$$
$$\overset{B_{10}H_{10}}{} \qquad\qquad\qquad \overset{B_{10}H_{10}}{}$$
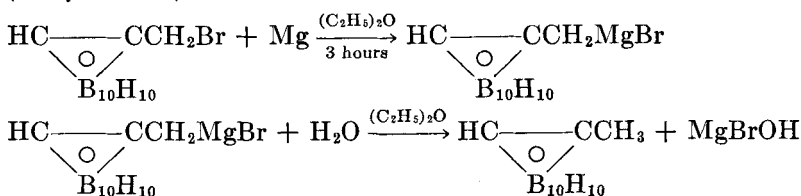
Methylcarborane [1-methyl-1,2-dicarbaclovododecaborane-(12)] may be prepared by hydrolysis of the Grignard reagent formed from the reaction of (bromomethyl)carborane with magnesium in the presence of diethyl ether.[2c,g,h]

Procedure

The reaction is carried out in a 1-l. three-necked flask equipped with a mechanical stirrer, reflux condenser, addition funnel, and nitrogen inlet (Fig. 11). A nitrogen atmosphere is strictly maintained throughout the course of the reaction. Clean magnesium chips, 6.1 g. (0.25 mol, 20% excess), and about

50 ml. of anhydrous diethyl ether (Mallinckrodt anhydrous ether, analytical reagent grade) are added to the thoroughly dried nitrogen-flushed flask. A solution of 50 g. (0.21 mol) of distilled (bromomethyl)carborane dissolved in 300 ml. of anhydrous diethyl ether is introduced into the addition funnel under a stream of nitrogen. The mixture of magnesium and ether is warmed to about 30°, and the Grignard reaction is initiated by rapid addition of about 50 ml. of the (bromomethyl)carborane solution to the stirred contents of the flask. (The checkers found it necessary to add an iodine crystal to start the reaction.) The addition of the carborane solution is continued dropwise with heating until the reflux temperature is reached. The heating mantle is then removed and the addition of the carborane solution is continued at a rate sufficient to maintain the reflux temperature. The total time of addition of the (bromomethyl)carborane solution is about 35 minutes. Upon completion of the addition, the stirred reaction mixture is again heated so that the reflux temperature is maintained. After 2½ hours, the solution is allowed to cool to room temperature and is decanted from the excess magnesium into a 2-l. beaker half filled with crushed ice. Two 50-ml. portions of diethyl ether are used to wash the remaining (carboranyl)magnesium bromide into the ice mixture. Hydrochloric acid (3 N) sufficient to dissolve the magnesium salts is added to the stirred ice mixture. The ether and water layers are separated, and the water layer is extracted three times with 75-ml. portions of diethyl ether. After the combined ether extracts are dried over anhydrous magnesium sulfate, the ether is removed by use of a rotary evaporator. Crystallization is accomplished by dissolving the product in 90 ml. of hot methanol and allowing the solution to cool slowly to 0°. Two additional crops may be obtained from the mother liquor. A portion of the methanol is removed, and water is added to the heated solution until it becomes cloudy. The solution is then allowed to cool to 0°. The combined crops are dried in a vacuum. The yield of

product is 31 g. (93%; checkers report 93%). The methyl-carborane purified in this fashion melts at 211 to 213°.

Properties

Methylcarborane is an air-stable, white crystalline solid which is soluble in common organic solvents. The infrared spectrum (Nujol mull) contains major absorption bands at 3.90 (s), 8.83 (w), 9.12 (w), 9.69 (w), 9.83 (w), 10.03 (w), and 13.85 (s) μ. The proton nuclear magnetic resonance spectrum of a carbon tetrachloride solution of methylcarborane contains a broad —CH resonance of intensity 1 at 6.52 τ and a —CH$_3$ resonance of intensity 3 at 8.02 τ.

D. 1,2-Dimethyl-1,2-dicarbaclovododecaborane(12)
(Dimethylcarborane)

$$\text{HC}\underset{\diagdown\underset{B_{10}H_{10}}{O}\diagup}{\text{———}}\text{CCH}_2\text{Br} + \text{Mg} \xrightarrow{\text{THF}} \text{BrMgC}\underset{\diagdown\underset{B_{10}H_{10}}{O}\diagup}{\text{———}}\text{CCH}_3$$

$$\text{BrMgC}\underset{\diagdown\underset{B_{10}H_{10}}{O}\diagup}{\text{———}}\text{CCH}_3 + \text{CH}_3\text{I} \xrightarrow{\text{THF}} \text{CH}_3\text{C}\underset{\diagdown\underset{B_{10}H_{10}}{O}\diagup}{\text{———}}\text{CCH}_3 + \text{MgBrI}$$
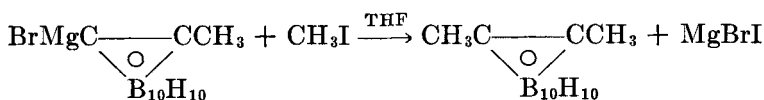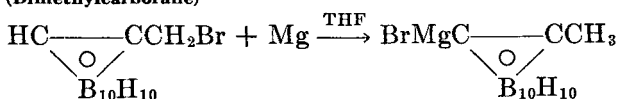
Dimethylcarborane [1,2-dimethyl-1,2-dicarbaclovododecaborane(12)][29] may be prepared by methylation of the Grignard reagent formed from the reaction of (bromomethyl)carborane with magnesium in the presence of tetrahydrofuran (THF).

Procedure

Tetrahydrofuran is distilled before use, in a nitrogen atmosphere, from lithium tetrahydroaluminate.* A 1-l. three-necked flask equipped with a mechanical stirrer, reflux condenser,

---

* The use of lithium tetrahydroaluminate for drying ethers can lead to explosions. It is essential that the distillation not be continued to a point where the volume of remaining solvent is low. The distillation must be effected in an inert atmosphere (nitrogen or argon).

addition funnel, and nitrogen inlet (Fig. 11) is thoroughly dried and flushed with nitrogen. The nitrogen atmosphere is strictly maintained throughout the course of the reaction. Into the flask is placed 6.1 g. (0.25 mol, 20% excess) of clean magnesium chips and about 50 ml. of tetrahydrofuran. Distilled (bromomethyl)carborane, 50 g. (0.21 mol), dissolved in 250 ml. of tetrahydrofuran is placed in the addition funnel under a stream of nitrogen. The rapid addition of about 50 ml. of the (bromomethyl)carborane solution to the stirred magnesium suspension is usually sufficient to cause initiation of the Grignard reaction. It may be necessary to heat the reaction mixture if the initial addition does not generate a self-sustaining reaction. Once the reaction has commenced, the rate of addition is controlled so that the heat of reaction is just sufficient to maintain the reflux temperature.

After the addition is complete (about 30 minutes), the flask is heated to maintain the reflux temperature for an additional $2\frac{1}{2}$ hours. The reaction mixture is allowed to cool to room temperature, and the solution is rapidly decanted from the excess magnesium into a second 1-l. three-necked flask equipped with a mechanical stirrer, addition funnel, Dry Ice condenser, and nitrogen inlet. A rapid stream of nitrogen is maintained through both flasks during the transfer. Methyl iodide, 48 g. (0.34 mol, 60% excess), is placed in the addition funnel under a stream of nitrogen and is added dropwise to the solution. When the solution begins to warm, the condenser is charged with a Dry Ice–isopropyl alcohol slurry. The addition rate of the methyl iodide is such that the reflux temperature is maintained. The addition takes about 30 minutes.

After the addition of methyl iodide, the solution is heated to the reflux temperature for an additional 3 hours. The reaction mixture is allowed to cool to room temperature and it is slowly added with stirring to about 400 ml. of chilled dilute (1 N) hydrochloric acid. The mixture is placed in a separatory funnel, and the carborane is extracted first with 250 ml. of diethyl ether

and then with three 75-ml. portions of diethyl ether. The combined ether extracts are washed once with 75 ml. of water, and the solution is dried over magnesium sulfate. The ether is removed by means of a rotary evaporator, and the product is crystallized from hot 95% ethanol. Two additional crops may be obtained from the mother liquor. A portion of the alcohol is removed, and water is added to the heated solution until it becomes cloudy. The solution is then allowed to cool to 0°. The crystallized material is dried in a vacuum. The yield of the product (m.p. 259 to 261°) is 33 g. (91%; checkers report 89%).

Properties

Dimethylcarborane is an air-stable, white, crystalline solid. It is soluble in common organic solvents. The infrared spectrum of the material in a Nujol mull contains major absorption bands at 3.90 (s), 8.40 (w), 9.82 (m), 10.55 (w), 10.90 (w), 12.71 (w), and 13.75 (m) μ. The proton nuclear magnetic resonance spectrum exhibits a —CH_3 resonance at 7.98 τ.

E. 1,2-Dimethyl-[3]-1,2-dicarbadodecahydroundecaborate(1—) Ion
[$B_9C_2H_{10}(CH_3)_2{}^-$]

$$B_{10}C_2H_{10}(CH_3)_2 + KOH + 3C_2H_5OH \xrightarrow{C_2H_5OH}$$
$$KB_9C_2H_{10}(CH_3)_2 + B(OC_2H_5)_3 + H_2 + H_2O$$
$$KB_9C_2H_{10}(CH_3)_2 + (CH_3)_3NHCl \xrightarrow{H_2O}$$
$$(CH_3)_3NHB_9C_2H_{10}(CH_3)_2 + KCl$$
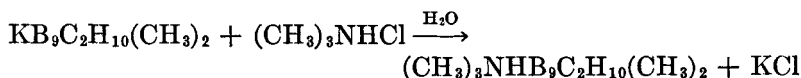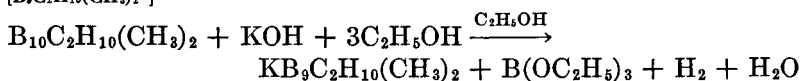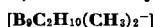
The selective basic degradation of 1,2-dicarbaclovododecarborane(12) and its *C*-methyl and *C*-phenyl derivatives has been recently reported.[3] The ethanolic potassium hydroxide degradation of *C,C'*-dimethyl-1,2-dicarbaclovododecaborane(12) and the isolation of the trimethylammonium salt of the resulting $B_9C_2H_{10}(CH_3)_2{}^-$ anion are described here as an illustration of this general reaction. The properties of the trimethylam-

monium salt of the $B_9C_2H_{12}^-$ anion and those of the tetra-
methylammonium salts of the $B_9C_2H_{12}^-$ and $B_9C_2H_{10}(CH_3)_2^-$
anions, obtained by analogous procedures, are also given.

Procedure

The reaction is carried out in a 500-ml. three-necked flask
equipped with a reflux condenser, mechanical stirrer, heating
mantle, and nitrogen inlet. The equipment is similar to that
pictured in Fig. 11, except that an addition funnel is not required.
In the reaction flask 20 g. (0.36 mol, 100% excess) of potassium
hydroxide is dissolved in 300 ml. of absolute ethanol. The
spare neck is closed with a ground-glass stopper, and the solu-
tion is stirred until it reaches room temperature. Addition of
the carborane to the warm basic solution may result in an initial
vigorous reaction. To this solution is added 30.0 g. (0.175 mol)
of solid dimethylcarborane. The solution is stirred for one
hour at room temperature and is then heated at the reflux
temperature for 14 hours or until hydrogen evolution has
stopped.

The reaction flask is allowed to cool and the condenser,
stirrer, and nitrogen inlet are removed. To the solution is
added 100 ml. of absolute ethanol, and a brisk stream of carbon
dioxide is passed through the solution to precipitate the excess
potassium hydroxide as potassium carbonate. Sufficient carbon
dioxide to precipitate the excess potassium hydroxide is con-
veniently obtained from about 150 g. of Dry Ice. The Dry
Ice is powdered and placed in a stoppered 500-ml. filter flask
with a line leading into the reaction solution. The insoluble
potassium carbonate is filtered and washed with four 50-ml.
portions of absolute ethanol. The combined filtrate and
washings are evaporated to dryness on a rotary evaporator
using a water aspirator vacuum and heat from a steam bath.
This yields a solid or semisolid cake containing some residual
potassium carbonate.

At this point the hygroscopic potassium salt may be isolated and dried,* or, more conveniently, the potassium salt may be dissolved in water and the carborane anion precipitated with one of a variety of large cations, such as the rubidium, cesium, tetramethylammonium, or trimethylammonium ions. The trimethylammonium salt of the carborane anion is useful because it is readily purified by recrystallization from water and may be easily converted in solution to salts containing other counterions.†

The $KB_9C_2H_{10}(CH_3)_2$ recovered from the ethanol solution is dissolved in 150 ml. of water, and a solution of 22 g. of trimethylammonium chloride in 100 ml. of water is added slowly with vigorous stirring. The precipitated salt is isolated by filtration, washed once with 50 ml. of cold water, and dried in vacuum over phosphorus(V) oxide. The yield of $(CH_3)_3NHB_9C_2H_{10}$-$(CH_3)_2$ is 37.8 g. (98%). To purify the salt by crystallization, a boiling solution of 38 g. of the salt in 2 l. of water is allowed to cool slowly to 0°. Eighty per cent of the material is recovered in the first crop. Successive crops of the trimethylammonium salt may be obtained, or the anion may be recovered as the less soluble tetramethylammonium salt by addition of an aqueous solution of tetramethylammonium chloride to the mother liquor. The tetramethylammonium salt may be recrystallized from an ethanol-water solution.

---

* The $KB_9C_2H_{10}(CH_3)_2$ is dissolved in ether, and the solution is filtered to remove residual potassium carbonate. The ether is removed and the resulting solid or semisolid is placed with about 700 ml. of dry benzene in a 1-l. three-necked flask equipped with a mechanical stirrer, an efficient distillation column, and a nitrogen inlet. The solution is stirred under a nitrogen atmosphere and the residual ether, alcohol, and water, as the benzene-water azeotrope, are distilled off. As these components are removed, the salt precipitates from the solution. Stirring prevents the formation of hot spots at points of deposition of the solid. The suspension is allowed to cool and the salt is isolated by filtration under a stream of nitrogen. If it is desired, further purification may be accomplished by extraction of the dried potassium salt with benzene from a Soxhlet thimble into a receiver equipped with a mechanical stirrer. The potassium salt may be mixed with anhydrous calcium chloride in the thimble to aid in maintaining anhydrous conditions.

† See the section on carbametallic derivatives in this series.

Properties

All these salts are white crystalline, air-stable, nonhygroscopic solids. The trimethylammonium salts, $(CH_3)_3NHB_9$-$C_2H_{10}(CH_3)_2$ and $(CH_3)_3NHB_9C_2H_{12}$, are soluble in acetone, methanol, and hot water; insoluble in benzene and other nonpolar solvents. The tetramethylammonium salts, $(CH_3)_4$-$NB_9C_2H_{10}(CH_3)_2$ and $(CH_3)_4NB_9C_2H_{12}$, are soluble in acetone, moderately soluble in boiling ethanol, and insoluble in water and benzene. The infrared spectra of the salts (Nujol mulls) contain major absorption bands for $(CH_3)_3NHB_9C_2H_{10}(CH_3)_2$ at 3.15 (m), 3.97 (s), 7.05 (w), 7.95 (w), 8.3 (w), 9.75 (m), 10.22 (m), 11.00 (w), 12.25 (w), 13.25 (w), 13.55 (w), and 14.7 (w) μ; $(CH_3)_4NB_9C_2H_{10}(CH_3)_2$ at 3.98 (s), 7.08 (w), 7.28 (m), 7.78 (w), 9.35 (w), 9.77 (m), 10.51 (s), 11.09 (w), and 11.82 (w) μ; $(CH_3)_3NHB_9C_2H_{12}$ at 3.22 (s), 3.99 (s), 7.10 (m), 7.99 (w), 8.48 (w), 9.18 (w), 9.71 (m), 10.24 (s), 11.00 (w), 11.45 (w), and 12.31 (w) μ; $(CH_3)_4NH_9C_2H_{12}$ at 4.00 (s), 7.06 (m), 7.27 (m), 7.78 (w), 8.50 (w), 9.18 (w), 9.72 (m), 10.20 (w), 10.50 (s), 10.73 (w), 11.37 (w), and 13.81 (w) μ.

F. Bis{[3]-1,2-dicarbaundecahydroundecaboranyl}iron(III)(1−) and Bis{[3]-1,2-dicarbaundecahydroundecaboranyl}cobalt(III)(1−) Ions

$[(\pi\text{-}B_9C_2H_{11})_2Fe]^-$ and $[(\pi\text{-}B_9C_2H_{11})_2Co]^-$

The [3]-1,2-dicarbaundecahydroundecaborate(2−) ion, B_9-$C_2H_{11}{}^{2-}$, has been found to form sandwich compounds with iron[5a] and cobalt.[5d] Two synthetic procedures, one in nonaqueous and the other in aqueous media, have been developed. The procedure in nonaqueous media is general, whereas that in aqueous media can be used only to prepare complexes which are not decomposed by base.* Both methods of preparation are

---

* These sandwich complexes have been prepared: $[(\pi\text{-}B_9C_2H_{11})_2M]^-$, $[(\pi\text{-}B_9C_2-H_{10}C_6H_5)_2M]^-$, $[(\pi\text{-}B_9C_2H_9(CH_3)_2)_2M]^-$ (M = Fe, Co; substituents are on the carbon atoms). The unsubstituted complexes of iron and cobalt and the phenyl-substituted complex of cobalt are stable toward base and may be prepared by either

detailed for $[(\pi\text{-}B_9C_2H_{11})_2Fe]^-$ but only the aqueous method is given for $[(\pi\text{-}B_9C_2H_{11})_2Co]^-$.

