INORGANIC SYNTHESES

Volume XI

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INORGANIC SYNTHESES

Volume XI

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PREFACE

This is the first volume of INORGANIC SYNTHESES that has a special section (Chap. 1) devoted to syntheses of compounds that are of particular interest in the solid state. We hope that more syntheses of this type will appear in future volumes. This volume is also notable for the inclusion of reliable methods for preparing certain coordination compounds which are presently of great interest because of their catalytic activity. (See Syntheses 18, 19, and 20.) Another unique feature is Chap. 4, which is devoted entirely to organometallic syntheses that illustrate the use of potassium hydroxide as a deprotonating agent.

The reader will notice, from the *Contents*, that the arrangement of the syntheses is rather arbitrary. It is advisable to seek particular compounds in the *Subject* or *Formula Indexes.* The indexes in this volume cover only this volume (Volume XI). The cumulative indexes of Volume X should be consulted for compounds in Volumes I through X, inclusively. It is planned that the indexes in Volumes XI through XV be cumulative back to Volume XI.

Inorganic Syntheses, Inc., is a nonprofit organization whose purpose is to help synthetic chemists. An annual publication schedule is being maintained, and the Editorial Board tries to restrict the syntheses to compounds which are of current research interest. Consequently, all chemists should look upon the series not only as a useful collection of recipes but also as a desirable publication medium for interesting syntheses. Prospective contributors are asked to heed the instructions in the Notice to Contributors which follows. Contributions and requests for information regarding the series should be addressed to Professor Stanley Kirschner, Department of Chemistry, Wayne State University, Detroit, Michigan 48202. The editors of Volumes XII and XIII will be Professors R. W. Parry and F. A. Cotton, respectively.

It is a pleasure to acknowledge the advice and help which I have received from the members of Inorganic Syntheses, Inc., during my editorship. I also wish to thank all the checkers of the syntheses, whose efforts are to a large extent responsible for the reliability of the procedures.

William L. Jolly

NOTICE TO CONTRIBUTORS

The INORGANIC SYNTHESES series is published to provide all chemists with reliable procedures for the preparation of important inorganic and organometallic compounds. It is hoped that qualified chemists will further this aim by submitting significant syntheses, by offering to check syntheses, and by suggesting possible improvements in the series.

The Editorial Board is anxious to include syntheses of compounds which are of general current interest and, when possible, procedures which can be extended to a series of related compounds. The procedures should be the best available at the time of publication. In evaluating a submitted synthesis, the Board takes into consideration the simplicity of the procedure, the yield and purity of the product, the availability of the starting materials, and, above all, the safety of the operations. Every synthesis must be satisfactorily reproduced in a laboratory other 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, Mich. 48202, U.S.A. The manuscript should be typewritten in English, using the format and style of the present volume. Nomenclature should conform to "The Definitive Rules for Nomenclature of Inorganic Chemistry," *J. Am. Chem. Soc.*, **82,** 5523 (1960). Abbreviations should conform to those used in the journal *Inorganic Chemistry*.

The *Introduction* should include a brief critical summary of any useful alternative procedures, together with the merits of the procedure presented. It should include an indication of the importance and utility of the product and a discussion of any potential hazards associated with the synthesis. The *Procedure* should present detailed and unambiguous laboratory directions and be written so that it anticipates possible mistakes and misunderstandings 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 those physical and chemical characteristics of the product that are relevant to judging its purity and to handling it in an intelligent manner.

CONTENTS

Corrections

COPPER(I) IODIDE

Submitted by G. B. KAUFFMAN*

The synthesis of copper(I) iodide [G. B. Kauffman et al., *Inorganic Syntheses,* **6,** 3 (1960)] can be carried out to give a quantitative yield of product if one-half the amount of potassium iodide specified in the Procedure is used. The correct equation is:

$$2CuSO_4 + 2KI + 2Na_2S_2O_3 \rightarrow 2CuI + K_2SO_4 + Na_2SO_4 + Na_2S_4O_6$$

Addition of the potassium iodide–sodium thiosulfate solution from a buret is unnecessary because the product is not appreciably soluble in moderate excesses of potassium iodide. The second and third sentences in the Procedure should be replaced by the following: "A second solution is prepared by dissolving 16.6 g. (0.10 mole) of potassium iodide and 25 g. of sodium thiosulfate 5-hydrate in 100 ml. of water. The second solution is added to the first with continuous rapid stirring."

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DICHLOROBIS(4-CHLOROBUTENYL)DIPALLADIUM(II)

Submitted by JOHN R. DOYLE*

The compound referred to as dichloro-(1,4-butadiene)palladium(II) in Volume VI[1] has been correctly formulated as dichlorobis(4-chlorobutenyl)dipalladium(II) by B. L. Shaw.[2] The second equation on page 218 of Volume VI should read:

$$2PdCl_2(C_6H_5CN)_2 + 2C_4H_6 \rightarrow (ClC_4H_6PdCl)_2 + 4C_6H_5CN$$

References

1. J. R. Doyle, P. E. Slade, and H. B. Jonassen, *Inorganic Syntheses,* **6,** 216 (1960).
2. B. L. Shaw, *Chem. Ind.* (*London*), 1190 (1962).

* The University of Iowa, Iowa City, Iowa 52240.

NITROGEN COMPOUNDS

In an introductory paragraph to the section on Nitrogen Compounds in Chapter 3 of *Inorganic Syntheses*, **10**, 129 (1967), the statement is made that, classically, triazanium chlorides have been prepared by the reaction of hydrazine with mixtures of chloramine and ammonia. In fact, the only known preparative method for these compounds is the one explicitly detailed by H. H. Sisler and K. Utvary in the synthesis of 2,2-dimethyltriazanium chloride. [H. H. Sisler and K. Utvary, *Inorganic Syntheses*, **10**, 129 (1967).]

Inorganic Syntheses, Volume XI
Edited by William L. Jolly

Chapter One

THE SOLID STATE

1. BARIUM AND STRONTIUM MOLYBDATES(IV)

$$H_2 + BaMoO_4 \rightarrow BaMoO_3 + H_2O$$
$$H_2 + SrMoO_4 \rightarrow SrMoO_3 + H_2O$$

Submitted by JOHN DELUCA,* AARON WOLD,* and LOTHAR H. BRIXNER†
Checked by GEORGE BOUCHARD, JR.,‡ and M. J. SIENKO‡

The synthesis of barium and strontium molybdates(IV) was first reported by Scholder, Klemm, and Brixner.[1,2] The compounds are of interest because they contain molybdenum in the +4 oxidation state. Both compounds have the undistorted cubic perovskite structure, which is ideal for studying cation-anion-cation (superexchange) interactions. The compounds also exhibit metallic behavior, thus permitting study of the role of *d* electrons in the conduction process.

Procedure

The alkaline earth molybdates(IV) are formed by the reduction at elevated temperatures of the corresponding molybdates(VI) in an argon-hydrogen atmosphere.

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† Pigments Department, E. I. du Pont de Nemours & Company, Experimental Station, Wilmington, Del. 19898.

‡ Cornell University, Ithaca, N.Y. 14850.

Preparation of Reactants. The $AMoO_4$-type molybdates(VI) (A = Ba, Sr) are prepared by precipitation from basic solution according to the equation:

$$A(NO_3)_2 + (NH_4)_2MoO_4 \rightarrow AMoO_4 + 2NH_4NO_3$$

Solutions of the alkaline earth nitrates (0.33 *M*) are prepared by dissolving 0.1 mole of the desired reagent-grade nitrate, $A(NO_3)_2$, in 300 ml. of distilled water. Concentrated ammonium hydroxide is added drop by drop to adjust the solution to pH 10, as measured by a strip of Hydrion paper.

Solutions (1 *M*) of ammonium molybdate, $(NH_4)_2MoO_4$, are prepared by adding 44.15 g. of reagent-grade ammonium heptamolybdate (paramolybdate), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, to a 500-ml. volumetric flask containing 300 ml. of distilled water. Concentrated ammonium hydroxide is added drop by drop until a clear solution is obtained with a $pH \approx 10$, as measured with a strip of Hydrion paper. Distilled water is added to bring the volume of the solution to 500 ml.

In basic solution the heptamolybdate goes to the molybdate according to the equation:

$$Mo_7O_{24}^{6-} + 8NH_3 + 4H_2O \rightarrow 7MoO_4^{2-} + 8NH_4^+$$

The precipitation reaction is carried out in basic solution to ensure that the alkaline earth molybdates are obtained with an $AO:MoO_3$ ratio of 1:1.[3,4] The 300 ml. of the basic solution of the desired alkaline earth nitrate is slowly added to 200 ml. of the basic molybdate solution in a 600-ml. beaker while continuously stirring with a magnetic stirrer. A precipitate of the alkaline earth molybdate, $AMoO_4$, forms immediately. The solution is stirred for one-half hour. The supernatant liquid is decanted, and the precipitate is washed by successive additions of 200-ml. portions of distilled water, followed by decantation. This procedure is repeated until the wash water is neutral, as determined with a strip of Hydrion paper. The precipitate is collected by filtration, and the white powder is dried overnight in an oven at 115°.