$(CH_3)_4N[(\pi\text{-}B_9C_2H_{11})_2Fe]$
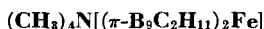
1. Preparation in Nonaqueous Media

$$Fe + 2FeCl_3 \xrightarrow{\text{THF}} 3FeCl_2$$

$$(CH_3)_3NHB_9C_2H_{12} + 2NaH \xrightarrow{\text{THF}} (CH_3)_3N + 2H_2 + Na_2B_9C_2H_{11}$$

$$2Na_2B_9C_2H_{11} + FeCl_2 \xrightarrow{\text{THF}} Na_2[(\pi\text{-}B_9C_2H_{11})_2Fe] + 2NaCl$$

$$Na_2[(\pi\text{-}B_9C_2H_{11})_2Fe] \xrightarrow{O_2,\ \text{THF}} Na[(\pi\text{-}B_9C_2H_{11})_2Fe]$$

$$Na[(\pi\text{-}B_9C_2H_{11})_2Fe] + (CH_3)_4NCl \xrightarrow{H_2O}$$
$$(CH_3)_4N[(\pi\text{-}B_9C_2H_{11})_2Fe] + NaCl$$
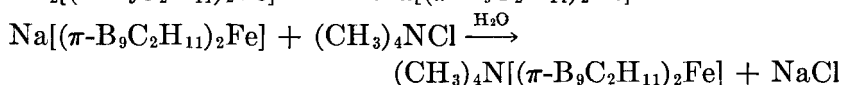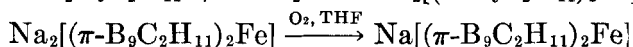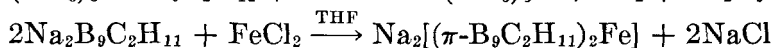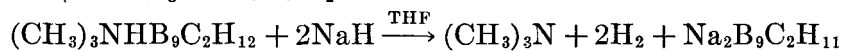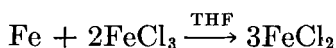
Procedure

The iron(II) chloride[7] is prepared from 1.5 g. (0.0268 mol) of iron powder (hydrogen-reduced, 100-mesh), 6.0 g. (0.370 mol) of anhydrous sublimed iron(III) chloride (Matheson, Coleman and Bell, reagent-grade), and 150 ml. of tetrahydrofuran (THF) freshly distilled under nitrogen from lithium tetrahydroaluminate or preferably calcium hydride.

The $Na_2B_9C_2H_{11}$ is prepared simultaneously under nitrogen in a 300-ml. three-necked round-bottomed flask equipped with a condenser, addition funnel, and a magnetic stirring bar. Sodium hydride, 1.51 g. (0.063 mol) (2.70 g. of a 56% dispersion in mineral oil), is washed twice with 30 ml. of THF to remove the mineral oil* and then is immediately washed with a total of

procedure. The phenyl- and dimethyl-substituted complexes of iron and the dimethyl complex of cobalt will not form in the strongly basic media of the aqueous preparation and the nonaqueous method must be employed in the preparation of these compounds.

* The sodium hydride dispersion is washed in the following manner. Into a beaker containing the sodium hydride–mineral oil dispersion, 30 ml. of THF is poured, the sodium hydride allowed to settle, and the THF decanted into a clean beaker. This procedure is repeated to complete the removal of mineral oil. The sodium hydride in the THF wash solutions may be destroyed by careful addition of isopropyl or butyl alcohol. ■ *Caution. Sodium hydride, when free from mineral oil, readily inflames in air on exposure to moisture.*

90 ml. of THF into the reaction flask. A solution of 5.0 g. (0.0259 mol) of $(CH_3)_3NHB_9C_2H_{12}$ dissolved in 75 ml. of THF is placed in the addition funnel and is added to the sodium hydride. Trimethylamine and hydrogen are briskly evolved and care must be taken during this addition or overflow due to foaming occurs. The reaction mixture is stirred at the reflux temperature (65°) under nitrogen for 3 hours or until no more gas is evolved. Although trimethylamine boils at 3°, it is not completely removed from the THF solution. Complete removal is achieved by passing a stream of nitrogen through one neck of the flask, over the solution, and out through the condenser during the final 30 minutes of the 3-hour reflux period.

After the reactions are complete, stirring is stopped, and both solutions are allowed to cool to room temperature. When the excess sodium hydride settles, the THF solution of Na_2B_9-C_2H_{11} is decanted into the iron(II) chloride–THF mixture under a flow of nitrogen. The solution immediately becomes very dark red. Slight heating may occur on mixing of the two solutions. The resulting mixture is stirred for one hour at room temperature under nitrogen.

When the reaction has been carried out with rigorous exclusion of oxygen, the species present in solution is $Na_2[(\pi\text{-}B_9C_2H_{11})_2Fe]$, which is readily converted to the oxidized form, $Na[(\pi\text{-}B_9C_2\text{-}H_{11})_2Fe]$ by stirring the reaction solution for 45 minutes in the presence of air. The reduced form has a pink-red color, whereas the oxidized form is Burgundy-red in color.

After oxidation is complete, the reaction solution is recovered by decantation into a 500-ml. round-bottomed flask; a magnet is used to retain the unreacted iron. The solvent is completely removed from the reaction mixture at ambient temperature using a rotary evaporator and a mechanical pump vacuum. The dark red crystalline residue is dissolved with agitation in 250 ml. of water. The solution is filtered through a layer of Celite (diatomaceous earth) and the residue in the filter funnel is washed with three 30-ml. portions of water.

The filtrate is washed in a separatory funnel with two 150-ml. portions of pentane and the pentane extract is discarded. The aqueous layer is again filtered through Celite, and $(CH_3)_4$-$N[(\pi\text{-}B_9C_2H_{11})_2Fe]$ is precipitated from the filtrate with 20 ml. of 50% aqueous tetramethylammonium chloride. The pinkish-red solid is collected by filtration and is washed three times with 30-ml. portions of water. In a 500-ml., round-bottomed flask, the product is dissolved in a mixture of 200 ml. of acetone and 80 ml. of water. The solvent is removed without heating using a rotary evaporator and water aspirator vacuum. The product separates from the solution as fine dark red plates. When the supernatant solution is still light red, the first crop of product is collected by filtration. The recovery of the product at this point is 3.12 g. (61%; the checkers report 54%). This material is sufficiently pure for most synthetic purposes. Successive crops of lighter-colored product, which are contaminated with unconverted $(CH_3)_4NB_9C_2H_{12}$, are obtained by further removal of solvent. The total yield of crude product is 3.72 g. (73%). Purification may be accomplished by alternate recrystallization from acetone–water and acetone–hexane: The solvent is allowed to evaporate slowly from these solutions at ambient conditions until crystallization occurs.

2. Preparation in Aqueous Media

$$(CH_3)_3NHB_9C_2H_{12} + NaOH \xrightarrow{H_2O} (CH_3)_3N + H_2O$$
$$+ NaB_9C_2H_{12}$$
$$NaB_9C_2H_{12} + NaOH \overset{H_2O}{\rightleftharpoons} Na_2B_9C_2H_{11} + H_2O$$
$$2Na_2B_9C_2H_{11} + FeCl_2 \xrightarrow{H_2O} Na_2[(\pi\text{-}B_9C_2H_{11})_2Fe] + 2NaCl$$
$$Na_2[(\pi\text{-}B_9C_2H_{11})_2Fe] \xrightarrow[H^+,\ Fe^{3+}]{O_2} Na[(\pi\text{-}B_9C_2H_{11})_2Fe]$$
$$Na[(\pi\text{-}B_9C_2H_{11})_2Fe] + (CH_3)_4NCl \xrightarrow{H_2O}$$
$$(CH_3)_4N[(\pi\text{-}B_9C_2H_{11})_2Fe] + NaCl$$
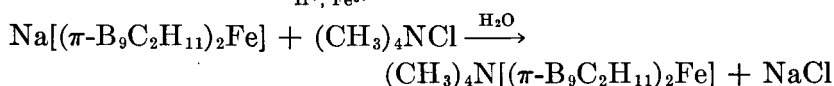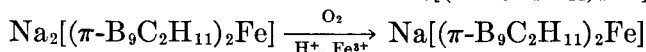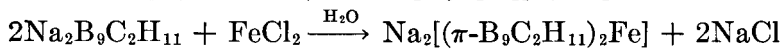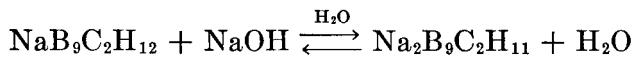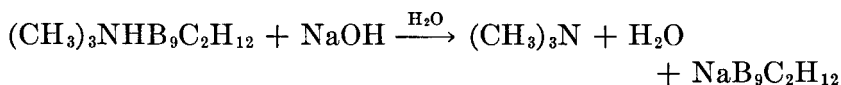
Procedure

In a 250-ml. round-bottomed flask, 2.96 g. (0.0155 mol) of $(CH_3)_3NHB_9C_2H_{12}$ is dissolved in 75 ml. of 50% aqueous

sodium hydroxide. The liberated trimethylamine is removed using a rotary evaporator. In a glass-stoppered, nitrogen-filled 500-ml. Erlenmeyer flask, 9.41 g. (0.0473 mol) of iron(II) chloride tetrahydrate (Baker and Adamson, reagent-grade) is dissolved in 25 ml. of water. The $Na_2B_9C_2H_{11}/NaB_9C_2H_{12}$ solution is heated to 70° on a steam bath and is added under a nitrogen atmosphere to the pale green iron(II) chloride solution. Iron(II) hydroxide immediately precipitates, and the reaction solution turns pink. The reaction solution is periodically agitated for 30 minutes. After the reaction is complete, the solution is diluted with 200 ml. of water and while still warm is filtered through a medium-porosity sintered-glass filter containing a layer of Celite. The residue in the filter funnel is washed three times with 20-ml. portions of hot water. The pink filtrate is acidified to pH 4 with 6 N hydrochloric acid using pH paper as an indicator. (Approximately 285 ml. of the hydrochloric acid is required.) About 0.3 g. of iron(III) chloride hexahydrate is added to catalyze the oxidation and air is passed through the solution for one hour. During the oxidation, the color of the solution changes from pink to red. The red solution is brought to pH 8 with aqueous sodium hydroxide, and the precipitated iron(III) hydroxide is removed by filtration. After precipitation with 20 ml. of 50% aqueous tetramethylammonium chloride, the pinkish-red product $(CH_3)_4N[(\pi\text{-}B_9C_2H_{11})_2Fe]$ is treated as in the nonaqueous procedure. The recovery of the first crop of product is 2.06 g. (69%; the checkers report 83% and they did not attempt a further recovery). The total yield of crude product is 2.50 g. (83%).

Properties

The tetramethylammonium salt is very soluble in acetone and acetonitrile, sparingly soluble in methylene chloride and boiling methanol, and insoluble in organic solvents such as benzene, hexane, and diethyl ether. The color of its solutions

is a deep red.   The infrared spectrum (Nujol mull) contains major absorption bands at 3.96 (vs), 8.26 (m), 8.53 (w), 8.72 (m), 8.98 (m), 9.11 (s), 9.33 (w), 9.80 (m), 10.00 (w), 10.21 (s), 10.55 (s), 10.88 (w), 11.28 (w), 11.42 (w), 11.64 (w), 13.34 (m), 13.88 (s), 14.49 (w), and 15.46 (m) μ.   The visible and ultraviolet absorption bands occur at 272 (ϵ = 21,200), 296 (18,000), 444 (585), and 530 (375, shoulder) mμ.

$(CH_3)_4N[(\pi\text{-}B_9C_2H_{11})_2Co]$

$$(CH_3)_3NHB_9C_2H_{12} + NaOH \xrightarrow{H_2O} (CH_3)_3N + H_2O$$
$$+ NaB_9C_2H_{12}$$
$$NaB_9C_2H_{12} + NaOH \underset{\longleftarrow}{\overset{H_2O}{\longrightarrow}} Na_2B_9C_2H_{11} + H_2O$$
$$4Na_2B_9C_2H_{11} + 3CoCl_2 \xrightarrow{H_2O} 2Na[(\pi\text{-}B_9C_2H_{11})_2Co]$$
$$+ Co + 6NaCl$$
$$Na[(\pi\text{-}B_9C_2H_{11})_2Co] + (CH_3)_4NCl \xrightarrow{H_2O}$$
$$(CH_3)_4N[(\pi\text{-}B_9C_2H_{11})_2Co] + NaCl$$
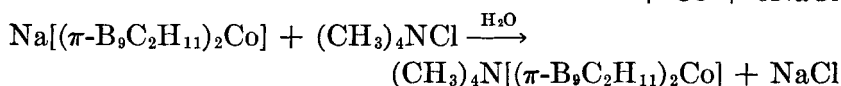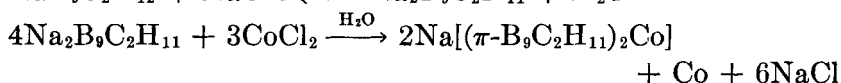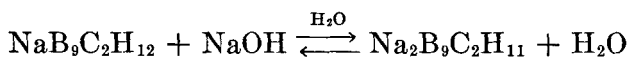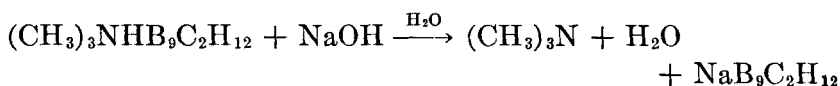
Procedure

The aqueous preparation of the cobalt complex is similar to that of the iron complex, but an internal redox reaction occurs which eliminates the necessity of catalyzed atmospheric oxidation and thus adjustment of pH.   Three (3.00) grams (0.0155 mol) of $(CH_3)_3NHB_9C_2H_{12}$ and 12.30 g. (0.0517 mol) of cobalt(II) chloride hexahydrate (Baker and Adamson, reagent-grade) are treated as in the aqueous preparation of $(CH_3)_4N[(\pi\text{-}B_9C_2\text{-}H_{11})_2Fe]$ except that a nitrogen atmosphere is not required. After the reaction is complete, the solution is diluted with 200 ml. of water and filtered while warm through a layer of Celite.   The residue in the filter funnel is washed with three 30-ml. portions of hot water.   The $(CH_3)_4N[(\pi\text{-}B_9C_2H_{11})_2Co]$ is precipitated from the basic yellow filtrate with 20 ml. of 50% aqueous tetramethylammonium chloride.   The yellow substance is then isolated and purified as in the nonaqueous

procedure for the iron complex. The yield of product is 2.66 g.
(86%).

Properties

The tetramethylammonium salt is very soluble in acetone and
acetonitrile, sparingly soluble in methylene chloride and boiling
methanol, and insoluble in organic solvents such as benzene,
hexane, and diethyl ether. The color of its solutions is a
yellow-orange. The infrared spectrum (Nujol mull) contains
major absorption bands at 3.98 (vs), 7.80 (w), 8.33 (m), 8.57
(w), 8.87 (m), 8.99 (w), 9.10 (s), 9.26 (w), 9.82 (m), 10.19 (s),
10.58 (s), 10.87 (w), 11.31 (s), 12.81 (w), 13.34 (m), 13.82
(m), 14.60 (m), and 15.50 (w) μ. The visible and ultraviolet
bands occur at 293 (ϵ = 45,000), 345 ($\sim$2000, shoulder), and
445 (440) mμ.

REFERENCES

1. J. A. POTENZA and W. N. LIPSCOMB: *Inorg. Chem.*, **3,** 1673 (1964).
2a. T. L. HEYING, J. W. AGER, JR., S. L. CLARK, D. J. MANGOLD, H. L. GOLD-
    STEIN, M. HILLMAN, R. J. POLAK, and J. W. SZYMANSKI: *ibid.*, **2,** 1089 (1963).
2b. H. SCHROEDER, T. L. HEYING, and J. R. REINER: *ibid.*, 1092 (1963).
2c. T. L. HEYING, J. W. AGER, JR., S. L. CLARK, R. P. ALEXANDER, S. PAPETTI,
    J. A. REID, and S. I. TROTZ: *ibid.*, 1097 (1963).
2d. S. PAPETTI and T. L. HEYING: *ibid.*, 1105 (1963).
2e. R. P. ALEXANDER and H. SCHROEDER: *ibid.*, 1107 (1963).
2f. M. M. FEIN, J. BOBINSKI, N. MAYES, N. SCHWARTZ, and M. S. COHEN: *ibid.*,
    1111 (1963).
2g. M. M. FEIN, D. GRAFSTEIN, J. E. PAUSTIAN, J. BOBINSKI, B. N. LICHSTEIN,
    N. MAYES, N. N. SCHWARTZ, and M. S. COHEN: *ibid.*, 1115 (1963).
2h. D. GRAFSTEIN, J. BOBINSKI, J. DVORAK, H. SMITH, N. SCHWARTZ, M. S.
    COHEN, and M. M. FEIN: *ibid.*, 1120 (1963).
2i. D. GRAFSTEIN, J. BOBINSKI, J. DVORAK, J. E. PAUSTIAN, H. F. SMITH, S.
    KARLAN, C. VOGEL, and M. M. FEIN: *ibid.*, 1125 (1963).
2j. S. PAPETTI, B. B. SCHAEFFER, H. J. TROSCIANIEC, and T. L. HEYING: *ibid.*,
    3, 1444 (1964).
2k. H. SCHROEDER, J. R. REINER, R. P. ALEXANDER, and T. L. HEYING: *ibid.*,
    1464 (1964).
2l. J. A. DUPONT and M. F. HAWTHORNE: *J. Am. Chem. Soc.*, **86,** 1643 (1964).
3. R. A. WIESBOECK and M. F. HAWTHORNE: *ibid.*, 1642 (1964).
4a. F. N. TEBBE, P. M. GARRETT, and M. F. HAWTHORNE: *ibid.*, 4222 (1964).

4*b*. F. N. TEBBE, P. M. GARRETT, and M. F. HAWTHORNE: *ibid.*, **88**, 607 (1966).
4*c*. F. N. TEBBE, P. M. GARRETT, D. C. YOUNG, and M. F. HAWTHORNE: *ibid.*, 609 (1966).
5*a*. M. F. HAWTHORNE, D. C. YOUNG, and P. A. WEGNER: *ibid.*, **87**, 1818 (1965).
5*b*. M. F. HAWTHORNE and T. D. ANDREWS: *ibid.*, 2496 (1965).
5*c*. M. F. HAWTHORNE and R. L. PILLING: *ibid.*, 3988 (1965).
5*d*. M. F. HAWTHORNE and T. D. ANDREWS: *Chem. Commun.*, **1965**, 443.
6. R. SCHAEFFER: *J. Am. Chem. Soc.*, **79**, 1006 (1957).
7. G. WILKINSON: *Org. Syn.*, **36**, 31 (1956).

18. DIBORON TETRACHLORIDE

Submitted by THOMAS WARTIK,* RICHARD ROSENBERG,* and WILLIAM B. FOX*
Checked by T. D. COYLE† and J. J. RITTER†

Although a chemical method for preparing diboron tetrachloride has been described,[1] electric-discharge procedures still provide the most convenient route to this substance for the average laboratory worker. Stock[2] used a discharge struck between zinc electrodes immersed in liquid boron trichloride to effect its reduction to diboron tetrachloride, but practically all preparative methods since reported[3] have involved passing the trichloride, in the vapor phase, between mercury electrodes. The over-all process may be described by the equation:

$$2BCl_3 + 2Hg \rightarrow B_2Cl_4 + Hg_2Cl_2$$
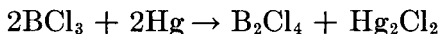
Optimum production rates have rarely been as much as 0.25 g./day per discharge tube.

The procedure described here involves the use of copper, rather than mercury, as a "chlorine-getter." In this case, presumably, the principal reaction is heterogeneous in nature and involves the attack of metallic copper by gaseous boron trichloride, according to the equation:

$$2BCl_3 + 2Cu \rightarrow B_2Cl_4 + 2CuCl$$
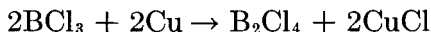
* Pennsylvania State University, University Park, Pa.
† National Bureau of Standards, Washington, D.C. 20234.

Because this reaction is not dependent upon a high concentration of vaporized metal, the temperature may be substantially lower than that called for when mercury is used. This circumstance permits higher discharge currents to be used without danger of cracking the reactor walls and, correspondingly, makes practicable the use of substantially higher boron trichloride pressures. The reduced temperature also substantially lowers the tendency for diboron tetrachloride, once formed, to undergo irreversible thermal decomposition. Finally, the present method makes practicable an arrangement which, effectively, permits from six to ten "discharge cells" to be operated in series within the same reactor.

With apparatus and procedures of the type to be described, diboron tetrachloride production rates approaching 1.0 g./hour may be anticipated with a new reactor tube. Yields decrease with aging, but relatively long service with a production rate no lower than 0.20 to 0.50 g./hour can generally be relied upon.

Procedure

The "cells-in-series" discharge tube, placed horizontally, is shown in Fig. 14. It consists of a water-jacketed tube, 130 cm. long, of 14-mm. i.d. fitted with 10 plugs of light copper turnings,* each about 5 cm. in length and spaced at intervals of 5 cm. (The checkers used six plugs in a tube 75 cm. long and 20 mm. i.d.) Before the terminal electrodes are sealed onto the discharge tube proper, the plugs are pushed into position with a long rod. To keep flow resistance at a minimum, the plugs should be loosely packed, but not so loosely that they will be blown out of position during the gas transfers.

The terminal plugs are connected directly to the tungsten electrodes by means of no. 18 copper wire. The latter is coiled

---

* Fisher Scientific copper (C-575) was used. As supplied, this metal is coated with oil, which must be removed by successive washings with a solvent such as chloroform. Failure to remove this oil will seriously interfere with the discharge tube operation.
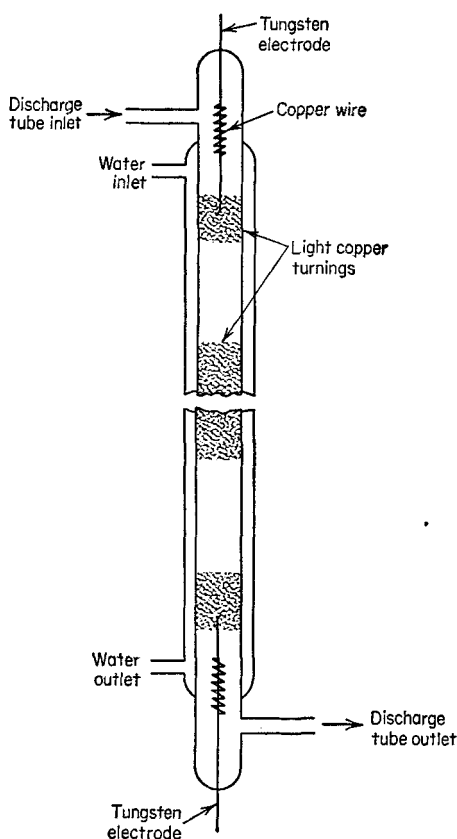
Fig. 14

tightly about the tungsten electrode, whose diameter may be in the range of 1 to 2 mm., and the coil is rendered rigid by flowing on soft solder. The free end of the copper wire is soldered to a strip of the terminal copper plug, which is then pushed into position in the discharge tube proper. The final seals are then made and the discharge tube is attached to the assembly shown in Fig. 15.

To achieve the discharge, a 60-cycle, 110-volt luminous-tube transformer with an output rating of 10,000 to 15,000 volts is adequate. The output potential is best controlled by activating

the primary through a variable transformer. Measurement of the output potential is not essential; it may be estimated from a knowledge of the voltage applied across the primary and the maximum rating of the luminous-tube transformer. Great care must be taken to avoid contact between the transformer leads and any metal parts except the electrodes themselves.

Commercially available boron trichloride is almost invariably contaminated with hydrogen chloride and occasionally with chlorine. Unless removed, the hydrogen chloride will produce hydrogen during the discharge process which inhibits the formation of diboron tetrachloride. Purification can be effected by subjecting the boron trichloride to long pumping at $-112°$ (melting carbon disulfide). Chlorine can be removed by agitating the boron trichloride with mercury in a sealed tube. When the vapor pressure at $0°$ is 477 mm., the reagent is ready to use.

Since boron trichloride reacts with many lubricants to form hydrogen chloride, the diboron tetrachloride synthesis is carried out in a grease-free system. A mercury float-valve vacuum system[4] depicted in Fig. 15 is employed here. The U-traps have a capacity of 50 ml. without plugging and tubes A and B have
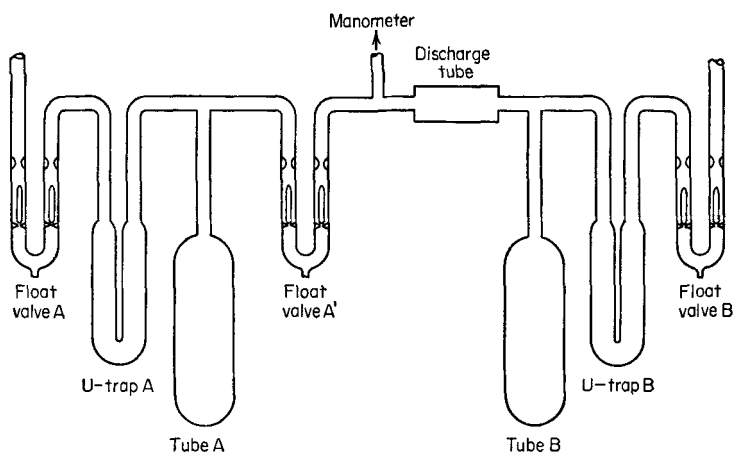
Fig. 15

a capacity of 250 ml.   (The checkers used fluorocarbon polymer needle valves and "O" ring joints with fluorocarbon elastomer "O" rings.)

Prior to introduction of the boron trichloride, the discharge system should be thoroughly evacuated.   Degassing of the walls can be hastened by flaming all components except the discharge tube, which can be freed of residual gases by turning on the discharge briefly.   About 150 ml. (liquid) of boron trichloride is condensed in tube *A* by cooling the latter with liquid nitrogen, and float valve *A* is closed.   (Float valve *A'* should be open at this point and float valve *B* should be closed.) The cold bath is now removed from tube *A*, and its contents are allowed to warm until the manometer reading is about 50 mm. At this juncture, an *empty* Dewar vessel at room temperature is raised about tube *A*, and tube *B* and U-trap *B* are cooled with liquid nitrogen.   Float valve *B* is then opened to the vacuum system in order to achieve continuous pumping during the initial stages of the boron trichloride transfer.

When the potential across the electrodes of the discharge tube is raised to an appropriate value, a greenish white glow will be noted in the spaces between the plugs of copper turnings. Direct concentrated arcing is not desirable, as it can lead to localized heating which can crack the glass discharge tube.   Any potential up to 12 kilovolts may generally be safely employed, and the rate of diboron tetrachloride production will be found to rise with increasing voltage.   The value of the boron trichloride pressure, within limits, does not appear to be critical, subject, of course, to the condition that it not be allowed to rise so high as to extinguish the discharge.   A pressure range of 15 to 30 mm. has been found to give satisfactory results.

Ordinary tap water flowing through the discharge-tube jacket has been found to provide adequate cooling.   The tap-water temperature has varied from 5 to 18° with no significant change in results.

Cooling U-trap *B* and evacuation during the initial stages of the discharge process is a precautionary measure to ensure removal of any hydrogen formed through the discharge-induced decomposition of residual hydrogen chloride. When gases noncondensable at −196° cease to be detected (a McLeod gage may be used), float valve *B* may be closed and the Dewar vessel around U-trap *B* may be lowered. All condensation will then occur in tube *B*. (U-trap *B*, in any event, is too small to accommodate the entire boron trichloride sample.)

If, during the transfer, the pressure of boron trichloride should fall much below 15 mm., the Dewar vessel surrounding tube *A* should be lowered until the pressure rises to a satisfactory value and then replaced by another empty Dewar vessel at room temperature. It is also possible to achieve a relatively constant temperature by allowing a slow stream of compressed air to exit from a tube leading to the bottom of the Dewar vessel.

After all the liquid has evaporated from tube *A* (1 to 5 hours, depending upon specific reaction conditions), the discharge current is interrupted. The Dewar vessel around tube *B* is removed and replaced by a bath at −80°, when the internal pressure reaches 5 to 10 mm. Tube *A* is cooled with liquid nitrogen to initiate back-transfer of the unchanged boron trichloride, which usually amounts to 95 to 97% of the amount originally charged. The less volatile diboron tetrachloride remains in tube *B*. This transfer is relatively slow, but since it requires no attention beyond making certain that both temperatures are maintained, it can be allowed to take place overnight. Owing to the fact that diboron tetrachloride does exert a small vapor pressure at −80° (about 0.1 mm.), it is best to terminate the transfer while 5 to 10 ml. of liquid still remains in tube *B*. Float valve *A'* is closed, and the crude product is condensed in another portion of the vacuum system for final purification. While this purification is being accomplished, the discharge synthesis procedure described above may be repeated.

Purification

The BCl_3-B_2Cl_4 mixture is best separated in a Stock-type fractionation train which utilizes mercury float valves.[4] The mixture is repeatedly passed, with pumping, through a series of U-traps at $-80°$ and $-196°$. These operations should be carried out as rapidly as possible to minimize passage of diboron tetrachloride through the U-trap at $-80°$ and should be continued until the diboron tetrachloride fraction (U-trap at $-80°$) exhibits a vapor pressure of 43 mm. at $0°$. Three to five such fractionations are generally required, and the yield of diboron tetrachloride ranges from 1.0 to 3.0 g. The separated boron trichloride may be saved for reuse in the discharge synthesis.

Liquid diboron tetrachloride decomposes relatively rapidly at room temperature, quickly turning from colorless to dark red in the process. The decomposition rate is insignificant at $-80°$, and this temperature is recommended for long-term storage.

Analysis

The vapor pressure at $0°$ (43 mm.) is generally a sufficient criterion for purity. (The checkers also used infrared spectroscopy and noted a trace of impurity of silicon tetrachloride.) Elemental analysis is readily accomplished by heating a weighed sample at $160°$ for 18 hours with a slight excess of water in a sealed glass tube.* A 15 to 20% excess of water over that required by the equation:

$$B_2Cl_4 + 6H_2O \rightarrow 2B(OH)_3 + 4HCl + H_2$$
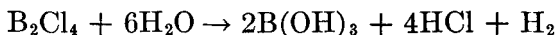
should be used. The analysis tube is opened to the vacuum system, the hydrogen collected and measured with a Toepler

---

* The heating time and temperature may be considerably reduced by using aqueous sodium hydroxide in place of water. However, this reagent also involves the danger of dissolving boron from borosilicate glasses.

pump, and the water–hydrogen chloride mixture evaporated from the residue and condensed in another portion of the apparatus. Chloride may be determined gravimetrically or volumetrically, and boric acid by titration in the presence of mannitol. Values should agree with those called for by the above equation by within 1%.

Properties

Although thermally rather unstable at room temperature, liquid diboron tetrachloride decomposes relatively slowly at temperatures below 0°. In the gas phase, the substance may be exposed to ambient temperatures for periods as long as 5 to 10 minutes without the risk of appreciable deterioration. The colorless substance melts[5] at −93.0° and its vapor pressures in the interval −63.5 to 22.5° are given by the equation:[3]

$$\log p_{mm} = -\frac{1753}{T} + 8.057$$

The principal infrared absorptions[6] (in cm.$^{-1}$) are 2041 (m), 1647 (m), 1319 (m), 1227 (m), 1026 (s), 950 (m), 917 (vvs), 818 (m), 745 (m), 730 (vvs), and 688 (s).

Owing to its extreme reactivity, diboron tetrachloride must always be handled in dry oxygen-free apparatus. *Sudden exposure to air has been known to result in detonation.*

REFERENCES

1. A. L. McCLOSKY, R. J. BROTHERTON, and J. L. BOONE: *J. Am. Chem. Soc.*, **83**, 4750 (1961).
2. A. STOCK, A. BRANDT, and H. FISCHER: *Ber.*, **58**, 653 (1925).
3. T. WARTIK, R. MOORE, and H. I. SCHLESINGER: *J. Am. Chem. Soc.*, **71**, 3265 (1949); G. URRY, T. WARTIK, and H. I. SCHLESINGER: *ibid.*, **76**, 5293 (1954).
4. R. T. SANDERSON: "Vacuum Manipulation of Volatile Compounds," John Wiley & Sons, Inc., New York, 1948.
5. M. J. LINEVSKY and T. WARTIK: *J. Phys. Chem.*, **62**, 1146 (1958).
6. D. E. MANN and L. FANO: *J. Chem. Phys.*, **26**, 1665 (1957).

19. n-BUTYLDICHLOROBORANE

$$Sn(n\text{-}C_4H_9)_4 + 2BCl_3 \rightarrow Cl_2Sn(n\text{-}C_4H_9)_2 + 2(n\text{-}C_4H_9)BCl_2$$

Submitted by KURT NIEDENZU,* JOHN W. DAWSON,* and PETER FRITZ†
Checked by EARL L. MUETTERTIES‡ and CONSTANCE M. WRIGHT‡

Three basic methods have been used for the preparation of organodihaloboranes, RBX_2: (1) the direct interaction of hydrocarbons with haloboranes, (2) the reaction of organometallic derivatives with haloboranes, and (3) the halogenation of organoboranes. One of the most convenient laboratory procedures involves the reaction of tetraorganotin derivatives with trihaloboranes, BX_3.[1-8] This reaction works particularly well for the preparation of alkyldihaloboranes as outlined below.