Preparation of Products. A platinum reaction boat is carefully cleaned before each run by allowing it to remain immersed in fused potassium disulfate (pyrosulfate), $K_2S_2O_7$, at least at red heat, for 15 minutes. ■ *A fume hood is necessary!* Upon removal from the disulfate, the platinum boat is immersed in boiling water for one-half hour in order to remove any traces of disulfate. Finally, the boat is rinsed well with distilled water and dried in a clean drying oven at 115°. Extreme care is taken not to touch or otherwise contaminate the boat. (This can be easily accomplished by using a clean white card to support the boat whenever it is necessary to transfer it. A stiff length of wire bent at one end to form a hook can be used to move and position the boat.) Samples that are used for the study of transport properties should be as pure as possible because these properties are influenced markedly by trace impurities.

The clean platinum boat is then transferred to the previously cleaned fused-silica combustion tube (see Fig. 1), where it is heated at 800° in air to constant weight. A sample of the desired molybdate(VI) is introduced into the boat. The sample is heated to constant weight under the same conditions.

The prepared sample is returned to the combustion tube, and the end caps are secured in place. The temperature controller is set to maintain the desired reaction temperature. A slow stream of an oxygen-free, water-free mixture of argon (85%) and hydrogen (15%) is allowed to flow continuously through the combustion tube. This mixture of gases can be used without special precautions because it is not flammable or explosive.* A reaction temperature of 1000° is used to prepare $BaMoO_3$, and $SrMoO_3$ forms at 950°. With a flow rate corresponding to about 100 bubbles/minute, a reaction time of 8–12 hours is required.

The progress of the reduction is checked by periodic weight-loss determinations. The reduction is assumed to have gone to completion when the weight of the reaction product lies within

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* Cylinders of the gas are available from Air Reduction Co., 150 E. 42nd St., New York, N.Y.

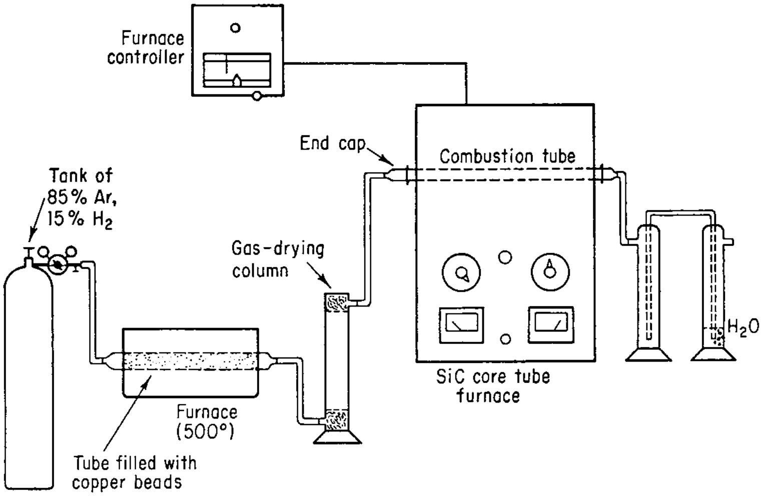

Fig. 1. Apparatus for the reduction of molybdates(VI) to molybdates(IV).

a fraction of a percent of the theoretical yield. The theoretical percent weight loss for $SrMoO_4$ is 6.46%; for $BaMoO_4$ it is 5.38%.

When a sample is removed from the combustion tube, care must be taken to prevent oxidation of the reduced sample. Before a sample boat is removed from the capped tube, it is allowed to cool to room temperature. This is accomplished by repositioning the combustion tube so that the sample boat is moved from the center of the furnace to a position outside of the furnace. The sample is allowed to remain in this position for one-half hour with the gas stream flowing over it before the end cap is removed and the boat is taken out.

If the sample requires further reduction, it is returned to the combustion tube and positioned just outside the furnace. The end cap is replaced, and the system is flushed with the gas mixture before again centering the boat in the hot zone of the furnace.

Properties

Barium molybdate(IV) is an intensely colored purple-red powder, and $SrMoO_3$ is a more intensely colored brick-red powder. The colors of both compounds become somewhat dulled upon exposure to air. The samples are best stored in sealed evacuated glass tubes. Samples prepared by the above procedure should be single-phase and homogeneous, as indicated by both microscopic and x-ray examination. Both compounds have the cubic perovskite structure. The cell parameters are 4.0400 ± 0.0003 A. and 3.9751 ± 0.0003 A. for $BaMoO_3$ and $SrMoO_3$, respectively. The lattice constants were calculated from x-ray diffraction patterns taken with a Philips 114.6-mm.-diam. camera at 25°, using K-α copper radiation ($\lambda = 1.5418$ A.). The α_1 and α_2 lines of the high-angle hkl reflections (422), (332), (420), and (411) were used for parameter determinations.[5] Accurate values were obtained by extrapolating a_0 vs. $\frac{1}{2}[(\cos^2\theta)/(\sin\theta) + \cos^2(\theta/\theta)]$, according to Nelson.[6]

Both $BaMoO_3$ and $SrMoO_3$ show metallic conductivity (resistivity increases with increasing temperature) over the temperature range −190 to 180°.

References

1. R. Scholder and W. Klemm, *Angew. Chem.*, **66,** 461–467 (1954).
2. R. Scholder and L. Brixner, *Z. Naturforsch.*, **10b,** 178–179 (1955).
3. E. Carrière and R. Lasri, *Compt. Rend.*, **207,** 1048–1049 (1938).
4. E. Carrière and A. Dautheville, *Bull. Soc. Chim. France*, **10,** 258 (1943).
5. L. H. Brixner, *J. Inorg. Nucl. Chem.*, **14,** 225–230 (1960).
6. J. B. Nelson and D. P. Riley, *Proc. Phys. Soc.*, **57,** 160 (1945).

2. CADMIUM DIGALLIUM(III) TETRASULFIDE

Submitted by A. G. KARIPIDES*† and A. V. CAFIERO*
Checked by AARON WOLD‡ and ROBERT KERSHAW‡

High-temperature chemical-transport reactions[1–3] afford a convenient means for the synthesis and crystal growth of a wide

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‡ Division of Engineering, Brown University, Providence, R.I. 02912.

variety of binary and ternary sulfides, selenides, tellurides, oxides, etc. Following Hahn[1] and Nitsche,[2] this preparation describes the synthesis and crystal growth of cadmium digallium(III) tetrasulfide, $CdGa_2S_4$, from gallium(III) sulfide and cadmium sulfide. The preparation of gallium(III) sulfide from gallium metal and hydrogen sulfide is also described.

The synthesis of cadmium digallium(III) tetrasulfide is carried out in an evacuated sealed tube in the presence of iodine. This allows the use of the same capsule for synthesis and crystal growth by chemical transport.[3] In this method the finely polycrystalline $CdGa_2S_4$ is transported through a temperature gradient with iodine. Iodine reacts with $CdGa_2S_4$ at the hotter end of the tube to form the respective volatile iodides and sulfur vapor. These species move through the temperature gradient to the cooler end of the tube, where reformation of $CdGa_2S_4$ occurs, often with the appearance of large crystals. Since the transporting agent, iodine, is released during recombination, only a small amount is needed to transport a large portion of starting material.

A. GALLIUM(III) SULFIDE

$$2Ga + 3H_2S \rightarrow Ga_2S_3 + 3H_2$$

Procedure

A quartz boat containing 5.57 g. (0.080 mole) of gallium metal* is placed in a silica-glass combustion tube. The combustion tube is placed in a tube-type furnace and fitted with a hydrogen sulfide inlet tube and paraffin-oil bubbler. The entire system which is to be heated is made of silica glass. The inlet tube should be long enough so that direct H_2S flow is over the gallium metal. All operations are performed in a well-

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* Alfa Inorganics, Inc., 2 Congress St., Beverly, Mass.; Gallard-Schlesinger Chemical Mfg. Corp., 580 Mineola Ave., Carl Place, L.I., N.Y.

ventilated hood because of the toxic nature of H_2S. The hydrogen sulfide* flow is started, and the temperature of the furnace is raised slowly to 950° and is held there for 2 hours. The furnace is then cooled to room temperature (H_2S flow continued); the product at this point is yellow because of the presence of gallium(II) sulfide. The mixture is ground in an agate mortar, returned to the combustion tube, and treated with H_2S as described above for an additional 3 hours. The product is again cooled under a hydrogen sulfide stream and removed at room temperature. Pure gallium(III) sulfide is white. If the product still has a yellow tinge, it is reground, and the process described is repeated. The yield is nearly quantitative.

B. CADMIUM DIGALLIUM(III) TETRASULFIDE

$$CdS + Ga_2S_3 \rightarrow CdGa_2S_4$$
$$CdGa_2S_4 + 4I_2 \rightleftarrows CdI_2 + 2GaI_3 + 4S$$

Procedure

A reaction tube is prepared as indicated in Fig. 2. The volume of the ampule *D* is determined, and the all-silica tube is thoroughly cleaned and dried before use. Before a seal is made at *A*, a small capsule *C* containing the correct amount of iodine is prepared and placed in the side chamber along with a steel bar *B*. For a reaction ampule *D* of volume 25 ml., the amount of iodine taken (5 mg./ml.) is 125 mg. (0.00049 mole). The iodine is contained in a thin-walled Pyrex tube under vacuum. Finally, a seal is made at *A* to close off the side chamber.

Cadmium sulfide† (1.226 g., 0.0085 mole) and gallium(III) sulfide (2.000 g., 0.0085 mole) are mixed thoroughly in an agate mortar. The powdered mixture is transferred to the reaction

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* Matheson Co., Inc., East Rutherford, N.J.