The use of organotin compounds for the preparation of organometallics and organometalloids appears to be quite versatile.[9] For example, alkyltetrafluorophosphoranes have been obtained from tetraalkyltin compounds and phosphorus(V) fluoride,[10] phenylmercury(II) chloride from tetraphenyltin and mercury(II) chloride,[11] and divinylbromoarsine from $(n\text{-}C_4H_9)_2\text{-}Sn(CH{=}CH_2)_2$ and arsenic(III) bromide.[12]

Procedure

■ *Caution. n-Butyldichloroborane is pyrophoric and must be handled with care (see Properties). All work should be conducted in a vented hood with a fire extinguisher readily available. After completion of the experiment, the apparatus should be cooled to room temperature while being flushed with inert gas. It should then be rinsed immediately with a copious amount of water.*

---

* Department of Chemistry, Duke University, and U.S. Army Research Office, Durham, N.C.

† Fa. Normag, Hofheim/Germany.

‡ Central Research Department, Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, Del.

A 500-ml. three-necked flask is fitted with a stirrer,* a 250-ml. dropping funnel (equipped with a pressure-equalizing side tube and a gas inlet tube at the top), and an efficient reflux condenser (cooled with water) which is topped with a Dry Ice condenser having a calcium chloride drying tube at the top. Ground-glass connections are lubricated with silicone stopcock grease. The apparatus is flushed with dry inert gas (nitrogen or argon) and is completely dried before use. The inert gas is introduced through the gas inlet at the top of the dropping funnel, and a slow gas flow is maintained throughout the operation.

The reaction vessel is cooled with a Dry Ice–methanol bath and is charged with 134 g. (approx. 1.15 mols) of boron trichloride.† Tetra-*n*-butyltin‡ (173.6 g., 0.5 mol) is placed in the dropping funnel and is added to the stirred boron trichloride over 15 minutes. After addition is complete, the cooling bath is removed and the mixture slowly warmed to room temperature and subsequently heated to reflux for 15 minutes. After the reaction mixture has cooled to room temperature, the inert gas flow is gradually increased and the reflux condenser quickly replaced by a distillation head connected to a condenser and a receiver (which is protected against atmospheric moisture with a calcium chloride drying tube). After the equipment has been thoroughly flushed with the inert gas, the flow is reduced and the reaction vessel is slowly heated. Excess boron trichloride is removed by the inert gas flow. On raising the temperature, distillation begins, and a crude fraction of *n*-butyldichloroborane is collected from about 75 to 110°, the major portion of the product distilling between 95 to 108°. The crude distillate is redistilled in a nitrogen atmosphere through a 25-mm. Widmer column to afford 100 to 110 g. (approx. 70 to 75% yield) of the pure product, b.p. 106 to 108°. The checkers report an 85% yield when the reaction was run at one-third

* Checkers used a mercury-sealed Hirshberg stirrer.
† C.P. grade, Matheson Company, East Rutherford, N.J.
‡ Columbia Organic Chemicals Co., Columbia, S.C.

scale and the product was distilled through a vacuum-jacketed Vigreaux column.

Properties

n-Butyldichloroborane is a white, mobile, strongly fuming liquid; it is easily and sometimes explosively hydrolyzed by moisture. Although the compound may be exposed *very briefly* to air at room temperature, it is pyrophoric and ignites on prolonged exposure. *n*-Butyldichloroborane should be handled and stored in an inert-gas atmosphere.

REFERENCES

1. H. D. KAESZ, S. L. STAFFORD, and F. G. A. STONE: *J. Am. Chem. Soc.*, **81**, 6336 (1959).
2. F. E. BRINCKMAN and F. G. A. STONE: *ibid.*, **82**, 6218 (1960).
3. K. NIEDENZU and J. W. DAWSON: *ibid.*, 4223 (1960).
4. J. E. BURCH, W. GERRARD, M. HOWARTH, and E. F. MOONEY: *J. Chem. Soc.*, **1960**, 4916.
5. A. B. BURG and J. R. SPIELMAN: *J. Am. Chem. Soc.*, **83**, 2667 (1961).
6. H. NÖTH and P. FRITZ: *Z. Anorg. Allgem. Chem.*, **322**, 297 (1963).
7. W. GERRARD, E. F. MOONEY, and R. G. REES: *J. Chem. Soc.*, **1964**, 740.
8. P. FRITZ, K. NIEDENZU, and J. W. DAWSON: *Inorg. Chem.*, **3**, 626 (1964).
9. R. K. INGHAM, S. D. ROSENBERG, and H. GILMAN: *Chem. Rev.*, **1960**, 459.
10. P. M. TREICHEL and R. A. GOODRICH: *Inorg. Chem.*, **4**, 1424 (1965).
11. K. A. KOCHESHKOV and A. N. NESMEYANOV: *J. Gen. Chem.* [*U.S.S.R (Engl. Transl.*)], **4**, 1102 (1934); *C.A.*, **29**, 3993 (1935).
12. L. MAIER, D. SEYFERTH, F. G. A. STONE, and E. G. ROCHOW: *J. Am. Chem. Soc.*, **79**, 5884 (1957).

Chapter Three

GROUP V COMPOUNDS

3A NITROGEN

In this section, syntheses of a variety of inorganic nitrogen compounds are described. The syntheses include those of triazanium chlorides; alkylamino derivatives of boron, arsenic, and tin; and trimeric and tetrameric boron-nitrogen ring structures as exemplified by borazine $(HNBH)_3$.

Classically, triazanium chlorides have been prepared by the reaction of hydrazine with mixtures of chloramine and ammonia. If the appropriately substituted hydrazine is available, this is still the method of choice for the synthesis of this class of compounds.

20. 2,2-DIMETHYLTRIAZANIUM CHLORIDE

$$(CH_3)_2NNH_2 + NH_2Cl \rightarrow [(CH_3)_2N(NH_2)_2]^+Cl^-$$
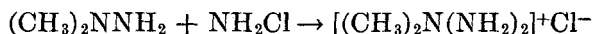
Submitted by H. H. SISLER and K. UTVARY*
Checked by T. E. GIER†

2,2-Disubstituted triazanium chlorides may be prepared by the reaction in benzene solution of unsymmetrically disubstituted

* Department of Chemistry, University of Florida, Gainesville, Fla.
† E. I. du Pont de Nemours & Company, Wilmington, Del.

hydrazines with mixtures of chloramide and ammonia.[1]   These compounds may also be prepared by the reaction of the chloramide-ammonia mixture with benzene solutions of appropriate N-disubstituted amino-1,3,2-dioxaphospholanes of the general formula:[1]

$$\begin{array}{c} CH_2-O \\ | \qquad\qquad \diagdown \\ \qquad\qquad\qquad P-NR_2 \\ | \qquad\qquad \diagup \\ CH_2-O \end{array}$$
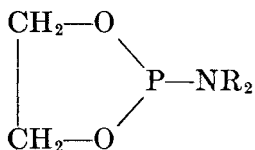
Among the triazanium chlorides prepared are

$$[(CH_3)_2N(NH_2)_2]Cl, \quad [(C_2H_5)_2N(NH_2)_2]Cl,$$

$$\left[\begin{array}{c} CH_2-CH_2 \\ | \qquad\qquad\diagdown \\ \qquad\qquad\qquad N(NH_2)_2 \\ | \qquad\qquad\diagup \\ CH_2-CH_2 \end{array}\right]Cl, \quad \left[\begin{array}{c} CH_2-CH_2 \\ \diagup\qquad\qquad\diagdown \\ O\qquad\qquad\qquad N(NH_2)_2 \\ \diagdown\qquad\qquad\diagup \\ CH_2-CH_2 \end{array}\right]Cl$$
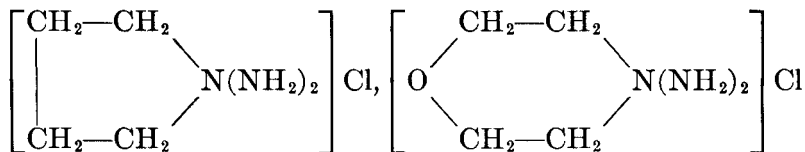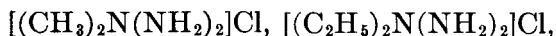
Since the aminophospholanes are relatively difficult to prepare, the reaction with the disubstituted hydrazine, if the latter is available, would be the method of choice.

Procedure

Three grams (0.1 mol) of anhydrous 1,1-dimethylhydrazine dissolved in 75 ml. of dry benzene is placed in a Minilab reaction flask.   The flask is immersed in an ice-water bath and the gas inlet tube connected to the outlet of a chloramide generator.[2]   The solution is then exposed to the effluent gases ($NH_2Cl + NH_3$) of the generator.   The chloramide content of the effluent gas has to be determined separately.[2]   After the solution has reacted with about 0.1 mol of chloramide, the cooling bath is removed, and the gas is bubbled through the mixture for another 5 to 10 minutes.   The reaction flask is then disconnected from the generator and allowed to remain at room temperature for about 12 hours, vented with a Drierite-filled

tube. After filtration, the residue is washed twice with 25 ml. of warm benzene and then extracted with 60 ml. of hot ethanol–acetone (1:1). Upon cooling in ice water, the triazanium chloride precipitates. Adding dry ether (100 ml.) gives another portion of the salt. The crude material is again recrystallized from ethanol–acetone–ether as described above. The yield is 30 to 50% of theory. *Anal.* Calcd. for $[(CH_3)_2N(NH_2)_2]^+Cl^-$: N, 37.66; Cl, 31.77. Found: N, 37.54; Cl, 31.91.

Properties

Pure dimethyltriazanium chloride decomposes at 133 to 134° (the checker reports 135 to 136°). The salt is very hygroscopic and should be stored in a desiccator. It is readily soluble in water, methanol, ethanol, and dimethyl sulfoxide. An aqueous solution is stable at room temperature. Free iodine is liberated from an acidic iodide solution, and this reaction makes it possible to determine the triazanium content.[3]

REFERENCES

1. K. Utvary and H. H. Sisler: *Inorg. Chem.,* **5,** 1835 (1966).
2. H. H. Sisler and G. Omietanski: Inorganic Syntheses, **5,** 92 (1957).
3. R. Gösl: *Angew. Chem. Intern. Ed. Engl.,* **1,** 405 (1962).

21. AMINO AND IMINO DERIVATIVES OF METALS AND METALLOIDS

Submitted by KURT MOEDRITZER*

Only recently, dialkylamino and alkylamino derivatives of many of the elements have been reported for the first time.

* Central Research Department, Monsanto Company, St. Louis, Mo.

Aminolysis of the corresponding halides is the preferred method for the synthesis of dialkylamino derivatives of boron,[1] silicon,[2] germanium,[3] phosphorus,[4] arsenic,[5] and sulfur.[6] (Dialkylamino)chlorosilanes are prepared stepwise by the reaction of silicon tetrachloride with dialkylamines. This method may be utilized equally well for the conversion of alkyl- or aryl-substituted halides [e.g., $(CH_3)_nSiCl_{4-n}$] or of oxide and sulfide halides (e.g., $POCl_3$ or $PSCl_3$) to the corresponding dialkylamino compounds.

Dialkylamino derivatives of elements located in the periodic table to the left or below those listed above cannot be prepared by the above method due to either the ionic character of some of the inorganic halides or the formation of stable metal halide–amine addition products. Therefore, other methods must be applied. Dialkylamino derivatives of tin[7] and antimony[8] are conveniently obtained by reaction of the corresponding halides with lithium dialkylamides. Others, such as the dialkylamino derivatives of aluminum,[9] are made by the interaction of the hydride with dialkylamines. Dialkylamino derivatives of beryllium[10] or lithium[11] result from the reaction of the respective alkyl derivative with a dialkylamine.

In reactions with metal or metalloidal halides, primary amines, because of their difunctionality, tend to yield more complex molecules, such as cyclic, cage, or polymeric structures. For example, cage-type structures[12,13] of the type $P_4(NCH_3)_6$ and $As_4(NCH_3)_6$ have been prepared by methylaminolysis of phosphorus(III) or arsenic(III) chloride, respectively, and cyclic structures of formula $(HNBCl)_3$[14] or $(RBNCl)_4$ have been prepared from boron halides and ammonium chloride or monoalkylamines.

REFERENCES

1. E. Wiberg and K. Schuster: *Z. Anorg. Allgem. Chem.*, **213**, 77 (1933); also see procedure given below, 21B.
2. H. Breederveld and H. I. Waterman: *Research (London)*, **5**, 537 (1952).
3. H. H. Anderson: *J. Am. Chem. Soc.*, **74**, 1421 (1952).

4. A. B. BURG and P. J. SLOTA, JR.: *ibid.*, **80**, 1107 (1958).
5. K. MOEDRITZER: *Chem. Ber.*, **92**, 2637 (1959); also see procedure given below, 21A.
6. E. S. BLAKE: *J. Am. Chem. Soc.*, **65**, 1267 (1943).
7a. I. M. THOMAS: *Can. J. Chem.*, **39**, 1386 (1961).
7b. K. JONES and M. F. LAPPERT: *J. Chem. Soc.*, **1965**, 1944.
8. K. MOEDRITZER: *Inorg. Chem.*, **3**, 609 (1964).
9. E. WIBERG and A. MAY: *Z. Naturforsch.*, **10b**, 234 (1955).
10. G. E. COATES and F. GLOCKLING: *J. Chem. Soc.*, **1954**, 22.
11. H GILMAN, N. N. CROUNSE, S. P. MASSIE, JR., R. A. BENKESER, and S. M. SPATZ: *J. Am. Chem. Soc.*, **67**, 2106 (1945).
12. R. R. HOLMES: *ibid.*, **83**, 1334 (1961).
13. H. J. VETTER, H. NÖTH, and W. JAHN: *Z. Anorg. Allgem. Chem.*, **328**, 144 (1964).
14. H. S. TURNER and R. J. WARNE: *J. Am. Chem. Soc.*, **87**, 6421 (1965).

A. Tris(dimethylamino)arsine

$$AsCl_3 + 6(CH_3)_2NH \rightarrow As[N(CH_3)_2]_3 + 3[(CH_3)_2NH_2]Cl$$

Submitted by KURT MOEDRITZER*
Checked by DONALD C. JICHA†

Tris(dimethylamino)arsine is prepared by dimethylaminolysis of arsenic(III) chloride in a suitable solvent.[1] The reaction is generally applicable since arsenic(III) iodide[2] and alkylhaloarsines[1] of the general formula R_nAsX_{3-n} ($n = 1$ or 2, $X = Cl$, Br, or I) have been reported to react similarly with secondary amines. In addition to dimethylamine, other secondary amines, such as diethylamine, have been used to prepare the corresponding tris(dialkylamino)arsine.[2,3] Tris(dialkylamino)arsines have also been prepared by transamination[4] of tris(dimethylamino)arsine with higher-boiling secondary amines such as diethylamine, di-*n*-butylamine, or piperidine.

Procedure

A mixture of 453 g. (2.5 mols) of freshly distilled arsenic(III) chloride and 4 l. of *n*-hexane is placed in a 5-l. four-necked flask

* Central Research Department, Monsanto Company, St. Louis, Mo.
† Department of Chemistry, University of North Carolina, Chapel Hill, N.C.

fitted with a reflux condenser, mechanical stirrer, thermometer, and gas inlet tube. A drying tube is attached to the outlet of the condenser to prevent moisture from entering the reaction vessel. The reaction flask is then cooled by an ice bath in order to maintain a temperature of *ca.* 5° inside the flask during the reaction. Dimethylamine* from a cylinder is passed slowly into the well-stirred solution after being dried by passing through a 1-m. drying tube filled with sodium hydroxide pellets. During the course of the reaction, a white precipitate of dimethyl-ammonium chloride is formed.

The reaction is complete when the clear supernatant solution in the reaction vessel no longer contains chlorine as detected by the addition of dilute nitric acid and silver nitrate solution to *ca.* 1-ml. of the clear solution withdrawn from the reaction flask. After the reaction is complete, the ice bath is removed, and stirring is continued for 2 hours at room temperature. After standing overnight, the dimethylammonium chloride is filtered and washed with *n*-hexane, with careful exclusion of the moisture of the atmosphere. The combined filtrates are distilled at atmospheric pressure to remove the solvent. The tris(dimethylamino)arsine distills at 36°/2 mm. (55 to 57°/10 mm.). The yield is 402 g. (78%).

Properties

Tris(dimethylamino)arsine (d_{20} 1.1248; n_D^{20} 1.4848)[3] is a colorless liquid which is readily hydrolyzed to form arsenic(III) oxide and dimethylamine when brought into contact with water. The compound is soluble in ethers and hydrocarbons. The product is at least 99.5% pure (with respect to hydrogen-containing impurities) as evidenced by the single sharp peak at −2.533 p.p.m. (relative to tetramethylsilane) seen in the proton nuclear magnetic resonance spectrum of the neat liquid.

* Matheson Company, East Rutherford, N.J., C.P. grade.

REFERENCES

1. K. MOEDRITZER: *Chem. Ber.*, **92**, 2637 (1959).
2. D. HASS: *Z. Anorg. Allgem. Chem.*, **325**, 139 (1963).
3. G. KAMAI and Z. L. KHISAMOVA: *Dokl. Akad. Nauk SSSR*, **105**, 489 (1955); *C.A.*, **50**, 1123h (1956).
4. H. J. VETTER, H. NÖTH, and U. HAYDUK: *Z. Anorg. Allgem. Chem.*, **331**, 35 (1964).

B. Tris(dimethylamino)borane

$$BCl_3 + 6(CH_3)_2NH \rightarrow B[N(CH_3)_2]_3 + 3[(CH_3)_2NH_2]Cl$$
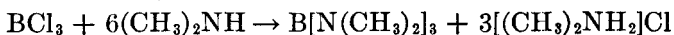
Submitted by KURT NIEDENZU* and JOHN W. DAWSON*
Checked by CONSTANCE M. WRIGHT†

Tris(dimethylamino)borane has been prepared by dimethyl-aminolysis of boron trichloride, with or without solvent,[1-5] and by the reaction of boron trifluoride with dimethylamine in the presence of a suitable Grignard reagent.[6] The procedure described here is a modification of the reaction of dimethylamine with boron trichloride in pentane as the solvent.

Procedure

A 2-l. three-necked flask is equipped with a stirrer, a 500-ml. dropping funnel protected by a calcium chloride drying tube, and a reflux condenser topped with a potassium hydroxide drying tube. The reaction vessel is cooled in an ice–salt bath and is charged with 500 ml. of dry pentane‡ and 293 g. (6.5 mols) of anhydrous dimethylamine. A solution of 117.2 g. (1 mol) of boron trichloride in 400 ml. of pentane, prepared by passing the gaseous chloride into chilled pentane, is added slowly with

---

* Department of Chemistry, Duke University, and U.S. Army Research Office, Durham. N.C.

† Central Research Department, E. I. du Pont de Nemours & Company, Wilmington, Del.

‡ Fisher Scientific Co., pentane (from petroleum), practical grade; dried over sodium wire and freshly distilled.

stirring over a period of 3 hours. The cooling bath is removed and the reaction mixture is allowed to reach room temperature. After standing overnight, the product is filtered in an inert atmosphere (dry-box) and the solid cake is washed several times with 50- to 100-ml. portions of pentane. The filtrates are combined, and most of the pentane is stripped off in a dry atmosphere until the volume of the remaining liquid is about 250 ml. If a small amount of dimethylammonium chloride precipitates, it should be filtered off and the filtrate distilled through a 250-mm. silver mantle column packed with stainless-steel helices under reduced pressure. The remainder of the pentane is collected in a large cooling trap, which is located between the distillation equipment and the vacuum pump and is cooled with Dry Ice–acetone. This trap may have to be emptied during the distillation. Care should be taken to keep any moisture from entering the equipment during this operation. After completion of the distillation, the equipment is flushed with dry air in order to avoid contamination of the product by hydrolysis. Yield: 100 g. (70%) of tris(dimethylamino)borane, b.p. 38° (9 mm.).

The synthesis was checked at one-fourth the above scale. The product was distilled through a vacuum-jacketed Vigreaux column to give 20 g. (0.14 mol) (56% yield based on the boron trichloride) of tris(dimethylamino)borane, b.p. 30°/5 to 6 mm.

Properties

Tris(dimethylamino)borane is a colorless liquid having a typical amine odor, b.p. 147°, n_D^{20} 1.4461. It is readily and quantitatively hydrolyzed. It is miscible without decomposition with most common nonprotonic anhydrous organic solvents.

REFERENCES

1. E. WIBERG and K. SCHUSTER: *Z. Anorg. Allgem. Chem.*, **213**, 77 (1933).
2. G. E. COATES: *J. Chem. Soc.*, **1950**, 3481.

3. H. J. BECHER: *Z. Anorg. Allgem. Chem.*, **287**, 285 (1956).
4. H. NÖTH and S. LUKAS: *Chem. Ber.*, **95**, 1505 (1962).
5. D. W. AUBREY, M. F. LAPPERT, and M. K. MAJUMDAR: *J. Chem. Soc.*, **1962**, 4088.
6. A. DORNOW and H. H. GEHRT: *Z. Anorg. Allgem. Chem.*, **294**, 81 (1958).

C. (Diethylamino)trimethylstannane

[(Diethylamino)trimethyltin]

$$(C_2H_5)_2NH + n\text{-}C_4H_9Li \rightarrow (C_2H_5)_2NLi + n\text{-}C_4H_{10}$$
$$(C_2H_5)_2NLi + (CH_3)_3SnCl \rightarrow (CH_3)_3SnN(C_2H_5)_2 + LiCl$$
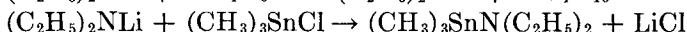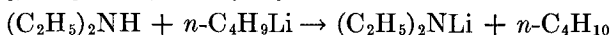
Submitted by C. M. WRIGHT* and E. L. MUETTERTIES*
Checked by T. J. PULLUKAT† and G. URRY†

The synthesis of dialkylamino derivatives of tin(IV)[1] can be readily accomplished by the reaction of the lithium salt of the amine and the corresponding chlorostannane.‡ An extensive series of representative aminostannanes of formula $R_nSn\text{-}(NR'_2)_{4-n}$ where $n = 0$ to 3 has been recently synthesized.[3] These compounds are very moisture-sensitive. ■ *Caution should be observed in the handling of these dialkylaminostannanes because of the recent report of mild explosions during the distillation of bis(dialkylamino)stannanes where temperatures were allowed to reach 200°, and during mild heating of chloroform solutions.*[4]

Procedure

The *n*-butyllithium in hexane was purchased from Foote Mineral Company, Exton, Pa. The diethylamine was dried over sodium hydroxide, and the solvents were dried over sodium metal.

* Central Research Department, Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, Del.
† Department of Chemistry, Purdue University, Lafayette, Ind.
‡ Attempted direct aminolysis of halostannanes yielded the corresponding amine adducts.[2]

A 250-ml. three-necked round-bottomed flask equipped with a dropping funnel with a pressure-equalizing side arm, a reflux condenser, a thermometer, and a magnetic stirrer was thoroughly flushed with nitrogen.   (A nitrogen atmosphere was maintained during the entire reaction.)

A 1.6 *M* solution (68.2 ml., 0.11 mol) of *n*-butyllithium in hexane was introduced into the flask by means of a syringe.   A solution of diethylamine (11.3 ml., 0.11 mol) in 20 ml. of ether was added with stirring over a 20-minute period to the flask, which was cooled with a Dry Ice–acetone bath during the addition.   The reaction mixture was then allowed to warm to room temperature.   A solution of trimethylchlorostannane (trimethyltin chloride) (19.9 g., 0.10 mol) dissolved in 50 ml. of ether was added to the lithium salt of the amine at such a rate as to cause slow reflux.   After the addition was complete, the solution was warmed at the reflux temperature for 2 hours and allowed to cool.   The mixture was filtered (medium-porosity glass frit) in a closed system under nitrogen, and the precipitate was washed with 20 ml. of petroleum ether.   The solvents were removed at 20°/40 mm., and the liquid remaining was transferred in a dry-box to a 25-ml. round-bottomed flask and distilled through a Vigreaux column at 36°/6 mm. to give 12.5 g. (53% yield) of (diethylamino)trimethylstannane. (Checkers report a 59% yield.)   *Anal.* Calcd. for $(CH_3)_3$-$SnN(C_2H_5)_2$: C, 35.7; H, 8.08; N, 5.95; Sn, 50.4.   Found: C, 35.9; H, 8.32; N, 6.08; Sn, 50.3.

Properties

(Diethylamino)trimethylstannane is a colorless liquid which boils at 36°/6 mm.   The compound is quickly hydrolyzed by moisture.   The proton nuclear magnetic resonance spectrum of a neat sample shows a CH_3—Sn resonance at 9.92 τ with H_{CH_3}—Sn^{119} splitting of 56.5 cycles and H_{CH_3}—Sn^{117} splitting of 54.0 cycles.   The ethyl resonance consists of a triplet at 9.10 τ

and a quartet at 7.15 τ with a H—H splitting of 7 cycles. The H_{CH_2}—Sn splitting is 44 cycles.

REFERENCES

1. I. M. THOMAS: *Can. J. Chem.*, **39**, 1386 (1961); G. J. M. VAN DER KERK, J. G. A. LUIJTEN, and M. J. JANSSEN: *Chimia (Aarau)*, **16**, 10 (1962); E. W. ABEL, D. BRADY, and B. R. LERWILL: *Chem. Ind. (London)*, **1962**, 1333.
2. R. K. INGHAM, S. D. ROSENBERG, and H. GILMAN: *Chem. Rev.*, **60**, 508 (1960).
3. K. JONES and M. F. LAPPERT: *J. Chem. Soc.*, **1965**, 1944; *ibid.*, **1965**, 2157; *Proc. Chem. Soc.*, **1962**, 358; *ibid.*, **1964**, 22; *J. Organomet. Chem.*, **3**, 295 (1965).
4. E. W. RANDALL, C. H. YODER, and J. J. ZUCKERMAN: *Inorg. Nucl. Chem. Letters*, **1**, 105 (1965).

D. B,B',B''-Trichloroborazine
(2,4,6-Trichloroborazine)

$$3BCl_3 + 3NH_4Cl \rightarrow (ClBNH)_3 + 9HCl$$
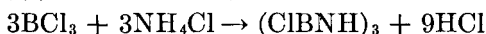
Submitted by KURT NIEDENZU* and JOHN W. DAWSON*
Checked by A. W. LAUBENGAYER†

The original method[1] reported for the preparation of B,B',B''-trichloroborazine involves the use of borazine. However, this procedure is not recommended because of the difficulty of preparing this heterocycle and its hydrolytic instability. More recently, this trichloroborazine has been prepared directly from ammonium chloride and boron trichloride at elevated temperatures with or without a solvent.[2–5] Ammonium chloride may be replaced by a primary aliphatic or aromatic amine or its hydrochloride, and organodihaloboranes can be used in place of the boron trichloride to give the respective N- and B-substituted borazines.[6] Boron tribromide has been used in analogous reactions to yield B,B',B''-tribromoborazines.[6]

* Department of Chemistry, Duke University, and U.S. Army Research Office, Durham, N.C.
† Department of Chemistry, Cornell University, Ithaca, N.Y.

Procedure

The reaction vessel consists of a 1-l. three-necked flask fitted with a stirrer. Another neck of the flask is provided with a water-cooled reflux condenser topped with a Dry Ice–acetone reflux head, the outlet of which is connected to a calcium chloride drying tube to prevent moisture from entering the apparatus. The third neck of the flask is fitted with a 10-cm. tube of 2.5 cm. o.d. and topped with a Dry Ice–acetone reflux head (cold-finger type). The outlet of the head is connected to a cooling trap having two outlets; one outlet is attached to a boron trichloride source and a tank of dry nitrogen is attached to the second outlet of the trap. The apparatus is completely dried before use, and a slow stream of nitrogen is maintained throughout the operation. All ground-glass connections are lubricated with silicone stopcock grease.

The ammonium chloride is dried at 110° for 24 hours. Reagent-grade chlorobenzene dried over sodium sulfate is distilled prior to use.

The reaction vessel is charged with 25 g. (0.47 mol) of ammonium chloride and 300 ml. of dry chlorobenzene, and the cooling trap with 67.5 g. (0.575 mol) of boron trichloride.* The contents of the reaction vessel are heated to gentle reflux with stirring. The cooling bath is then removed from the trap while the nitrogen stream is regulated to carry the boron trichloride slowly past the cold finger into the reaction vessel over a period of 4 to 5 hours. The rate of addition of the boron trichloride is controlled by regulating the temperature of the trap. After addition is complete, the mixture is refluxed for another 12 to 15 hours until the evolution of hydrogen chloride has practically ceased. The solution is filtered hot (100°) in an inert atmosphere (dry-box), and the solvent is removed from the filtrate under reduced pressure. The remaining solid is

* C.P. grade, Matheson Co., East Rutherford, N.J.

sublimed at 40° in high vacuum to yield 10 to 13 g. (about 40% yield) of B,B',B''-trichloroborazine, m.p. 83 to 84°.

Properties

B,B',B''-Trichloroborazine forms white crystalline needles, m.p. 83.9 to 84.5°. It is extremely sensitive to moisture and decomposes violently in water. It is soluble without decomposition in anhydrous nonprotonic organic solvents such as benzene, ethyl ether, and carbon tetrachloride. B,B',B''-Trichloroborazine is readily reduced with alkali metal hydroborates to yield borazine, $(HBNH)_3$.[7,8] The boron-bonded chlorine can be replaced by fluorine through the action of metal fluorides upon the trichloroborazine.[9,10] With amines, the latter reacts to yield B,B',B''-triaminoborazines.[11,12] The substitution of chlorine in N-substituted B,B',B''-trichloroborazines by organic groups is most easily achieved by the Grignard method[13-15] but has also been effected by the use of organolithium compounds.[16]

REFERENCES

1. E. WIBERG and A. BOLZ: *Ber. Deut. Chem. Ges.*, **73**, 209 (1940).
2. C. A. BROWN and A. W. LAUBENGAYER: *J. Am Chem. Soc.*, **77**, 3699 (1955).
3. H. J. EMELEUS and G. J. VIDELA: *J. Chem. Soc.*, **1959**, 1306.
4. L. F. HOHNSTEDT and D. T. HAWORTH: *J. Am. Chem. Soc.*, **82**, 89 (1960).
5. G. L. BRENNAN, G. H. DAHL, and R. SCHAEFFER: *ibid.*, 6248 (1960).
6. K. NIEDENZU and J. W. DAWSON: "Boron-Nitrogen Compounds," Springer-Verlag OHG, Berlin, Heidelberg, New York, 1965.
7. L. F. HOHNSTEDT and D. T. HAWORTH: *Chem. Ind. (London)*, **1960**, 559; *J. Am. Chem. Soc.*, **82**, 89 (1960).
8. G. H. DAHL and R. SCHAEFFER: *J. Inorg. Nucl. Chem.*, **12**, 380 (1960).
9. K. NIEDENZU: *Inorg. Chem.*, **1**, 943 (1962).
10. A. W. LAUBENGAYER, K. WATTERSON, D. R. BIDINOSTI, and R. F. PORTER: *ibid.*, **2**, 519 (1963).
11. K. NIEDENZU and J. W. DAWSON: *J. Am. Chem. Soc.*, **81**, 3561 (1959).
12. W. GERRARD, H. R. HUDSON, and E. F. MOONEY: *J. Chem. Soc.*, **1962**, 113.
13. A. GROSZOS and S. F. STAFIEJ: *J. Am. Chem. Soc.*, **80**, 1357 (1958).
14. H. J. BECHER and S. FRICK: *Z. Anorg. Allgem. Chem.*, **295**, 83 (1958).
15. G. E. RYSCHKEWITSCH, J. J. HARRIS, and H. H. SISLER: *J. Am. Chem. Soc.*, **80**, 4515 (1958).
16. J. H. SMALLEY and S. F. STAFIEJ: *ibid.*, **81**, 582 (1959).

E. Borazine

$$(ClBNH)_3 + 3NaBH_4 + 3(n\text{-}C_4H_9)_3N \rightarrow$$
$$(HBNH)_3 + 3NaCl + 3(n\text{-}C_4H_9)_3N \cdot BH_3$$
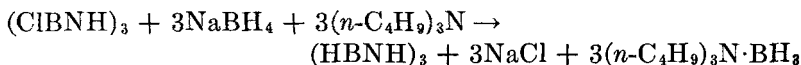
Submitted by KURT NIEDENZU* and JOHN W. DAWSON*
Checked by EARL L. MUETTERTIES† and JAMES SHERMAN†

Borazine originally was obtained by the reaction of ammonia with diborane.[1] Mixtures of lithium or sodium tetrahydroborate with ammonium chloride also have been pyrolyzed to yield this product.[2] More recently, the reduction of B,B',B''-trichloroborazine with alkali metal hydroborates has proved to be a convenient laboratory-scale method for the preparation of this compound.[3-7] The procedure described herein is a variation of the last method as reported by Dahl and Schaeffer.[7] This method is effective for the synthesis of N-substituted alkyl- and arylborazines, i.e., compounds of the formula $(HBNR)_3$ where R is CH_3, C_2H_5, C_6H_{11}, C_6H_5, $p\text{-}C_6H_4CH_3$, or $p\text{-}C_6H_4OCH_3$.[5]

Procedure

The required working time is 3 to 4 hours. All equipment is thoroughly dried prior to use and is flushed with an inert gas (argon or nitrogen). Commercial sodium hydroborate is used without purification. The dimethyl ether of diethylene glycol (diglyme) is refluxed over calcium hydride for 8 hours and subsequently distilled over lithium tetrahydroaluminate (lithium aluminum hydride). Commercial tri-n-butylamine is refluxed with acetic anhydride and distilled at atmospheric pressure.

* Department of Chemistry, Duke University, and U.S. Army Research Office, Durham, N.C.
† Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Del.

B,B',B''-Trichloroborazine* is sublimed at 40° in high vacuum (m.p. 83 to 84°).

A 2-l. three-necked flask is equipped with a stirrer, a reflux condenser (topped with a potassium hydroxide drying tube), and a 750-ml. dropping funnel (equipped with a pressure-equalizing side tube and a gas inlet tube at the top). A slow stream of dry nitrogen (or argon) introduced through the gas inlet is maintained throughout the operation.