† Alfa Inorganics, Inc., Ventron Corp., Metal Hydride Div., 8 Congress St., Beverly, Mass.

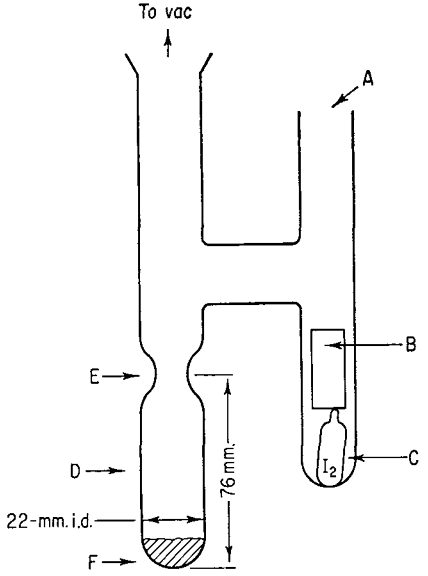

Fig. 2. Apparatus for the preparation of cadmium digallium(III) tetrasulfide.

ampule *D* by means of a long-stem funnel. The tube is attached to the vacuum system, and the entire tube and contents are degassed by slight warming. Evacuation is continued, and when complete (10^{-3} mm. or less),* the stopcock to the vacuum system is closed, and the iodine capsule *C* is broken by impact, using a strong magnet to raise the steel bar *B*. The iodine is then quickly sublimed through the arm, using a liquid nitrogen trap at *F*. The ampule is then sealed off at *E*, and is placed in the gradient-free region of the furnace.† The temperature is

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* The transport tube used by the checkers was 11 mm. i.d. × 20 cm. long, having a volume of 18 ml. The amount of iodine used was 90 mg. (5 mg./ml.). The sample was evacuated to less than 10^{-5} torr, and outgassed at 150° for 4 hours before the tube was sealed off.

† The checkers used a two-zone Hevi-Duty MK2012 furnace. The temperatures of the growth and charge zones were controlled with two West JP Guardsman controllers. The temperature gradient could then be readily set and maintained. In addition, the use of a two-zone furnace eliminated the need of cooling the sample twice and reversing the tube in the furnace. After the tube was placed in the Hevi-Duty furnace, the firing schedule was as follows: Initially, the growth zone was held for 20 hours at 800° and the charge zone at 700°. This allowed for reaction of the starting materials, and also back-transported any nuclei. The

raised to 700°, and the reaction is allowed to proceed for 8 hours or, for convenience, overnight. The furnace is cooled to room temperature, and the ampule is removed. The product appears as a pale yellow powder. The same tube is used as the crystal-growth vessel.

For best-quality crystal growth the end of the ampule must be free of sites of crystallization. To ensure the complete absence of microscopic seeds at the growth end, a reverse transport is performed initially. The ampule is placed in a furnace with the growth end at 700° and the other end at 600° or lower. The reverse transport is allowed to continue for several hours. Any microscopic cadmium digallium(III) tetrasulfide seeds are thereby rapidly transported back to the cooler end. The ampule is cooled to room temperature, and the above arrangement is reversed. The tube is then ready for final crystal growth. The end containing the polycrystalline $CdGa_2S_4$ is held at 700°, and the opposite growth end is kept at 675°. The temperature gradient may be achieved by utilizing the natural gradient present in a Kanthal wire-wound single-core furnace. While the central region of such a furnace is gradient-free, the natural temperature drop near the ends of the furnace provides a convenient means for obtaining a number of gradients. For the 100° or more gradient the ampule's cool end is placed very near the end of the core. The 25° gradient is sufficient for chemical transport and crystal growth. A larger gradient may be used, and transport is more rapid, although polycrystalline formation is encouraged. For the indicated temperatures, transport is allowed to proceed for 4 days; then the furnace is cooled slowly to room temperature, and the ampule is removed. The light yellow crystals* of $CdGa_2S_4$ appear at the cool end. Excess

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growth zone was then lowered to 675°, and the charge zone was maintained at 700°. After 100 hours both zones were allowed to cool to room temperature, and the ampule was removed.

[*] Using an ampule of 22 mm. i.d., crystals *ca.* 6 × 2 × 2 mm. have been obtained; using an ampule of 11 mm. i.d., crystals *ca.* 3 × 0.5 × 0.5 mm. have been obtained.

iodine may easily be sublimed from the crystals before the ampule is opened.

Properties

The ternary sulfide, $CdGa_2S_4$, forms pale yellow tetragonal crystals with $a = 5.56$ A. and $c = 10.1$ A. Single-crystal x-ray analysis is in agreement with the reported unit-cell dimensions.[1] The light yellow color of the crystals is probably due to the presence of a small amount of iodine. The crystals are piezoelectric. The crystalline compound is stable toward air and water at room temperature.

References

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2. R. Nitsche, H. U. Bölsterli, and M. Lichtensteiger, *J. Phys. Chem. Solids*, **21**, 199 (1961).
3. H. Schafer, "Chemical Transport Reactions," Academic Press Inc., New York, 1961.

3. SINGLE CRYSTALS OF TRIIRON TETRAOXIDE

$$3Fe_2O_3 + CO \xrightarrow{CO_2} 2Fe_3O_4 + CO_2$$

Submitted by ROBERT KERSHAW* and AARON WOLD*
Checked by NORIO TASHIMA† and EPHRAIM BANKS†

Chemical-transport reactions have been used[1] to prepare single crystals of triiron tetraoxide (magnetite) and other ferrites, which comprise the majority of all known ferrimagnetic mate-

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† Polytechnic Institute of Brooklyn, Brooklyn, N.Y. 11201.

rials. Previously, Smiltens[2] had prepared well-characterized triiron tetraoxide single crystals, using a modified Bridgman-Stockbarger technique. The crystals were grown under a carbon dioxide atmosphere; then carbon monoxide was introduced, and the ratio of these gases was changed gradually as the temperature was varied during the cooling process. This procedure yielded stoichiometric crystals. The techniques of flame fusion[3] and hydrothermal growth[4] have also been used to grow magnetite single crystals, but their quality, in general, has usually been poor. The work of Darken and Gurry[5] suggested that stoichiometric magnetite powder could be prepared by heating iron(III) oxide in an atmosphere of CO and CO_2. Pure Fe_3O_4 was prepared by this method.

In this procedure, crystals of Fe_3O_4 are grown by the method of chemical transport, as outlined by Hauptman.[1] The powdered charge material reacts with the transporting agent to form a more volatile compound. This vapor diffuses along the tube to a region of lower temperature, where some of the vapor undergoes the reverse reaction. The starting compound is reformed, and the transport agent is liberated. The latter then diffuses to the hot end of the tube and again reacts with the charge. Under the proper conditions the compound may be deposited as crystals. The transport of Fe_3O_4 using HCl as the transport agent occurs by the reversible reaction:

$$Fe_3O_4 + 8HCl \rightleftarrows FeCl_2 + 2FeCl_3 + 4H_2O$$

The same transport procedure has been used to prepare crystals of other ferrites, such as $NiFe_2O_4$.

Procedure

A weighed silica boat (10 cm. long × 2 cm. wide × 1.3 cm. deep) is filled with approximately 3 g. (0.0188 mole) of iron(III) oxide* and placed in a silica combustion tube. The tube is

* Johnson Matthey Company, 608 5th Ave., New York, N.Y.

heated in a tube furnace, under a slow flow of dry oxygen, to 610° for 3 hours. The tube is then shifted so that the boat is outside the furnace. When the boat has cooled, it is removed and weighed quickly to obtain the actual weight of Fe_2O_3 used.

The boat is returned to the furnace, and the gas train, shown in Fig. 3, is connected. A mixture of carbon monoxide and carbon dioxide* in the ratio of 1:2 is passed over the sample. After all air has been flushed out of the tube, the furnace is heated to 610°, and the reduction is allowed to proceed for 8 hours. The sample is quenched by shifting the combustion tube to bring the boat outside the furnace, and the gas flow is immediately changed to nitrogen by turning the stopcock. When cool, the boat is removed and weighed. The composition of the powder may be determined by the weight change, since each oxygen atom lost corresponds to the reduction of two Fe(III) ions to two Fe(II) ions.

Single-crystal Growth. The transport tube is prepared by closing one end of a 25-cm. length of 13-mm.-i.d. silica tubing and sealing the other end to an $\frac{18}{9}$ Vycor ball joint. After the tube has been cleaned with aqua regia and dried, a 1-g. charge of Fe_3O_4 is added through a long-stemmed funnel, and the tube

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* Matheson Co., Inc., East Rutherford, N.J.

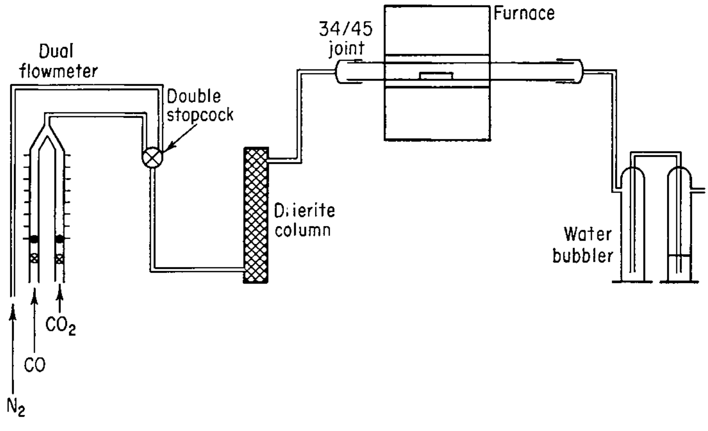

Fig. 3. Gas train used to prepare Fe_3O_4.