The flask is charged with a solution of 77 g. of sodium hydro-borate (25% excess) in 600 ml. of diglyme and is cooled with a bath maintained at 0°; 380 g. (about 25% excess) of tri-n-butylamine is added with vigorous stirring. A solution of 100 g. of B,B',B''-trichloroborazine in 250 ml. of diglyme is added dropwise to the reaction vessel over a period of 1 to 2 hours. After addition is complete, stirring and cooling are continued for another 30 minutes. The reaction vessel is then attached to a 40-cm. Widmer column which is connected to a cooling trap (cooled with Dry Ice–methanol) and to a high-vacuum source (1 mm. or better). The product is distilled from the reaction vessel which is allowed to reach room temperature and then is gradually heated to 40 to 50°; borazine and some by-products are collected in the trap. The crude borazine is redistilled in a dry argon atmosphere at atmospheric pressure through a 25-cm. silver mantle column (filled with stainless-steel helices) topped with a partial take-off head, while the receiving flask is cooled with an ice-salt bath. Approximately 18 to 20 g. of borazine (about 41 to 46% yield), b.p. 54 to 55°, is collected. (The checkers ran the reaction on one-fourth the scale outlined here and obtained a yield of 4.27 g. (39%) of purified borazine. The product was distilled through a vacuum-jacketed Vigreaux column.)

Properties

Borazine is a colorless liquid, m.p. −58°, b.p. 55°. It is very susceptible to hydrolysis and undergoes partial decomposition

* U.S. Borax Research Corp., Anaheim, Calif.

on storage.   Several explosions of highly purified 5-ml. samples sealed in ampules occurred when the material was stored for several weeks on a laboratory shelf in a normally illuminated laboratory; samples kept in darkness were safely stored for several months.

Borazine is miscible with anhydrous nonpolar organic solvents. Its chemical and physical properties have been studied in great detail.[8]

REFERENCES

1. A. STOCK and E. POHLAND: *Ber. Deut. Chem. Ges.*, **49B**, 2215 (1926).
2. G. W. SCHAEFFER, R. SCHAEFFER, and H. I. SCHLESINGER: *J. Am. Chem. Soc.*, **73**, 1612 (1951).
3. R. SCHAEFFER, M. STEINDLER, L. HOHNSTEDT, H. S. SMITH, JR., L. B. EDDY, and H. I. SCHLESINGER: *ibid.*, **76**, 3303 (1954).
4. H. J. EMELÉUS and G. J. VIDELA: *J. Chem. Soc.*, **1959**, 1306.
5. L. F. HOHNSTEDT and D. T. HAWORTH: *J. Am. Chem. Soc.*, **82**, 89 (1960).
6. D. T. HAWORTH and L. F. HOHNSTEDT: *Chem. Ind. (London)*, **1960**, 559.
7. G. H. DAHL and R. SCHAEFFER: *J. Inorg. Nucl. Chem.*, **12**, 380 (1960).
8. K. NIEDENZU and J. W. DAWSON: "Boron-Nitrogen Compounds," Springer-Verlag OHG, Berlin, Heidelberg, New York, 1965.

F. *sym*-N,N',N'',N'''-Tetra-*t*-butyl-B,B',B'',B'''-tetrachloroperhydro-tetrazatetraborocine

$$4BCl_3 + 4(C_2H_5)_3N \rightarrow 4(C_2H_5)_3N \cdot BCl_3$$
$$4(C_2H_5)_3N \cdot BCl_3 + 4(C_2H_5)_3N + 4t\text{-}C_4H_9NH_2 \rightarrow$$
$$(ClBN\text{-}t\text{-}C_4H_9)_4 + 8(C_2H_5)_3N \cdot HCl$$
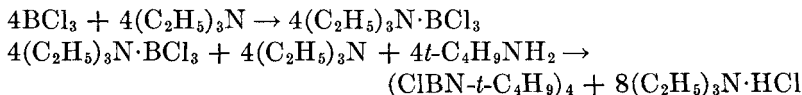
Submitted by A. MELLER* and E. SCHASCHEL*
Checked by KURT NIEDENZU† and JOHN W. DAWSON†

Compounds belonging to the borazine structural class which is based on a six-membered ring of alternating boron and nitrogen atoms are readily prepared by a number of reactions including

* Department of Inorganic and General Chemistry, Technical University of Vienna, Vienna, Austria.

† Department of Chemistry, Duke University, and U.S. Army Research Office, Durham, N.C.

thermal dehydrohalogenation of amine-boranes and amino-boranes. Analogous compounds based on the eight-membered ring system, i.e., *sym*-tetrazatetraborocines, are less accessible. The synthesis of one has been described in a patent[1] but no procedure of good reproducibility has been presented. However, the reaction of tertiary alkyl primary amines with the triethyl-amine–boron trichloride complex in the presence of excess triethylamine gives good yields of the tetrazatetraborocine if performed in the following way.

Procedure

The reaction is effected in all-glass equipment with standard ground-glass joints. The reagents are dried in the following fashion: triethylamine is distilled from a potassium hydroxide–potassium mixture; *t*-butylamine is distilled from barium oxide; and reagent-grade toluene is distilled from metallic potassium. The commercial grade of boron trichloride is used directly without any purification.

A 5-l. three-necked flask is fitted with a stirrer (which may be of the glass-sleeve type lubricated with paraffin oil, or a mercury-sealed Hirshberg stirrer), an efficient condenser fitted with a calcium chloride drying tube, and a gas inlet tube. The gas inlet tube is connected with polyethylene tubing through a small bubble counter containing a nonvolatile hydrocarbon to the cylinder of boron trichloride.

Two liters of toluene are added to the reaction flask* and the boron trichloride cylinder is placed on a balance. The reaction flask is then cooled with a Dry Ice–ethanol or Dry Ice–acetone mixture. The gas cylinder valve is opened, and the boron trichloride is condensed in the toluene. After 117 g. (1 mol) of boron trichloride has been introduced, the cylinder valve is

---

* The checkers used half the amount of chemicals described here. The total time required for the preparation under these conditions was about 48 hours, of which 6 required direct participation of the experimentalist.

closed, the cylinder is disconnected, and a slow stream of nitrogen is passed through the reaction mixture for about 1 minute.*

The inlet tube is then replaced by a 300-ml. dropping funnel containing 202 g. (2 mols) of triethylamine. The triethylamine is added dropwise to the reaction mixture. During the addition, the reaction mixture is stirred and cooled by ice or cold water. After addition of the triethylamine, 73 g. (1 mol) of *t*-butyl-amine is added through the dropping funnel over a period of one hour. The slurry is stirred for 2 hours at room temperature and then finally heated to reflux for a period of 40 hours.

The reaction mixture is filtered through a sintered-glass funnel in a dry atmosphere such as may be maintained in a dry-box. The insoluble material is washed with 200 ml. of toluene. The washings and the filtrate are taken to dryness by distillation under reduced pressure at about 90 to 100°. The solid residue is recrystallized twice from dry carbon tetrachloride and then dried in high vacuum at 50 to 100° for a period of 6 hours. The yield of *sym-N,N',N'',N'''*-tetra-*t*-butyl-*B,B',B'',B'''*-tetra-chloroperhydrotetrazatetraborocine is 96 g. (60%).

Properties

sym-N,N',N'',N'''-Tetra-*t*-butyl-*B,B',B'',B'''*-tetrachloroper-hydrotetrazatetraborocine is a colorless crystalline material that readily dissolves in nonpolar organic solvents; its solubility in polar media is quite low. This compound tends to separate from solution with retention of solvent molecules. For example, the phase that separates out from carbon tetrachloride contains 2 mols of the solvent.[2] The unsolvated product melts with some decomposition around 200°; however, a reproducible melting point of 248° is observed under vacuum conditions. It sublimes at 135°/0.01 mm. although degradation proceeds at a moderate rate under these conditions. The structure of an

---

* The checkers drew the proper amount of boron trichloride into a graduated cold trap and added it to the precooled toluene.

eight-membered ring of alternating boron and nitrogen atoms has been established for tetrazatetraborocines through an x-ray analysis.[3]

The hydrolytic stability of *sym-N,N',N'',N'''*-tetra-*t*-butyl-*B,B',B'',B'''*-tetrachloroperhydrotetrazatetraborocine is quite good; solutions of the compound in aqueous dioxane show only a low rate of hydrolysis even under reflux conditions.[2] The chlorine atoms in this ring structure are not readily replaced by alkyl groups or by hydrogen atoms; there is no evidence of reaction with lithium alkyls, Grignard reagents, or alkali metal tetrahydroborates.[2] However, the chlorines are readily displaced by treatment with certain pseudohalides, for example, isocyanate, isothiocyanate, isoselenocyanate, and azide.[2,4]

A recent, authoritative account of tetrazaborocine chemistry has been presented by Turner and Warne.[5]

REFERENCES

1. British patent number 937,430 (Sept. 18, 1963).
2. H. S. TURNER and R. J. WARNE: *Advan. Chem.*, **42**, 290 (1963).
3. P. T. CLARKE and H. M. POWELL: Abstr. of papers, XIXth International Congress of Pure and Applied Chemistry, p. 202, London, 1963.
4. British patent number 946,989 (Jan. 15, 1964).
5. H. S. TURNER and R. J. WARNE: *J. Chem. Soc.*, **1965**, 6421.

3B PHOSPHORUS

22. SUBSTITUTED DIFLUORO- AND DICHLOROPHOSPHINES

Submitted by J. G. MORSE,* K. COHN,* R. W. RUDOLPH,* and R. W. PARRY*
Checked by W. MAHLER†

Substituted dihalophosphines of the general formula X_2PY are known where X is either chlorine or fluorine and Y is either an

* Department of Chemistry, University of Michigan, Ann Arbor, Mich.
† Central Research Department, E. I. du Pont de Nemours & Company, Wilmington, Del.

alkylamino group or another halogen atom.   Some members of the series, particularly those where Y is Br or I, are of limited stability.   In general, these substituted dihalophosphines may be prepared by a group-interchange reaction of the form:

$$2X_3P + Y_3P \rightleftharpoons 3X_2YP$$
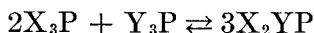
but the product is usually a complex mixture which is difficult to separate.   The substituted fluorophosphines of the general formula F_2PX where X is another halogen atom can also be prepared by the partial fluorination of the appropriate phosphorus trihalide, PX_3, but again a complex mixture usually results.[1,2,3]

An alternative general procedure for X_2PY compounds, which minimizes the separation problem, can be based upon the reactions of (dimethylamino)dichlorophosphine, $Cl_2PN(CH_3)_2$.[4,5,6] The latter compound can be prepared in yields above 90% by the action of dimethylamine on a slight excess of phosphorus trichloride.   Ether has been used as a solvent,[7] but the reaction of neat liquids is somewhat simpler and gives substantially higher yields of pure product.   The synthesis of $Cl_2PN(CH_3)_2$ and its conversion in steps to $F_2PN(CH_3)_2$, then F_2PCl, F_2PBr, or F_2PI are described here.

Data from this laboratory and others[8,9,10] indicate that the general procedure outlined for the synthesis of F_2PX compounds may be extended to the synthesis of the oxy derivatives of pentavalent phosphorus such as F_2ClPO and Cl_2FPO, but the detailed directions are not given here.   The mixed oxyhalides of phosphorus, like the corresponding mixed halophosphines, have not been obtained easily in pure form from complex reaction mixtures.[11,12]

■ *Caution.   Since many of the fluoro derivatives of the oxygen acids of phosphorus are known[10] to be extremely TOXIC and since detailed and reliable toxicity data on all the compounds considered here are not available, all these fluorophosphine derivatives should be handled as though they were highly toxic materials.*
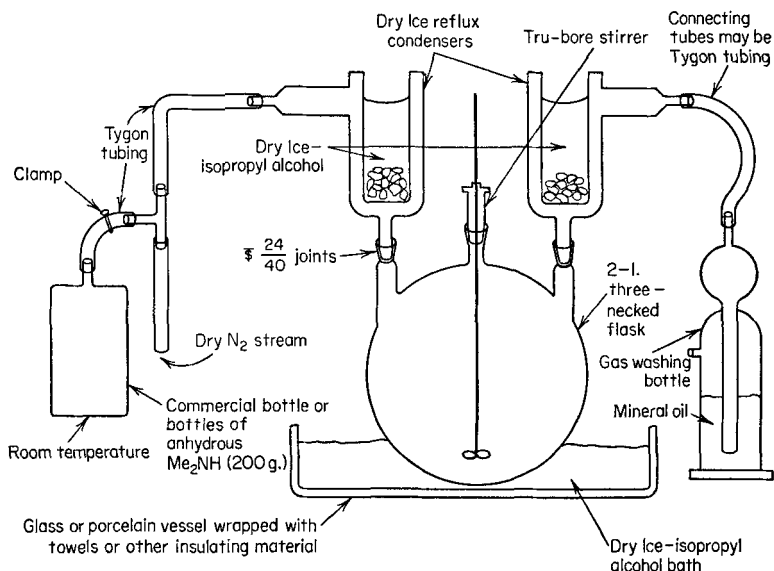
Fig. 16

A. (Dimethylamino)dichlorophosphine*

$$PCl_3 + 2HN(CH_3)_2 \rightarrow Cl_2PN(CH_3)_2 + [(CH_3)_2NH_2]Cl$$

Procedure

The apparatus shown in Fig. 16 is set up in the fume hood. The equipment is flushed with dry nitrogen, then a 200-ml. portion (314.8 g., 2.29 mols) of phosphorus trichloride is placed in the 2-l. reaction flask. The flask is partially immersed in the Dry Ice–isopropyl alcohol bath; the clamp to the alkylamine container is opened; and a stream of dry nitrogen is passed through the system at a rate of about 30 cc./minute measured at S.T.P. The nitrogen stream sweeps the anhydrous amine (200 g.) from the bottle into the reactor. The amine usually condenses on one of the two cold fingers of the reactor and drips into the chilled stirred phosphorus trichloride solution. Finely divided dimethylammonium chloride precipitates immediately.

* This was run by the checker on one-fourth scale.

The anhydrous dimethylamine may be obtained in convenient 100-g. bottles from Eastman Organic Chemicals, or any other source of pure dimethylamine may be utilized. *The nitrogen flow rate is important.* If the flow rate is too high, large amounts of the amine hydrochloride will be entrained, and the outlet tube will be blocked. At still higher flow rates, amine may pass through the reactor unchanged and low yields will result.

The addition of dimethylamine is usually completed within 3 hours. The reaction mixture is then stirred under nitrogen for an additional 3 hours while the system warms slowly to room temperature. The reflux condenser on the exit side (the right) of the reactor is quickly replaced by a distillation apparatus suitable for fractionation. The reaction mixture is then distilled under dry nitrogen at a pressure of 1 atmosphere. The fraction boiling at 149 to 151°/745 mm. is collected as product. In a typical experiment, this fraction weighed 304.8 g. or 94% of theory based on the dimethylamine used. *Anal.* Calcd. for $(CH_3)_2NPCl_2$: C, 16.46; H, 4.14; N, 9.60; Cl. 48.58. Found: C, 16.39; H, 4.16; N, 9.30; Cl, 48.68.

Properties

The product is a water-white liquid with an obnoxious odor. It boils at 150°/760 mm. It is reactive toward water and amines, and reacts slowly with atmospheric oxygen. On long standing, it deposits small amounts of dimethylammonium chloride.

B. (Dimethylamino)difluorophosphine

(Dimethylamino)difluorophosphine has been prepared directly from phosphorus trifluoride and dimethylamine[5,6] and also by the action of dimethylamine on (trichloromethyl)difluorophosphine.[13]   The most convenient procedure yet reported[4] appears to be the fluorination of $Cl_2PN(CH_3)_2$ using ant mony trifluoride or sodium fluoride as a fluorinating agent.

Procedure

$$(CH_3)_2NPCl_2 + 2NaF \xrightarrow{\text{Sulfolane}} (CH_3)_2NPF_2 + 2NaCl$$
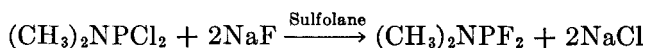
■ *Caution.* *(Dimethylamino)difluorophosphine is TOXIC. All procedures should be carried out in a good fume hood.*

The apparatus consists of a 2-l., three-necked, round-bottomed flask equipped with a mechanical stirrer, a pressure-equalized dropping funnel through which dry nitrogen can be added, and a reflux condenser, and is to be maintained at 0°. The outlet tube on the reflux condenser leads to a large U-tube trap, fitted with stopcocks on both sides, and immersed in a Dry Ice–isopropyl alcohol bath. The U-trap vents to a mineral oil bubbler. (See Fig. 17.) Sodium fluoride, 454 g. (10.8 mols) is added to the flask followed by approximately 1200 ml. of tetramethylene sulfone.* The system is then flushed thor-

---

* Available from Special Products Division, Phillips Petroleum Company, Bartlesville, Okla., under the name "Sulfolane."
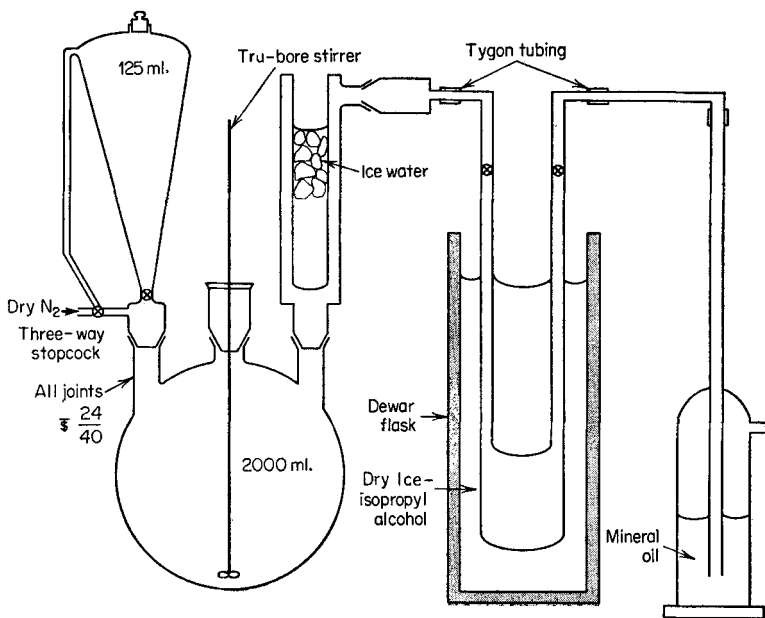
Fig. 17

oughly with dry nitrogen. (The nitrogen flow should continue throughout the reaction at a rate of 100 to 200 cc./minute S.T.P.) The 438 g. (3.00 mols) of (dimethylamino)dichloro-phosphine is added dropwise to the stirred suspension of sodium fluoride, present in about 1.8:1 excess.