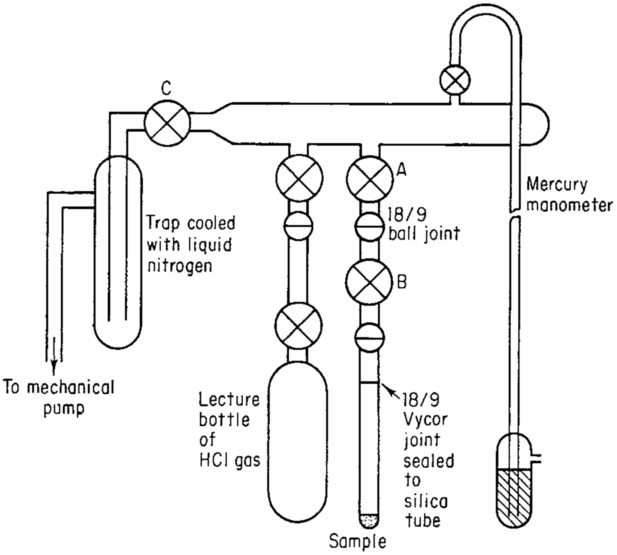

Fig. 4. Vacuum system used to prepare transport tubes.

is connected to stopcock *B* on the vacuum system shown in Fig. 4. When the pressure in the system has been reduced to less than 10^{-3} mm., the sample is outgassed by heating to about 300°. Stopcock *C* is then closed, and the system is pressurized with hydrogen chloride gas* to a pressure of 10 mm., as measured with the mercury manometer. Stopcocks *A* and *B* are then closed, the joint between them is separated, and the transport tube is sealed off to a length of 20 cm. with an oxy-hydrogen flame. This tube is then centered in the transport furnace, and the temperature-controller thermocouples are placed at its ends. A Hevi-Duty MK2012 furnace, rewired to give two independently controllable temperature zones, may be used in these experiments. It has been found that a 2-cm.-thick firebrick baffle was needed at the junction of the two zones in order to obtain a satisfactory temperature profile in this relatively large diameter (6 cm.) furnace. The temperature of the empty, or

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* Matheson Co., Inc., East Rutherford, N.J.

growth, zone is raised to 1000°, while the end of the tube with the powder, or charge, zone is left at room temperature. This back transport lasts for 24 hours, and cleans the growth zone of stray nuclei by causing them to transport to the charge zone, where they cannot interfere with crystal growth. The growth-zone temperature is then lowered to 750°, and the charge zone raised to 1000°. Transport is allowed to proceed for 10 days, after which time the charge-zone temperature is reduced to 750°. In about one hour, when equilibrium has been reestablished, both heaters are turned off. When the furnace has cooled to room temperature (usually overnight), the transport tube is removed and opened.

Properties

Triiron tetraoxide produced as described is a black, strongly magnetic powder. The x-ray powder-diffraction pattern can be indexed on the basis of a cubic unit cell with $a_0 = 8.396$ A. The crystals grown by chemical transport are well-formed octahedra, with shiny faces measuring up to 5 mm. across. When the crystals are ground up and x-rayed, the resulting pattern is identical with that of the starting material. Total iron may be determined by titrating a reduced solution (silver reductor) with cerium(IV). Iron(II) may be determined by dissolving the sample in a vanadium(V) solution and titrating with permanganate. *Anal.* Calcd. for Fe_3O_4: total Fe, 72.36; Fe(II), 24.12. Found (powder): total Fe, 72.66; Fe(II), 23.78. Found (crystal): total Fe, 72.83; Fe(II), 23.65.

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Chapter Two

BORON-HYDROGEN COMPOUNDS

4. DIBORANE

$$KBH_4 + H_3PO_4 \rightarrow \tfrac{1}{2}B_2H_6 + H_2 + K^+ + H_2PO_4^-$$

Submitted by **ARLAN D. NORMAN***† and **WILLIAM L. JOLLY***
Checked by **DENNIS SATURNINO**‡ and **SHELDON G. SHORE**‡

Diborane can be prepared by a variety of methods, the most common being the reduction of boron trihalides with active metal hydrides[1,2] and the reaction of hydroborate salts with boron trifluoride,[1,3] tin(II) chloride,[4] sulfuric acid,[5] methanesulfonic acid,[6] orthophosphoric acid,[6,7] or polyphosphoric acid.[7] Although diborane is commercially available in bulk quantities, we have found the reaction of potassium hydroborate, KBH_4, with 85% orthophosphoric acid to be convenient for the rapid preparation in a vacuum line of small quantities of this material.§

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§ It is unsafe to accumulate large quantities (more than 0.02 mole) of diborane in the laboratory. When it is desired to use large amounts of diborane as an intermediate, with the generated diborane being passed directly into a reaction mixture, the $NaBH_4$-BF_3 procedure of Zweifel and Brown[3] can be used.

Using this method, diborane is obtained in only 40–50% of the theoretical yield; however, the absence of volatile solvents, the high purity of the product, and the simplicity of the reaction apparatus make this method superior.

By using approximately 100% orthophosphoric acid,[7] the yield of diborane is increased to 60–65%. However, under these conditions extensive foaming occurs, necessitating the use of an overhead stirrer in the reaction apparatus. The advantage of this increased yield is offset by the relative unavailability of the more concentrated acid and the increased difficulty of stirring.

■ **Caution.** *This synthesis is not suitable for the preparation of diborane in a flow system at atmospheric pressure because flaming of the reaction mixture and/or the formation of unwanted reduction products (i.e., phosphine) may occur. Inasmuch as diborane reacts violently with oxygen and is extremely poisonous, it must be handled either in a vacuum line or an oxygen-free reaction system at all times.*

Procedure

A 500-ml. reaction vessel equipped with an efficient magnetic stirrer and a sidearm addition tube, as shown in Fig. 5, is connected to a vacuum line in such a way that the volatile reaction products can be removed through a series of four U-tube traps. A plug of glass wool in the neck of the reaction vessel prevents traces of nonvolatile materials from being carried into the vacuum line. It is also convenient to have a mercury manometer in the system so that gas pressure can be monitored during the reaction. Thirty milliliters of reagent-grade orthophosphoric acid (85% H_3PO_4) is poured into the reaction vessel, 1.6 g. (0.0297 mole) of fresh carbonate-free potassium hydroborate* is placed in the sidearm, the sidearm is attached to the

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* Metal Hydrides Inc., Beverly, Mass.

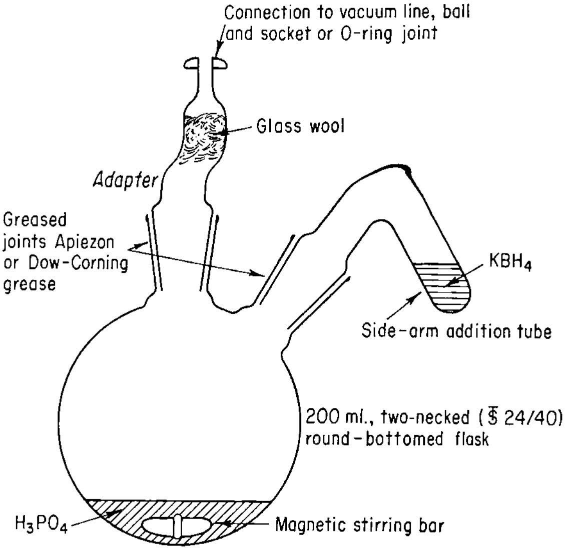

Fig. 5. Apparatus for the preparation of diborane.

reaction vessel as shown in Fig. 5, and the reaction vessel is evacuated for a period of 0.5 hour. At the end of this time the trap nearest the reaction vessel is cooled to −78° (Dry Ice–acetone mixture) and the three remaining traps are cooled to −196° (liquid nitrogen).

Diborane production is begun by carefully rotating and tapping the sidearm until the powdered potassium hydroborate begins to drop onto the surface of the rapidly stirred acid. Gas evolution begins immediately, and foaming of the reaction mixture occurs. For maximum yield and minimum foaming, care should be taken to avoid the sudden addition of large quantities of potassium hydroborate. The potassium hydroborate should be added slowly enough (over a period of 1–1.5 hours) so that the pressure in the reaction system never exceeds 5 mm. and the layer of foam never becomes thicker than 2.5 cm.*

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* The potassium hydroborate can be added more rapidly (over a period as short as 20 minutes) if a lower yield (*ca.* 25%) is acceptable.

Pumping is continued for 15–30 minutes after the last of the potassium hydroborate has been added, in order to ensure complete removal of the diborane prior to detachment of the reaction vessel from the vacuum line. The condensate in the −78° trap consists mainly of water and traces of trapped diborane, and can be discarded. The diborane, condensed in the −196° traps, is purified by passage through a −111.6° (carbon disulfide slush) into a −196° trap. Traces of material which condense at −111.6° may be discarded. Typically, from 6 to 7 mmoles of diborane is obtained from this reaction. The reaction may be conveniently scaled up (by no more than a factor of 3!) for the preparation of larger quantities, provided that a correspondingly larger reaction vessel is used to accommodate the additional foam.