After the addition of $Cl_2PN(CH_3)_2$ is complete, the reaction mixture is heated to 50 to 60° for one hour. The water is then drained from the reflux condenser, and the dropping funnel is replaced with a tube by means of which dry nitrogen can be bubbled through the mixture. With the mixture maintained at 50 to 60°, the (dimethylamino)difluorophosphine is carried into the U-tube trap by the nitrogen stream. This should be continued for a period of several hours to ensure a good yield. The U-tube trap is then attached to a vacuum system, and the contents are distilled through U-traps held at $-45°$ (chlorobenzene slush), at $-78°$ (Dry Ice–isopropyl alcohol), and at $-196°$ (liquid nitrogen). The fraction held in the $-78°$ trap is quite pure $F_2PN(CH_3)_2$. It may be further purified by distillation through a trap held at $-63°$ (chloroform slush), a trap held at $-95°$ (toluene slush), and a trap held at $-196°$ to catch the more volatile components. The product is retained at $-95°$.

In a typical experiment, the $-95°$ fraction weighed 157.5 g., 46.4% of theory based on the $Cl_2PN(CH_3)_2$ used. [This corresponds to 43.8% based on the amount of dimethylamine used to prepare the $Cl_2PN(CH_3)_2$.] *Anal.* Calcd. for F_2-$PN(CH_3)_2$: N, 12.39; P, 27.4; F, 33.6. Found: N, 12.40; P, 27.3; F, 33.0.

This preparation was checked on a one-tenth scale and the observed yield was 53%.

Properties

(Dimethylamino)difluorophosphine is a water-white liquid with the following physical constants: melting point, $-86°$;

vapor pressure, 25.9 mm./ $-23°$, 93.4 mm./0°, and 259.2 mm./ 22.1°; extrapolated normal boiling point, 47°; index of refraction at 25°, 1.3580. It is very reactive to water, amines, and moist air, and reacts slowly with atmospheric oxygen. *Because of its high vapor pressure, it should only be handled in a well-ventilated fume hood.* It can be stored in a sealed container at room temperature, or at $-78°$ in a glass vessel with a greased stopcock.

C. Halodifluorophosphines

All the halodifluorophosphines may be synthesized by the general reaction:

$$F_2PNR_2 + 2HX \rightarrow F_2PX + [R_2NH_2]X$$
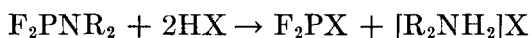
Since some of the reagents and products have both a relatively high vapor pressure and a high toxicity, a standard high-vacuum system[14,15] is recommended for carrying out the reactions and separating the products. Because some of the reactants and products attack mercury on long exposure, it is desirable to *avoid* mercury float valves and to protect manometers with stopcocks until pressure measurements are to be made. Essentially the same basic procedure is used for the preparation of chloro-, bromo-, and iododifluorophosphine.

1. Chlorodifluorophosphine

Procedure

In a typical experiment, a 12.18-mmol sample of hydrogen chloride is frozen into a 500-ml. reaction bulb on the vacuum system. (Liquid nitrogen is the refrigerant.) An 8.22-mmol sample of (dimethylamino)difluorophosphine* is then frozen into the bulb, the stopcock to the bulb is closed, and the system is allowed to warm slowly to 25°. Reaction is indi-

---

* The quantity of $F_2PN(CH_3)_2$ specified is in excess of the stoichiometric quantity. This slight excess assists in subsequent fractionation.

cated by the formation of clouds of amine hydrochloride. The system is held at 25° for about 15 minutes after the cloud in the reactor has settled. The products are then removed under vacuum into the vacuum line. Products from the reaction vessel (at 25°) are led through U-traps maintained at −112° (carbon disulfide slush), −160° (2-methylbutane slush), and −196° (liquid nitrogen). This procedure gives 6.05 mmols of pure chlorodifluorophosphine in the −160° trap. The yield is 99% on the basis of the hydrogen chloride charged. The excess of $F_2PN(CH_3)_2$ is retained at −112°, and a trace of phosphorus trifluoride is obtained in the −196° trap.

Properties

The chlorodifluorophosphine prepared in this manner has a vapor pressure of 312.0 mm. at −63.6° (chloroform slush). The infrared spectrum of the vapor shows absorptions at the following frequencies: 864.5 (s), 853.5 (vs), 543.7 (s), and 412.5 (m) cm.$^{-1}$ in the 4000 to 200 cm.$^{-1}$ region. Disproportionation of the liquid is fairly rapid; contact of the vapor with mercury also appears to hasten disproportionation. Thus chlorodifluorophosphine is best prepared just prior to use. It may be stored at −196°.

2. Bromodifluorophosphine

Procedure

The preparation and separation of products are conducted exactly as outlined for chlorodifluorophosphine except that hydrogen bromide is substituted for hydrogen chloride. Care should be taken to obtain pure hydrogen bromide.* (We have noted that some commercially available samples are contam-

* Pure hydrogen bromide can be conveniently prepared from the bromination of tetrahydronaphthalene as described by D. R. Duncan, INORGANIC SYNTHESES, **1**, 151 (1939).

inated with hydrogen chloride.)   Typically, a 7.01-mmol sample of bromodifluorophosphine is isolated at $-160°$ when 14.08 mmol of HBr and 7.82 mmol of $F_2PN(CH_3)_2$ are used as starting materials.   This corresponds to a 99% conversion of the hydrogen bromide.

Properties

The bromodifluorophosphine prepared as outlined above displayed a vapor pressure of 183 mm. at $-45.2°$ (chlorobenzene slush) (190 mm. in reference 2).   The infrared spectrum of the vapor shows absorptions at 858.9 (s), 851.0 (vs), 459.3 (s), and 391.3 (m) cm.$^{-1}$ in the 4000 to 200 cm.$^{-1}$ range.   As with the chloro derivative, bromodifluorophosphine is best prepared just before use and contact with mercury should be minimized.

3. Iododifluorophosphine

Procedure

This procedure differs from those outlined for the bromo and chloro derivatives in that an appreciable excess of (dimethylamino)difluorophosphine *cannot* be used because it is difficult to separate from iododifluorophosphine by fractional condensation.   Typically, (dimethylamino)difluorophosphine (6.38 mmol) and hydrogen iodide* (12.76 mmol) are condensed into a 500-ml. reaction bulb and allowed to warm slowly to 25°.   As reaction ensues,† the white solids are discolored by formation of red phosphorus triiodide which probably results from a disproportionation: $3PF_2I \rightarrow 2PF_3 + PI_3$.   Thus, when the products are separated by fractional condensation through $-126°$ (methylcyclohexane slush) to $-196°$, an appreciable amount of

---

* See C. J. Hoffman, INORGANIC SYNTHESES, **7**, 180 (1963).

† The checker observed this reaction to be quite vigorous but did not detect the formation of red phosphorus triiodide.

phosphorus trifluoride (0.25 mmol) is retained at −196°. The desired iododifluorophosphine (5.98 mmol) is held in the −126° U-tube. The yield is 94% based on the amount of (dimethyl-amino)difluorophosphine taken.

Properties

The iododifluorophosphine prepared as described above displays a vapor pressure of 74.5 mm. at −22.9° (carbon tetrachloride slush). The infrared spectrum of the vapor shows absorptions at 850.4 (s), 845.3 (vs), 411.8 (m), and 378.5 (m) cm.$^{-1}$ in the 4000 to 200 cm.$^{-1}$ region. Since iododifluoro-phosphine reacts with mercury, their contact should be avoided. The disproportionation of the vapor is enhanced at higher pressures, i.e., when p_0 = 37 mm., *ca.* 1% decomposition after 1 day, and when p_0 = 280 mm., *ca.* 6% decomposition after 1 day. Iododifluorophosphine is best prepared just before use. It may be stored at −196°.

REFERENCES

1. H. S. Booth and A. R. Bozarth: *J. Am. Chem. Soc.*, **61**, 2927 (1939).
2. H. S. Booth and S. G. Frary: *ibid.*, 2934 (1939).
3. R. R. Holmes and W. P. Gallagher: *Inorg. Chem.*, **2**, 433 (1963).
4. R. Schmutzler: *ibid.*, **3**, 415 (1964).
5. Sr. M. A. Fleming: doctoral dissertation, University of Michigan, 1963.
6. R. G. Cavell: *J. Chem. Soc.*, **1964**, 1996.
7. A. B. Burg and P. J. Slota: *J. Am. Chem. Soc.*, **80**, 1107 (1958).
8. Z. Skrowaczewska and P. Mastalery: *Roczniki Chem.* **29**, 415–430 (1955).
9. G. Schrader: British Intelligence Objectives Subcommittees Report 714, 47, (1947); *Chem. Rev.*, **48**, 225 (1951).
10. M. Pianka: *J. Applied Chem. (London)*, **5**, 109 (1955).
11. M. L. Delwaulle and F. Francois: *Compt. Rend.*, **222**, 1173 (1946).
12. H. S. Booth and C. G. Seegmiller: *J. Am. Chem. Soc.*, **61**, 3120 (1939); *ibid.*, 2937 (1939).
13. J. F. Nixon and R. G. Cavell: *J. Chem. Soc.*, **1964**, 2469.
14. R. T. Sanderson: "Vacuum Manipulation of Volatile Compounds," John Wiley & Sons, Inc., New York, 1948.
15. W. L. Jolly: "Synthetic Inorganic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N.J., 1960.

23. TRIPHENYLPHOSPHINE SELENIDE

$$(C_6H_5)_3P + KSeCN \xrightarrow{CH_3CN} (C_6H_5)_3PSe + KCN$$
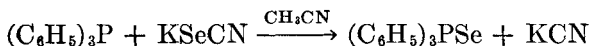
Submitted by PHILIP NICPON* and DEVON W. MEEK*
Checked by BRUCE M. FOXMAN† and F. A. COTTON†

Tertiary phosphine selenides have been prepared either by direct fusion of the tertiary phosphine with elemental selenium[1] or by refluxing the phosphine with selenium in an inert solvent.[2] In the case of a solid phosphine, such preparations often require numerous and time-consuming extractions to obtain the pure phosphine selenide.

The reaction of triphenylphosphine with potassium selenocyanate rapidly produces quite pure material in almost quantitative yield. The procedure outlined below is simple and appears to be particularly advantageous for preparation of selenide derivatives of solid phosphines.‡ Actual working time required for the synthesis is $1\frac{1}{2}$ to 2 hours, and the total elapsed time is less than 1 day.

■ *Although no extensive data are available for evaluating the toxicity of phosphine selenides, these compounds are similar to organophosphates and -thiophosphates, many of which are insecticides and related to the so-called "nerve gases."[3] A high toxicity for mammals has been noted in* $(RO)_2P(Se)X$ *compounds.[3] Consequently, the phosphine selenides should be handled carefully.*

Procedure

Triphenylphosphine (13.1 g., 0.05 mol) is dissolved in 60 ml. of warm ($\sim$60°) purified acetonitrile[4] in a 250-ml. Erlenmeyer

---

* The Ohio State University, Columbus, Ohio.
† Massachusetts Institute of Technology, Cambridge, Mass.
‡ Phosphines which are oxidized by air must be protected with a nitrogen atmosphere during the initial phase of the synthesis.

flask. A solution of potassium selenocyanate* (7.2 g., 0.05 mol, in 60 ml. of acetonitrile) is added rapidly with magnetic stirring. The white compound will begin crystallizing almost immediately. The mixture is stirred for one hour while it cools to room temperature; the solvent is then completely evaporated *in a hood.* The solid residue is transferred to a sintered-glass funnel and washed with six 50-ml. portions of distilled water to remove potassium cyanide and then with 10 ml. of cold absolute ethanol and finally with anhydrous ethyl ether. ■ *Caution. Since potassium cyanide is produced in the reaction, the filtrate and funnels must be handled carefully to prevent contact with acids.* (Alternatively, the phosphine selenide may be extracted from the potassium cyanide with benzene and then recovered by evaporating the benzene solution to dryness.)

The crude product, after drying for 12 hours over P_4O_{10} *in vacuo,* melts at 183 to 186°. The yield is 16.3 to 16.5 g. (96 to 97%).† An analytical sample can generally be obtained by one recrystallization from absolute ethanol; m.p. 187 to 188° (literature values 184 to 186°,[5] 187 to 188°[6]). *Anal.* Calcd. for $C_{18}H_{15}PSe$: C, 63.35; H, 4.43; Se, 23.11. Found: C, 63.36; H, 4.45; Se, 23.00.

Properties

Triphenylphosphine selenide crystallizes from absolute ethanol as small white needles which melt at 187 to 188°. The compound is very soluble in dichloromethane; moderately soluble in hot methanol, hot ethanol, hot acetonitrile, hot benzene, and hot 1-butanol; and insoluble in ether and water. The PSe infrared stretching frequency occurs at 562 cm.$^{-1}$ (Nujol mull).

The following phosphine selenides were prepared in 90 to

---

* Potassium selenocyanate was obtained from Alfa Inorganics, Inc.

† The checkers used Eastman White Label acetonitrile without purification and obtained 15.6 g. (92%) of crude material melting at 183 to 186°. After one recrystallization from absolute ethanol, the melting point was raised to 186.5 to 187.5° and the analytical data were quite satisfactory.

95% yields by the above procedure:[7] tri-*p*-tolylphosphine selenide, m.p. 198 to 198.5°; tri-*m*-tolylphosphine selenide, m.p. 139 to 140°; diphenyl[3-(dimethylamino)propyl]phosphine selenide, $(C_6H_5)_2P(Se)CH_2CH_2CH_2N(CH_3)_2$, m.p. 90 to 91°; and ethylenebis(diphenylphosphine selenide), $(C_6H_5)_2P(Se)CH_2CH_2P(Se)(C_6H_5)_2$, m.p. 194 to 195°.

The phosphine selenides form coordination complexes with Ag(I), Hg(II), Cd(II), Pd(II), and Pt(II) salts.[8,9]

REFERENCES

1. R. A. ZINGARO and R. E. McGLOTHLIN: *J. Chem. Eng. Data*, **8**, 226 (1963).
2. G. M. KOSOLAPOFF: "Organophosphorus Compounds," p. 98, John Wiley & Sons, Inc., New York, 1950.
3. W. O. NEGHERBON: "Handbook of Toxicology," Vol. III, Insecticides, pp. 536–569, W. B. Saunders Company, Philadelphia, Pa., 1959.
4. W. S. MUNEY and J. F. COETZEE: *J. Phys. Chem.*, **66**, 89 (1962).
5. A. MICHAELIS and H. SODEN: *Ann. Chem.*, **229**, 295 (1895).
6. C. SCRETTAS and A. F. ISBELL: *J. Org. Chem.*, **27**, 2573 (1962).
7. P. NICPON and D. W. MEEK: *Inorg. Chem.*, **5**, 1297 (1966).
8. P. NICPON and D. W. MEEK: paper presented at the 151st meeting of the American Chemical Society, Pittsburgh, Pa., March, 1966.
9. P. NICPON and D. W. MEEK: *Chem. Commun.*, **1966**, 398.

3C ARSENIC

24. *o*-PHENYLENEBIS(DIMETHYLARSINE)

$$(CH_3)_2As(O)OH + 2Zn + 4HCl \rightarrow$$
$$(CH_3)_2AsH + 2ZnCl_2 + 2H_2O$$
$$(CH_3)_2AsH + Na \xrightarrow{\text{tetrahydrofuran}} NaAs(CH_3)_2 + \tfrac{1}{2}H_2$$
$$2NaAs(CH_3)_2 + o\text{-}Cl_2C_6H_4 \rightarrow o\text{-}[(CH_3)_2As]_2C_6H_4 + 2NaCl$$
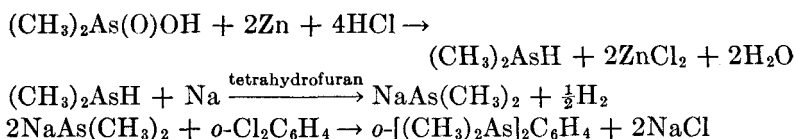
Submitted by R. D. FELTHAM* and WILLIAM SILVERTHORN*
Checked by F. N. JONES†

The bidentate ligand *o*-phenylenebis(dimethylarsine) (DAS) was first prepared by Chatt and Mann.[1] A wide variety of

* University of Arizona, Tucson, Ariz.
† Central Research Department, Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, Del.

interesting complexes of this ligand have subsequently been prepared and investigated by Nyholm and co-workers.[2] The original preparation of this compound consisted of four steps with an over-all yield of 20%. The low yield of this time-consuming synthesis has prevented the wide use of DAS as a chelating ligand. It was therefore desirable to find more direct and general methods for the preparation of DAS. A rapid two-step synthesis of this useful ligand is described below.