Properties

Diborane prepared by this method has a vapor pressure at −111.6° of 225 ± 1 mm., a value identical with that reported in the literature.[8] The infrared spectrum[9] shows absorptions at 3670(w), 2625(s), 2558(s), 2353(w), 1853(m), 1602(vs), 1197(s), 1178(s), 1154(s), and 973(m, sh) cm.$^{-1}$. The mass spectrum has peaks from m/e 10–13 and from m/e 21–27, attributable to BH_x^+ and $B_2H_x^+$ ions, respectively. A small peak at m/e 44 arising from a trace of carbon dioxide ($<0.1\%$) is also observed in some cases.

Diborane may be stored in the gas phase at room temperature for several days without appreciable decomposition. On long standing, hydrogen and higher boron hydrides are formed. These decomposition products may be removed by freezing the material at −196°, pumping off the hydrogen, and then distilling the diborane through a −130° trap (*n*-pentane slush) into a −196° trap.

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5. *closo*-1,2-DICARBADODECABORANE(12)

[*1,2-Dicarbaclovododecaborane*(*12*)]

Submitted by CHARLES R. KUTAL,* DAVID A. OWEN,* and LEE J. TODD*
Checked by ROBERT C. STAFFORD† and NEIL R. FETTER†

Two methods have been reported for the preparation of *closo*-1,2-dicarbadodecaborane(12) (*ortho*-carborane). The first procedure involves the direct reaction of acetylene with a (Lewis base)$_2$B$_{10}$H$_{12}$ compound.[1–4] The second procedure involves the oxidative degradation of 1,2-bis(hydroxymethyl)-*closo*-1,2-dicarbadodecaborane(12).[3]

The first method requires a rather elaborate apparatus for the purification and handling of gaseous acetylene; the second method is simpler and possibly safer. This synthesis is a modification of the second method, which gives reproducible yields of good-quality carborane.

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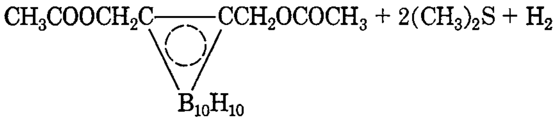
A. 1,2-BIS(ACETOXYMETHYL)-*closo*-1,2-DICARBADODECABORANE(12)

$$B_{10}H_{14} + 2(CH_3)_2S \xrightarrow{C_6H_6} [(CH_3)_2S]_2B_{10}H_{12} + H_2$$

$$[(CH_3)_2S]_2B_{10}H_{12} + CH_3COOCH_2C \equiv CCH_2OCOCH_3 \xrightarrow{C_6H_6}$$



$$CH_3COOCH_2C\text{—}CCH_2OCOCH_3\ (B_{10}H_{10}) + 2(CH_3)_2S + H_2$$

Procedure

In a dry 1-l. three-necked flask fitted with a magnetic stirrer and reflux condenser topped with a nitrogen inlet are placed 61.2 g. (0.50 mole) of sublimed decaborane* and 320 ml. of benzene which has been dried by percolation through Linde 4-A molecular sieve. Dimethyl sulfide (88.2 ml., 1.2 moles) is added by syringe to the reaction flask. The mixture is stirred at reflux for 6 hours. During this period, the solution turns yellow, and hydrogen is evolved. The reaction flask is cooled to room temperature, and 86.7 g. (0.510 mole) of 2-butyne-1,4-diol diacetate† is added through the condenser in one portion. The added reagent is washed down the condenser with 30 ml. of dry

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* ■ **Caution.** *The decaborane is purified by sublimation at 60° at 10^{-4} mm. The sublimation apparatus should be situated in a hood which is well shielded. If air should accidentally contact decaborane at elevated temperatures, a violent oxidative decomposition might result. Decaborane is toxic; therefore one should avoid breathing the vapor or allowing the compound to contact the skin.*

† The 2-butyne-1,4-diol diacetate (b.p. 92–94°/3 mm.; m.p. 30–31°) is prepared by esterification of 2-butyne-1,4-diol with acetyl chloride in pyridine. The ester is stored in a vacuum desiccator over phosphorus pentaoxide. The 2-butyne-1,4-diol may be purchased from General Aniline and Film Corporation.

benzene. The mixture is stirred at room temperature until the mild exothermic reaction subsides. Then the mixture is refluxed for another 10 hours. After the reflux period, the dimethyl sulfide and benzene are removed under vacuum with a rotary evaporator.* The reaction flask containing the remaining orange liquid is fitted with a reflux condenser and magnetic stirrer. Methanol, 150 ml., is slowly added† at room temperature to the flask with stirring. The mixture is stirred at room temperature for 5 hours and then cooled to approximately −10° (rock-salt–ice bath). A light yellow solid crystallizes from solution.‡ Additional product is obtained from the filtrate by cooling to −10° and adding water to the mixture drop by drop.§ The crude, dry, light yellow product (108 g., 75% yield) can be further purified by recrystallization from methanol. It may be used without further purification in part B.

Properties

The 1,2-bis(acetoxymethyl)-*closo*-1,2-dicarbadodecaborane(12) is an air-stable white crystalline solid, m.p. 42–43°. It is soluble in most common organic solvents and insoluble in water. The infrared spectrum of the compound in carbon tetrachloride solution contains absorption bands at λ max. 3000(w), 2550(s), 1740(s), 1430(s), 1380(m), 1360(m), 1210(s), and 1060(m) cm.$^{-1}$. The proton nuclear magnetic resonance spectrum ($CDCl_3$ solution) exhibits peaks at 5.32 (CH_2) and 7.88 (CH_3) τ.

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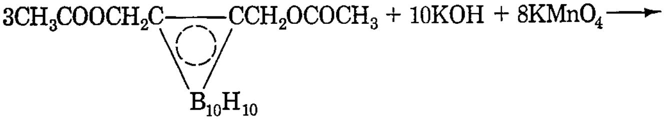
* ■ **Caution.** *The boron hydride products should be concentrated at as low a temperature as possible under vacuum to avoid the possibility of an explosion. A safety shield is recommended.*

† Methanol is used to decompose boron hydride by-products to borates and hydrogen. This reaction can be very vigorous, and the solution may reach reflux temperatures.

‡ In some instances vigorous scratching is required to obtain crystallization.

§ If too much water is added initially, a viscous oil is obtained instead of crystals.

B. *closo*-1,2-DICARBADODECABORANE(12)



$$3CH_3COOCH_2C\text{—}CCH_2OCOCH_3 \,(B_{10}H_{10}) + 10KOH + 8KMnO_4 \longrightarrow$$

$$3B_{10}C_2H_{12} + 6CH_3COOK + 8MnO_2 + 6K_2CO_3 + 8H_2O$$

Procedure

In a 3-l. three-necked flask fitted with a stirrer and gas exit tube are placed 108 g. (0.375 mole) of 1,2-bis(acetoxymethyl)-*closo*-1,2-dicarbadodecaborane(12) and 1.7 l. of 20% potassium hydroxide solution. The mixture is stirred at room temperature for 5 hours or until an immiscible layer (the carborane diester) is no longer present. The reaction flask is then cooled with an ice bath, and 400 g. (2.53 mole) of finely divided potassium permanganate is added slowly with stirring over an 8-hour period.* The temperature is maintained between 0 and 10° during the reaction. The mixture is transferred to a 4-l. beaker, which is maintained at 0°, and approximately 350 g. of potassium disulfite is added. This is followed by addition of approximately 600 ml. of ice-cold 35% sulfuric acid.† A yellow solid (crude carborane) collects on the surface of the light pink solution. The solid is

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* The finely divided potassium permanganate must be added slowly or it will form large chunks of only partially consumed oxidant. After the 8-hour period, if the liquid phase is not green (presence of MnO_4^{2-} ion), the desired oxidation reaction is incomplete, and the product will be difficult to purify. Addition of more potassium permanganate is recommended.

† This part should be carried out in the hood *immediately* after the oxidation reaction. Remaining oxidant will slowly destroy some of the product if the mixture is allowed to stand. The amounts of acid and disulfite recommended above may not be sufficient to remove the MnO_2, and additional small amounts of these reagents may be required.

collected and mixed with 100 g. of 8-mesh anhydrous calcium chloride. This mixture is extracted with *n*-pentane for 28 hours, using a Soxhlet extractor. The colorless carborane separates from the pentane extract, and is isolated by filtration and dried. Carborane of analytical purity is obtained by sublimation (45°/0.01 mm.). The overall yield is 32.4 g. (45% based on decaborane).*

Properties

closo-1,2-Dicarbadodecaborane(12) is an air-stable, white, sublimable solid, m.p. 320°.† This compound is very soluble in benzene, ethers, and alcohols and less soluble in aliphatic hydrocarbons. The infrared[5,6] and ^{11}B nuclear magnetic resonance spectra[7] have been reported.

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* The checkers obtained yields of carborane from two preparations of 47.5 and 46% with melting points of 300 and 297°, respectively, after extraction from pentane.

† The melting point must be obtained in an evacuated sealed tube. The melting point is a very strict criterion of purity. Impurities which depressed the melting point as much as 25° could not be detected in the infrared spectrum or the elemental analysis.

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6. POLYHEDRAL HYDROBORATES, UNDECAHYDROUNDECABORATE, NONAHYDRONONABORATE, AND OCTAHYDROOCTABORATE

($B_{11}H_{11}{}^{2-}$, $B_9H_9{}^{2-}$, *and* $B_8H_8{}^{2-}$)

Submitted by **F. KLANBERG** and **E. L. MUETTERTIES***
Checked by **ALFRED L. MOYE†** and **JAMES C. CARTER†**

Polyhedral hydroborate anions (commonly referred to as polyhedral borane anions in the current literature) of generic formula $B_nH_n{}^{2-}$ have assumed an unusual status in inorganic chemistry within recent years, not only because of their high thermal and hydrolytic stability, but also because of the wide range of geometries which the boron atom skeletons in compounds of the series $B_nH_n{}^{2-}$ ($n = 6$–12) can adopt.[1,2] Convenient syntheses for the $B_{10}H_{10}{}^{2-}$ and $B_{12}H_{12}{}^{2-}$ polyhedral ions,[3,4] as well as for the polyhedral fragment ions $B_3H_8{}^-$ and $B_{11}H_{14}{}^-$, have already been described.[4] The preparations described below capitalize on the ready availability of salts of the last two ions and provide experimentally simple routes to the nonahydrononaborate, $B_9H_9{}^{2-}$, octahydrooctaborate, $B_8H_8{}^{2-}$, and undecahydroundecaborate, $B_{11}H_{11}{}^{2-}$, anions. The dry pyrolysis of CsB_3H_8 is also of interest for the preparation of the decahydrodecaborate anion because it circumvents the use of decaborane, an expensive and occasionally scarce compound, as a starting material in the synthesis of $B_{10}H_{10}{}^{2-}$.

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A. CESIUM TETRAMETHYLAMMONIUM UNDECAHYDROUNDECABORATE $Cs[(CH_3)_4N]B_{11}H_{11}$

$$[(CH_3)_3NH]B_{11}H_{14} + 2NaOH \rightarrow Na_2B_{11}H_{13} + 2H_2O + (CH_3)_3N$$
$$Na_2B_{11}H_{13} + H_2SO_4 \rightarrow NaB_{11}H_{14} + NaHSO_4$$
$$NaB_{11}H_{14} + 2CsOH \rightarrow Cs_2B_{11}H_{13} + NaOH + H_2O$$
$$Cs_2B_{11}H_{13} \rightarrow Cs_2B_{11}H_{11} + H_2$$

The cesium salt of $B_{11}H_{13}^{2-}$ decomposes under vacuum at about 250° with the liberation of 1 mole of hydrogen per mole of cesium salt.[1] The solid residue consists substantially of the cesium salt of $B_{11}H_{11}^{2-}$. This salt can be isolated as such by fractional crystallization,[1] but it is more convenient to separate the anion $B_{11}H_{11}^{2-}$ from the by-products by precipitation as the sparingly soluble cesium tetramethylammonium salt. By-products in the crude pyrolysis mixture are cesium salts of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$. In order to minimize the formation of these ions, it is necessary to use starting material, $Cs_2B_{11}H_{13}$, of high purity. A procedure to prepare this salt from salts of the previously published[4] ion $B_{11}H_{14}^{-}$ is therefore described first.

Procedure

In a well-ventilated hood, 19 g. (0.100 mole) of trimethylammonium tetradecahydroundecaborate, $[(CH_3)_3NH]B_{11}H_{14}$, prepared as described,[4] is dissolved in 200 ml. of 2 *M* sodium hydroxide, and the solution is heated to boiling for 15–20 minutes. Liberated trimethylamine is swept away during the boiling. The hot solution is filtered, and 40 g. (0.267 mole) of cesium fluoride dissolved in 25 ml. of water is added to the filtrate. The mixture is cooled to nearly 0°, and the resulting precipitate of crude $Cs_2B_{11}H_{13}$ is collected by filtration and redissolved in about 200 ml. of near-boiling water. The hot solution is then treated *drop by drop* with 2 *M* sulfuric acid.* Consecutive drops of

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* Sulfuric acid should not be replaced by other mineral acids. Hydrochloric acid is especially detrimental because it eventually leads to the formation of the $Cs_2B_{11}H_{13}\cdot CsCl$ double salt.

sulfuric acid should be added only when the foaming of the solution after each addition has subsided and the malodorous, presumably toxic, fumes have escaped. The addition of sulfuric acid is continued until the pH of the solution remains 4–5. The solution is then slowly cooled to 0°, whereupon platelike crystals of $CsB_{11}H_{14}$ crystallize. The yield is 14.0 g.

This salt of $B_{11}H_{14}^-$ is reconverted to the cesium salt of $B_{11}H_{13}^{2-}$ by recrystallization from 150 ml. of hot 2 *M* cesium hydroxide solution. Dicesium tridecahydroundecaborate is precipitated by slowly cooling the strongly basic solution to 0°. This purification procedure is then repeated in exactly the same fashion as described above. A useful visual criterion for the purity of the resulting $Cs_2B_{11}H_{13}$ is its crystal habit. Pure $Cs_2B_{11}H_{13}$ crystallizes in bundles of intertwined *needles* which are colorless to just faintly yellowish. The final product is dried at 100°/0.001 mm. The yield is 15.0 g. (0.038 mole) of $Cs_2B_{11}H_{13}$ (38%). *Anal.* Calcd. for $Cs_2B_{11}H_{13}$: B, 29.9; H, 3.3; hydrolytic H_2, 1379 ml./g. Found: B, 30.5; H, 3.5; hydrolytic H_2, 1357 ml./g.

The $Cs_2B_{11}H_{13}$ thus obtained is pyrolyzed as follows: A 100-ml. oval-shaped flask is charged with 5.6 g. (0.014 mole) of $Cs_2B_{11}H_{13}$. The flask is attached to a vacuum line, evacuated, and gradually heated to a maximum temperature of 270° by means of an oil bath. Hydrogen evolution begins slowly around 150°, proceeds briskly around 230°, and levels off at higher temperatures. Over a period of 3 hours, 346 ml. (0.015 mole) of hydrogen is generated. The solid reaction product is dissolved in 50 ml. of hot water, and the solution is filtered.* The filtrate is treated with a solution prepared by dissolving 10 g. of crystalline tetramethylammonium hydroxide 5-hydrate, $(CH_3)_4NOH \cdot 5H_2O$, in 20 ml. of water, and the mixture is cooled to nearly 0°. The resulting precipitate is filtered off and recrystallized from 75 ml. of hot water. By slowly cooling the

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* The solution is usually milky white because of the presence of colloids. A filter aid such as Celite may be used to assist in the filtration.

solution, 2.0 g. of large mother-of-pearl-like crystals of cesium tetramethylammonium undecahydroundecaborate is obtained. An additional crop of 1.8 g. of less well developed crystals is isolated by reduction of the volume of the mother liquor in a rotating evaporator. The total yield is 80%, based on the amount of $Cs_2B_{11}H_{13}$ used. *Anal.* Calcd. for $Cs[(CH_3)_4N]B_{11}H_{11}$: Cs, 39.4; C, 14.3; H, 6.9; N, 4.2; B, 35.3; hydrolytic H_2, 1528 ml./g. Found: Cs, 38.3; C, 14.8; H, 6.8; N, 4.2; B, 35.6; hydrolytic H_2, 1528 ml./g.

Properties

Crystals of $Cs[(CH_3)_4N]B_{11}H_{11}$ are monoclinic, with the parameters $a = 12.59$, $b = 5.69$, $c = 5.68$, $\beta = 96.62°$, and $Z = 1$. The density is 1.368 g./cm.^{3}. The ^{11}B n.m.r. spectrum of the $B_{11}H_{11}^{2-}$ ion shows two doublets at +35.0 and +47.4 p.p.m. (Chemical shifts relative to trimethyl borate as external standard.) The two ^{11}B—H coupling constants are 125 c.p.s., and the relative intensities of the two doublets are 10:1. The ultraviolet spectrum of salts of $B_{11}H_{11}^{2-}$ in aqueous solution shows only end absorption at 2250 A. Infrared absorptions due to the $B_{11}H_{11}^{2-}$ ion occur at 2450 cm.$^{-1}$ with a slight shoulder at 2360 cm.$^{-1}$, at 1060 with a distinct shoulder at 1020 cm.$^{-1}$, and at 720 cm.$^{-1}$. It may be noted that the infrared spectrum of the anion $B_{11}H_{13}^{2-}$ is practically identical with that of the anion $B_{11}H_{11}^{2-}$, except for the appearance of another band at 1117 cm.$^{-1}$ in the spectrum of $B_{11}H_{13}^{2-}$.

B. DICESIUM NONAHYDRONONABORATE, $Cs_2B_9H_9$

$$20CsB_3H_8 \rightarrow 2Cs_2B_9H_9 + 2Cs_2B_{10}H_{10} + Cs_2B_{12}H_{12} + 10CsBH_4 + 34H_2$$

The course of the thermolysis of the $B_3H_8^-$ ion is known to be strongly dependent on reaction conditions. The principal factors affecting both composition and relative yields of the products are temperature, solvent, and especially the cation associated with the $B_3H_8^-$ anion. If pure alkali metal salts of $B_3H_8^-$ are heated to about 230° in the absence of a solvent, good conversions to the nonahydrononaborate anion, $B_9H_9^{2-}$, are obtained.[1] Solid by-products in the reaction are salts of the anions $B_{10}H_{10}^{2-}$, $B_{12}H_{12}^{2-}$, and BH_4^-; large amounts of hydrogen are also generated. The equation given above for this heterogeneous reaction should not be taken too literally and should not be used to calculate "theoretical" yields. However, the yields of the individual products do not vary significantly throughout independent runs. The cesium salt is used in the synthesis described below because of the great ease and convenience of the work-up procedure. Other alkali metal salts (K^+, Rb^+) of $B_3H_8^-$ behave analogously. The reaction can be conducted safely in simple apparatus and does not make great demands on the experimenter's time (2–3 hours). It should be borne in mind, however, that the heating of borane salts, especially in large quantities, is always a *potentially* hazardous operation which should be done in an efficient hood with adequate shielding.