Procedure

■ *Caution. The arsenic compounds used here are extremely toxic and must be handled only in an efficient hood. Dimethylarsine is particularly dangerous because of its volatility (b.p. 36°/760 mm.) and its spontaneous flammability.*

Dimethylarsine can be prepared in high yield from cacodylic acid. This preparation has been carried out using several different quantities of materials. We recommend the following procedure which uses the apparatus shown in Fig. 18. The 1-l. three-necked flask is equipped with a dropping funnel, nitrogen inlet, gas outlet, and mechanical stirrer.* Plastic (Tygon) tubing must be used for all connections because dimethylarsine attacks rubber. The small trap *A* should have a volume of 30 to 50 ml. below the inlet tube. Drying tube *B* is made from size 35/25 spherical joints.† Trap *C* must have a volume of at least 100 ml. below the outlet tube; trap *C* plus the tubing and screw clamps at *D* and *E* are weighed before the run. The 1-l. flask is charged with 300 ml. of distilled water, 135 g. (0.98 mol) of cacodylic acid, and finally 225 g. of

---

* The zinc dust tends to clump badly; therefore, good mechanical agitation is essential. The stirrer seal should prevent appreciable leakage; a Tru-bore stirrer is satisfactory.

† An ordinary calcium chloride drying tube with a rubber stopper can be used but is less satisfactory.
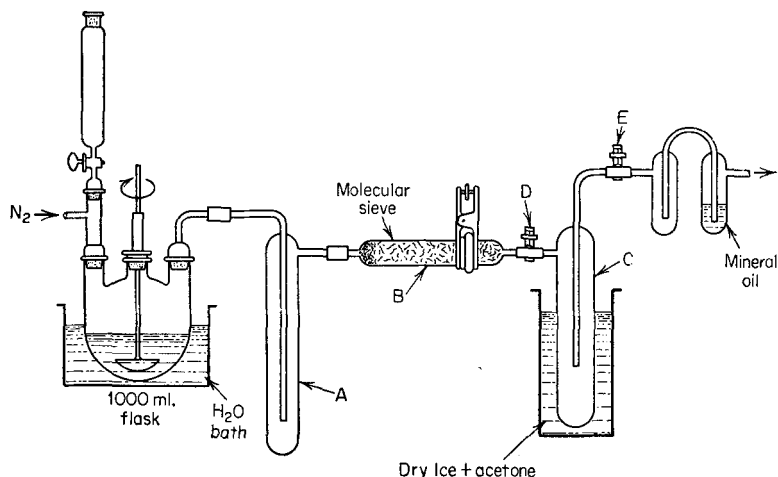
Fig. 18

zinc dust. ■ *Caution. Dimethylarsine begins to evolve slowly as soon as the zinc dust is added.* A stream of nitrogen slow enough to give 10 to 40 bubbles per minute in the bubbler is started and maintained throughout the reaction. The water bath surrounding the flask is heated to 40°, and 600 ml. of concentrated hydrochloric acid is added dropwise over a period of 45 minutes. The heat of the reaction will maintain the temperature of the water bath at 40 to 45°. When the addition is complete, the nitrogen stream is continued for 15 minutes. The clamp at *D* is closed. The arsine generator is demounted (■ *Caution, dimethylarsine*). Trap *C* is allowed to warm to room temperature as gases escape through the bubbler. The clamp at *E* is closed, and trap *C* plus the product and the tubing and clamps at *D* and *E* are weighed. The yield is 90 to 98 g. (87 to 94% based on cacodylic acid).

A 1-l. three-necked flask equipped with a nitrogen inlet, a high-speed stirrer,* and a Dewar condenser having a gas outlet

---

* A "Stir-o-Vac" stirrer obtained from Cole-Parmer Instrument and Equipment Company, Chicago, Ill. 60626, was satisfactory.

Dry Ice/acetone

Mineral oil

N₂ or
(CH₃)₂AsH/N₂

Petroleum
ether bath
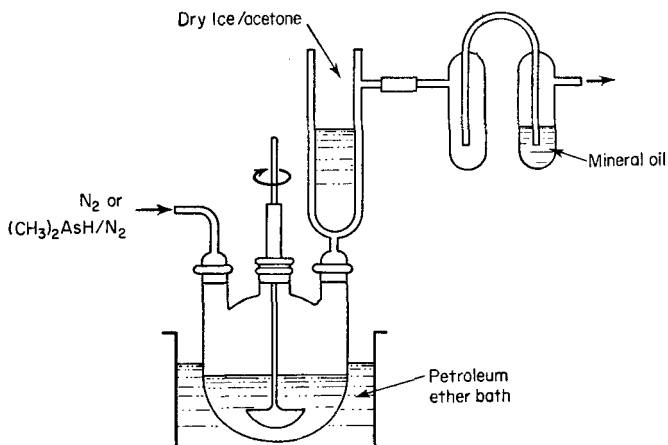
Fig. 19

(Fig. 19) is charged with 23.0 g. (1 mol) of sodium metal and 200 ml. of toluene. Sodium sand* is prepared under nitrogen in this flask in the usual manner.[3]   After the mixture cools to room temperature, most of the toluene is removed by means of a pipet, with a rapid flow of nitrogen through the flask.   Next, 200 ml. of tetrahydrofuran is added.   The system is flushed with nitrogen and the Dewar condenser is charged with Dry Ice–acetone.   The trap containing the dimethylarsine is placed in a water bath and connected to the round-bottomed flask. The dimethylarsine is swept by nitrogen flow into the sodium dispersion over a period of 60 to 90 minutes,† with the water bath at 40 to 50°.   The reaction is immediate and exothermic but not violent.   After the distillation of the dimethylarsine is complete,‡ the dimethylarsine inlet tube is replaced by a 125-ml.

---

* A 50% dispersion of sodium in paraffin, which was obtained from Alfa Inorganics, Inc., can be used successfully instead of the freshly prepared sodium sand.

† Faster addition of dimethylarsine causes aggregation of sodium.

‡ A small amount of higher-boiling liquid remains in the trap.   This residue is spontaneously flammable; it can be disposed of by opening both ends of the trap to air in the hood.

dropping funnel. A bath of ligroin (b.p. 60 to 90°) is placed around the round-bottomed flask. Then 76 g. (0.5 mol) of *o*-dichlorobenzene is added slowly over a period of 1 to 2 hours. The temperature of the bath is maintained between 20 and 25° by the addition of Dry Ice. The temperature in the flask will be warmer. After completing the addition of *o*-dichlorobenzene, the mixture is stirred for one hour and then the tetrahydrofuran is removed by vacuum distillation. Water (300 ml.) is added,* the mixture is again stirred for one hour, and the lower layer is allowed to settle. The lower layer is transferred by means of a pipet to a nitrogen-swept flask equipped for vacuum distillation through a Vigreaux column.† The product is fractionated, and the fraction boiling at 97 to 101°/1.1 mm. is collected. The yield is 40 to 54 g. (28 to 38% over-all).

Properties

DAS has $n_D^{25°}$ 1.6156 and $d_{25°}$ 1.3992; the nuclear magnetic resonance spectrum has a singlet at 8.83 τ and an A_2B_2 pattern at 2.62 τ. Although DAS is very oxygen-sensitive, it is readily stored in sample bottles with serum caps. Complexes of many metals have been prepared; exceptions include scandium, yttrium, lanthanum, and zinc.

REFERENCES

1. J. Chatt and F. G. Mann: *J. Chem. Soc.*, **1939**, 610.
2. For a partial listing of DAS complexes see: F. P. Dwyer and D. P. Mellor: "Chelating Agents and Metal Chelates," pp. 129–132, Academic Press Inc., New York, 1964.

* ■ *Caution. Water should be added slowly at first as small pieces of sodium may be present in the mixture. The checker destroyed sodium by adding 50 ml. of ethanol and stirring for one hour before removing tetrahydrofuran.*

† The checker used a 1.3- × 46-cm. spinning-band column. He obtained 40 g. (28%) of DAS boiling at 111 to 111.5°/2.5 mm.

3. W. JOLLY: "Synthetic Inorganic Chemistry," p. 161, Prentice-Hall, Inc., Englewood Cliffs, N.J., 1960.

CORRECTION

In the synthesis procedure for chlorine(IV) oxide in Volume IV, page 153, the required approximate amount of sodium chlorite should be 0.13 g. instead of 1.3 g.

SUBJECT INDEX

Names used in the cumulative Subject Index for Volumes I through X are based for the most part upon those adopted in Volume II (Appendix, page 257; see also the heading *Nomenclature* in this index), with a few changes that have been standardized and approved since publication of Volume II. No major changes seemed to be required for general conformity with the "Definitive Rules for Nomenclature of Inorganic Chemistry," 1957 Report of the Commission on the Nomenclature of Inorganic Chemistry of the International Union of Pure and Applied Chemistry, *J. Am. Chem. Soc.*, **82**, 5523–5544 (1960).

In line, to some extent, with *Chemical Abstracts* practice, more or less inverted forms are used for many entries; for example, silanes, germanes, phosphines, and the like; organic compounds; metal alkyls, aryls, 1,3-diketone and certain other derivatives: *Sodium, cyclopentadienyl-; Manganese, bis(2,4-pentanedionato)-* (instead of *Manganese(II) acetylacetonate*). In this way, or by the use of formulas, many entries beginning with numerical prefixes are avoided; thus: Bromogallate(III), tetra-; Cyanotungstic acid, $H_4W(CN)_8$. Numerical and some other prefixes are also avoided by restricting entries to group headings where possible: *Cobalt carbonyls* as the only entry for $[Co(CO)_3]_4$, with the formula given there; *Silicon chlorides; Sodium periodates* for the meta- and para-(ortho-); *Sodium sulfites* including $NaHSO_3$.

Boldface type is used to indicate individual preparations described in detail, whether for numbered syntheses or for intermediate products (in the latter case, usually without stating the purpose of the preparation). Group headings, as *Calcium orthophosphates*, are in lightface type unless all the formulas under them are boldfaced. Under a few general headings like *Ammonium compounds, substituted*, reference is made to a table of such compounds instead of listing all of the specific compounds that could be entered under the heading. However, each specific compound is entered in the Formula Index.

Under other general headings, such as *Chromium(III) complex compounds* and *Ammines*, used for grouping coordination compounds of similar types with names considered unsuitable for individual headings, formulas or names of specific compounds are not usually given. Hence it is imperative to consult the Formula Index for entries for specific complexes. The decision as to names of acids (and their salts and other derivatives) suitable for index entries has been based largely on the *Chemical Abstracts* list of anions ("The Naming and Indexing of Chemical Compounds from Chemical Abstracts," 1962, Appendix III, page 73N). Thus halo, cyano, oxalato, and a few other complexes are entered only under their specific names: *Potassium hexachlororhenate(IV); Potassium tetraoxalatouranate(IV)*. [One exception is the handling of phosphorus acid derivatives, such as thio, halo, amido,

for which names like *Sodium thiophosphate* have been preferred, with sometimes duplicate entries for the "new" organic phosphorus names (*CA, ibid.*, §407), as *Sodium phosphorothioate.*] In other cases, the cation has been omitted as of no significance on the basis of the emphasis given to a complex anion (as with less well-known ones): $[N(C_2H_5)_4]_2[MnI_4]$ is entered in the Subject Index only under Iodomanganate(II), tetra- (but the full formula beginning with $[MnI_4]$ is given in the Formula Index); $[(C_2H_5)_3NH]_2B_{12}H_{12}$ is entered as Decaborate, dodecahydro-, $B_{12}H_{12}{}^{2-}$ (and as $B_{12}H_{12}{}^{2-}$ in the Formula Index).

Two entries are made for compounds having two cations. Unsatisfactory names that have been retained for want of better ones or as synonyms are placed in quotation marks.

As in *Chemical Abstracts* indexes, headings that are phrases are alphabetized straight through, letter by letter, not word by word, whereas inverted headings are alphabetized first as far as the comma and then by the inverted part of the name. Roman numerals in Stock names are ignored in alphabetizing unless two or more names are otherwise the same. Footnotes are indicated by *n.* following the page number.

FORMULA INDEX

The chief aim of this Formula Index, like that of other formula indexes, is to help in locating specific compounds, or even groups of compounds, that might not be easily found in the Subject Index, or in the case of compounds in tables or of many complex coordination compounds, not to be found at all in the Subject Index. *All* specific compounds, or in some cases ions, with definite formulas (or even a few less definite) are entered in this index, whether entered specifically in the Subject Index or not. As in the latter index, **boldface type** is used for formulas of compounds or ions whose preparations are described in detail, in at least one of the references cited.

Wherever it seemed best, formulas have been entered in their usual form (*i.e.*, as used in the text) for easy recognition: PbO_2, $EuSO_4$, Si_2Cl_6, $ThOBr_2$. However, for compounds containing the more uncommon elements and groupings and also for complexes, the significant or central atom has been placed first in the formula in order to throw together as many related compounds as possible. This procedure usually involves placing the cation last (often of relatively minor interest, especially in the case of alkali and alkaline earth metals), or dropping it altogether: $[PtCl_4]K_2$; $[Al(C_2O_4)_3]K_3 \cdot 3H_2O$; $[Co(enta)]_2Ba$; $B_{12}H_{12}{}^{2-}$. The guiding principle in these decisions has been the chapter in the text in which the preparation of the compound in question is described. Where there is likely to be almost equal interest in two or more parts of a formula, two or more entries have been made: $AgClO_3$ and ClO_3Ag; Al_2Se_3 and Se_3Al_2; SF_6 and F_6S (halides other than fluorides are entered only under the other elements or groups in most cases); $NaNH_2$ and NH_2Na; NH_2SO_3H and $(SO_3H)NH_2$; $[(\pi\text{-}B_9C_2H_{11})_2Fe]^-$ and $[Fe(\pi\text{-}B_9C_2H_{11})_2]^-$.

Formulas for organic compounds are structural or semistructural so far as feasible: $CH_3COCH_2COCH_3$. Consideration has been given to probable interest for inorganic chemists, *i.e.*, any element other than carbon, hydrogen, or oxygen in an organic molecule is given priority in the formula if only one entry is made, or equal rating if more than one entry: $Zr(C_5H_7O_2)_4$, but $NaC\equiv CH$ and $CH\equiv CNa$. Names are given only where the formula for an organic compound, ligand, or radical may not be self-evident, but not for frequently occurring relatively simple ones like C_5H_5N (pyridine), $C_5H_7O_2$ (2,4-pentanedionato), C_5H_5 (cyclopentadienyl).

The formulas are listed alphabetically by atoms or by groups (considered as units) and then according to the number of each in turn in the formula rather than by total number of atoms of each element; formulas with special isotopes follow

197

the usual ones.   This system results in arrangements such as the following:

$NH_2SO_3NH_4$
$(NH_2)_2C_2H_4$ (instead of $N_2H_4C_2H_4$ or $N_2H_8C_2$)
NH_3

$Si(CH{=}CH_2)Cl_3$ FNa
$Si(CH_3)Cl_3$ FH
$Si(CH_3)_3Cl$ $F^{18}H$
$Si(C_2H_4Cl)Cl_3$ $F^{18}Na$
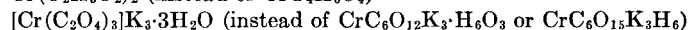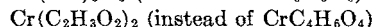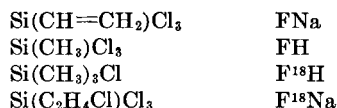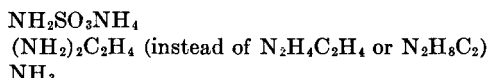
$Cr(CN)_6K_3$ (instead of $CrC_6N_6K_3$)
$Cr(C_2H_3O_2)_2$ (instead of $CrC_4H_6O_4$)
$[Cr(C_2O_4)_3]K_3 \cdot 3H_2O$ (instead of $CrC_6O_{12}K_3 \cdot H_6O_3$ or $CrC_6O_{15}K_3H_6$)
$[Cr(en)_2Cl_2]Cl \cdot H_2O$ ("en" is retained for simplicity and is alphabetized as such rather than as $C_2H_4(NH_2)_2$ or $(NH_2)_2C_2H_4$.   Similarly, "dien" stands for diethylenetriamine, "enta" for the anion $[-CH_2N(CH_2CO_2)_2]_2^{4-}$ of ethylenediaminetetraacetic acid, "o-phen" for o(or 1,10)-phenanthroline, "pn" for 1,2-propanediamine (propylenediamine), and "tetren" for tetraethylenepentamine.)
Footnotes are indicated by *n.* following the page number.