Procedure

An oval-shaped or round-bottomed flask of about 100 ml. volume is charged with 37.8 g. (0.218 mole) of cesium octahydrotriborate, CsB_3H_8[2]. The flask is attached to a vacuum line of sufficient total volume to hold about 10 l. of gas, preferably in several interconnected reservoirs of 2- to 3-l. volume each, and evacuated. A large O-ring joint with a spring clamp on the pyrolysis flask is recommended to prevent the possibility of very rapid hydrogen evolution blowing the flask off the line. Stopcocks should be of at least 4-mm.-bore, and there should be no constrictions between the flask and the expansion volume. It is possible to run the reaction with continuous removal of the hydrogen generated, but this is impractical because the rate of hydrogen evolution may temporarily exceed the pumping capacity, and the progress of the reaction cannot be monitored by means of pressure measurements.

The flask is immersed into an oil bath such that the level of the oil reaches *above* the layer of CsB_3H_8, and is heated to a temperature of 230° over a period of 30–45 minutes. Hydrogen evolution begins slowly around 180°, proceeds very vigorously above 210°, and then ceases relatively abruptly.* After the hydrogen evolution has ceased, the heating bath is removed, and the hydrogen (7.75 l., 0.346 mole) is removed by evacuation. The solid pyrolysate is suspended in 180 ml. of water (vigorous gas evolution may occur!), and the slurry is briefly (1–2 minutes) heated to boiling. The hot suspension is sucked through a filter funnel. The insoluble residue, which consists of crude $Cs_2B_9H_9$, is recrystallized from 300–320 ml. of near-boiling water. Rapid filtration of the hot solution through a large Büchner funnel and slow cooling of the ensuing clear filtrate gives relatively large (1–3 mm.), glittering, faintly yellowish crystals of dicesium nonahydrononaborate. One recrystallization usually suffices to give material of high purity, but the operation may be repeated if necessary. The yield of $Cs_2B_9H_9$ is 5.5 ± 0.4 g. (0.015 mole), occasional extremes of 4.9 and 6.3 g. having been encountered. *Anal.* Calcd. for $Cs_2B_9H_9$: Cs, 71.4; B, 26.2; H, 2.4; hydrolytic H_2, 1143 ml./g. Found: Cs, 71.6; B, 26.3; H, 2.5; hydrolytic H_2, 1148 ml./g.

Properties

Crystals of $Cs_2B_9H_9$ are tetragonal with $a = 6.50$ and $c = 12.06$ A.; there are two formula units per unit cell. The density is 2.43 g./cc. The stereochemical arrangement of the nine boron atoms in the $B_9H_9^{2-}$ anion is a tricapped trigonal prism of D_{3h} symmetry. The ^{11}B n.m.r. spectrum of the $B_9H_9^{2-}$

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* Some borane salt may be carried with the gas stream to distant parts of the vacuum line. This is effectively prevented by inserting a *loose* plug of glass wool into the neck of the reaction flask.

ion shows two doublets at $\delta = +21.5$ p.p.m. and $\delta = +39.6$ p.p.m., with $^{11}B—H$ coupling constants of 133 and 124 c.p.s., respectively. The relative intensities of the two doublets are 3 and 6. In aqueous solution, the anion $B_9H_9^{2-}$ absorbs ultraviolet radiation at 2250 A.; the molar extinction coefficient of the cesium salt is $\epsilon = 3950$. The infrared spectrum of $Cs_2B_9H_9$ (Nujol mull) shows a characteristic sharp spike at 2540 cm.$^{-1}$, as well as another strong broad band in the B—H stretching region with maxima at 2478, 2445, and 2415 cm.$^{-1}$; other bands occur at 1050(w), 995 with a shoulder at 960, 882(m), and at 760(w) cm.$^{-1}$ with a shoulder at 745 cm.$^{-1}$. The anion $B_9H_9^{2-}$ is degraded by hydrogen ions in aqueous solution with evolution of hydrogen.

Salts of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ can be isolated from the crude reaction mixture in the following manner. The filtrate from the crude $Cs_2B_9H_9$ isolation step is cooled to about 0° in an ice bath. The precipitating solid consists largely of the known double salt $Cs_2B_{12}H_{12}\cdot CsBH_4$. It is purified by treating it with 80 ml. of 2 *M* hydrochloric acid (■ ***caution:*** *heavy foaming*), and recrystallization of the resulting double salt $Cs_2B_{12}H_{12}\cdot CsCl$ from 30–50 ml. of hot water. The yield of pure $Cs_2B_{12}H_{12}\cdot CsCl$ is about 1 g. (0.002 mole).

The filtrate from the $Cs_2B_{12}H_{12}\cdot CsBH_4$ isolation step is then treated with a solution of *ca.* 10 g. of tetramethylammonium chloride in 20 ml. of water. The resulting precipitate is recrystallized from 150 ml. of hot water to give 3.7 ± 0.5 g. (0.010 mole of large micalike plates of cesium tetramethylammonium decahydrodecaborate, $Cs[(CH_3)_4N]B_{10}H_{10}$.)

C. DICESIUM OCTAHYDROOCTABORATE, $Cs_2B_8H_8$

$$Na_2B_9H_9 + O_2 + H_2O \rightarrow Na_2B_8H_8 + B(OH)_3$$
$$Na_2B_8H_8 + 2Cs^+ \rightarrow Cs_2B_8H_8 + 2Na^+$$

The nonahydrononaborate anion, $B_9H_9^{2-}$, is selectively degradable to give another polyhedral anion, octahydrooctaborate, $B_8H_8^{2-}$. An intermediate in this reaction is a paramagnetic species exhibiting a complex e.s.r. spectrum which has been ascribed[2] to the anion radical of formula $B_8H_8^-$. The reaction is effectively carried out using the hydrated sodium salt $Na_2B_9H_9 \cdot xH_2O$, where $2 < x < 4$.

Procedure

Dicesium nonahydrononaborate (10 g., 0.027 mole) is dissolved in 1000 ml. of water at 70–80°. The solution is passed through a sodium ion-exchange column which is prepared as follows: A glass column of about 300 mm. length and 25 mm. diameter is filled with commercial ion-exchange resin.* A solution of 100 g. of sodium chloride in about 300 ml. of water is passed through the column, which is then washed out with a sufficiently large volume of distilled water to ensure the absence of chloride ion in the effluent. The column is then treated with approximately 100 ml. of 2 *M* sodium hydroxide solution, and washing is continued until the pH of the runoff is about 8.

The hot aqueous $Cs_2B_9H_9$ solution is passed through this column at a moderately rapid rate (10–15 ml./minute), and the column is finally washed with 600 ml. of warm (50–60°) water. The combined eluate is evaporated to dryness on a rotating evaporator using an oil-pump vacuum and a trap cooled in a Dry Ice–acetone bath. The remaining solid is dried at 120° and 0.001 mm. pressure to give 4.3–5.1 g. of white, free-flowing, powdery solid of composition $Na_2B_9H_9 \cdot xH_2O$ $(2 < x < 4)$.

The hydrated disodium nonahydrononaborate thus obtained is stirred with 300–350 ml. of 1,2-dimethoxyethane (practical grade) at a temperature of 70° for 15 minutes. Stirring is best done manually with a glass rod, which allows larger lumps to be crushed. When all (or nearly all) solid has dissolved, the burgundy-red solution is filtered, and a stream of air is bubbled through the filtrate for about 2 hours. Gradually, the red color

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* Rexyn 101 (H), research grade, may be used.

vanishes. The saturation with air is stopped at a point when the red coloration has just disappeared and the mixture becomes milky white. Cesium hydroxide solution (100 ml., 0.5 *M*) is then added, and the resulting sludgy precipitate is collected by filtration on a Büchner funnel and recrystallized from 100 ml. of warm (70–80°) water* and dried in a vacuum. The yield of $Cs_2B_8H_8$ is 3.2–3.8 g. (0.010 mole), corresponding to an overall conversion of 40% based on the $Cs_2B_9H_9$ used. *Anal.* Calcd. for $Cs_2B_8H_8$: B, 24.0; H, 2.2; hydrolytic H_2, 1057 ml./g. Found: B, 24.2; H, 2.5; hydrolytic H_2, 1059 ml./g.

Properties

Dicesium octahydrooctaborate forms white, velvetlike, nontransparent crystals, the density of which is 2.34 g./cc. In an evacuated sealed tube, $Cs_2B_8H_8$ is stable up to 600°. The anion $B_8H_8^{2-}$ is rapidly degraded by hydrogen ions in water. The structure of the anion (in the tetraamminezinc salt) in the solid state has been shown to be that of a slightly distorted dodecahedron of D_{2d} symmetry.

The ^{11}B n.m.r. spectrum of the anion in solution consists of one doublet at $\delta = 24.1$ p.p.m., with a B—H coupling constant of 128 c.p.s. The ultraviolet spectrum in water cuts off at 2000 A.

A Nujol mull of $Cs_2B_8H_8$ shows the following bands in the sodium chloride region of the infrared spectrum: 2480(vs), 2450(vs), 1138(m), 1000(vw), 950(vw), 900(w), 860(w), 834(vw), and 715 $cm.^{-1}$.

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* Boiling of the solution is to be avoided because decomposition of $B_8H_8^{2-}$ in aqueous solution becomes appreciable at high temperature.

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7. *C*-AMMINECARBAUNDECABORANE(12) DERIVATIVES AND CESIUM TRIDECAHYDROCARBAUNDECABORATE(1-)

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The preparation of a series of aminecarboranes of the type $B_{10}H_{12}CNH_2R$ from decaborane and alkyl isocyanides has been reported.[1] A more convenient preparation of this class of aminecarboranes, which gives the parent member $B_{10}H_{12}CNH_3$, has also been reported.[2] Procedures for preparation of the aminecarboranes, their methylation, and subsequent deamination of the *C*-(trialkylamine)carbaundecaborane(12) are described here.

A. *C*-AMMINECARBAUNDECABORANE(12)

$$B_{10}H_{14} + 2NaCN \rightarrow Na_2B_{10}H_{13}CN + HCN$$

$$Na_2B_{10}H_{13}CN \xrightarrow[\text{exchange}]{H^+\text{-ion}} B_{10}H_{12}CNH_3$$

Procedure

■ **Caution.** *These preparations must be conducted in well-ventilated hoods. Decaborane is a very toxic material and should be handled with gloves. In addition, significant quantities of*

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hydrocyanic acid are liberated in the initial step, during the ion exchange, and during the first evaporation.

Sodium cyanide (25 g., 0.51 mole) is dissolved in 400 ml. of water in an 800-ml. beaker. Purified* decaborane (20 g., 0.0164 mole) is added, and the mixture is stirred for one hour or until the decaborane dissolves. The solution is filtered and, in an efficient hood, passed through a 40-mm.-diam. ion-exchange column packed with 500 ml. of a strongly acidic ion-exchange resin, such as Rexyn 101 (H). A minor amount of bubbling may occur during this ion exchange, but it is generally not troublesome. If too narrow a column is used, the bubbling may cause separation of the column packing. The column is rinsed down with water until a total of 2500 ml. of effluent has been collected. This is placed in a porcelain evaporating dish and evaporated to dryness on a steam bath.† The evaporation residue consists of 22 g. of $B_{10}H_{12}CNH_3$, contaminated with a small amount of boric acid. The latter is removed by breaking up the residue, which is usually obtained as a hard cake, and extracting it with three 100-ml. portions of ether at room temperature. The extracts are clarified by filtration through diatomaceous earth. The filtrate is concentrated in a rotary evaporator until a solid or semisolid residue is obtained. The final traces of ether are removed by redissolving this residue in 25 ml. of water and reevaporating to dryness. The final product is dried at 100° under vacuum to obtain 20 g., 82%, of $B_{10}H_{12}CNH_3$, which does not melt below 400°. *Anal.* Calcd. for $B_{10}H_{12}CNH_3$: B, 72.5; C, 8.0; H, 10.1; N, 9.4. Found: B, 73.0; C, 8.0; H, 10.1; N, 9.4.

Properties

C-Amminecarbaundecaborane(12) is a colorless crystalline solid which does not melt below 400°. It is characterized by its

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* Decaborane can be satisfactorily purified by sublimation at 65–75° under high vacuum or by recrystallization from heptane.

† The initial stages of the evaporation may be accomplished using a hot plate at low heat.

infrared spectrum, which, in a Nujol mull, has absorptions at 3200(m), 3160(m), 3100(mw), 2570(m), 2530(s), 1575(mw), 1160(w), 1120(w), 1020(m), 995(m), 960(w), 930(w, broad), 860(w), 840(w), 810(w), 760(w), 750(w), 710(w, broad), and 695(w) cm.$^{-1}$, disregarding the Nujol regions. It is soluble in water and polar organic solvents and is ionized by base to form $B_{10}H_{12}CNH_2^-$. It reacts with various transition-metal halides in the presence of base to form π-bonded sandwich species, exemplified by $(B_{10}H_{10}CNH_3)_2Fe^-$ and $(B_{10}H_{10}CNH_3)_2Ni$.[3]

B. *C*-(TRIMETHYLAMINE)CARBAUNDECABORANE(12)

$$B_{10}H_{12}CNH_3 + 3(CH_3)_2SO_4 + 6NaOH \rightarrow 2B_{10}H_{12}CN(CH_3)_3 + 3Na_2SO_4 + 6H_2O$$

Procedure

A solution of 5.0 g. (0.0335 mole) of $B_{10}H_{12}CNH_3$ in 200 ml. of 10% aqueous sodium hydroxide is prepared in a 300-ml. Erlenmeyer flask. Dimethyl sulfate (6 ml.) is added, and the solution is stirred. After 10 minutes a second 6-ml. portion of dimethyl sulfate is added, and stirring is continued for 40 minutes. The resulting mixture is filtered, and the filter cake is washed with seven 150-ml. portions of water. The resulting solid is dried at 80° under vacuum for 16 hours to obtain 5.4 g., 84%, of $B_{10}H_{12}CN(CH_3)_3$, which is indistinguishable by infrared analysis from recrystallized material. Recrystallization can be achieved by dissolving 1 g. of the crude product in 15 ml. of boiling acetonitrile, filtering, and adding water (about 2 ml.) to the boiling solution until incipient precipitation is reached. The solution is then allowed to cool, and is filtered to obtain 0.56 g. of crystalline product. *Anal.* Calcd. for $B_{10}H_{12}CN(CH_3)_3$: B, 56.5; C, 25.1; H, 11.0; N, 7.3. Found: B, 56.1; C, 25.8; H, 11.0; N, 7.5.

The behavior of $B_{10}H_{12}CN(CH_3)_3$ when it is heated is dependent on the rate of heating. With comparatively fast heating (10–15 minutes to reach 340°), complete melting is observed at

346–347° for the crude material and at 348° for the recrystallized product. With slow heating (approximately one hour to reach 340°), only a slight sintering and darkening is observed at 355°, with no further change to 400°.

Properties

C-(Trimethylamine)carbaundecaborane(12) is a colorless crystalline solid. It is insoluble in water and moderately soluble in polar organic solvents.

C. *C*-(*n*-PROPYLAMINE)CARBAUNDECABORANE(12)

$$n\text{-}C_3H_7NC + B_{10}H_{14} \rightarrow B_{10}H_{12}CNH_2C_3H_7$$

Procedure

The reaction is carried out in a 3-l. three-necked flask equipped with a mechanical stirrer, pressure-equalized dropping funnel, reflux condenser, and a nitrogen inlet.* In the flask is dissolved 212 g. (1.73 mole) of sublimed decaborane† in 1 l. of dry benzene. In the dropping funnel is placed 160 g. (2.31 mole) of *n*-propyl isocyanide.‡ An ice bath is placed around the flask, and the *n*-propyl isocyanide is added with stirring over a 4-hour period. The initial colorless solution will develop a deep red-purple color, and then a white solid will separate from solution. After the addition period, the ice bath is removed, the mixture is stirred for another hour, and then allowed to stand for an hour. The solid is isolated by filtration, washed with 800 ml. of ben-

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* This reaction should be done in a well-ventilated hood.

† The decaborane is purified by sublimation at 60° and 10^{-4} mm.

‡ The *n*-propyl isocyanide is prepared by the method of Jackson and McKusick,[4] using 490 g. (2.8 mole) of *n*-propyl iodide and 454 g. (3.3 mole) of silver cyanide. It is observed that, after a long induction period, the reaction becomes quite violent. It is suggested that one half of the propyl iodide be added initially and the other half be added drop by drop over a 2-hour period. The dry product is used without the final fractional distillation indicated in the reference.

zene, and air-dried on the filter. The crude light tan $B_{10}H_{12}CNH_2C_3H_7$ is obtained in 94% yield (312 g.) based on decaborane. The product can be purified by crystallization from hot water.

Properties

C-(*n*-Propylamine)carbaundecaborane(12) is an air-stable white crystalline solid, m.p. 220–222°. It is soluble in acetone, methanol, tetrahydrofuran, and hot water; insoluble in benzene. The infrared spectrum (Nujol and hexachlorobutadiene mulls) contains major absorption bands at 3191(vs), 3124(s), 3008(w), 2992(w), 2982(m), 2956(w), 2896(w), 2555(vs), 2000(w), 1578(s), 1476(m), 1405(m), 1366(m), 1027(m), 1011(s), 850(m), 756(m), and 649(m) $cm.^{-1}$. This compound reacts with various transition-metal halides in the presence of base to form π-bonded sandwich species such as $(B_{10}H_{10}CNH_2C_3H_7)_2Ni$ and $(B_{10}H_{10}CNH_2C_3H_7)_2Co^-$.[5]

D. *C*-(DIMETHYL-*n*-PROPYLAMINE)CARBAUNDECABORANE(12)

$$B_{10}H_{12}CNH_2C_3H_7 + 2CH_3I + 2NaHCO_3 \xrightarrow{THF/H_2O} B_{10}H_{12}CN(CH_3)_2C_3H_7 + 2NaI + 2CO_2 + 2H_2O$$

This methylation reaction can be more economically accomplished using sodium hydroxide and dimethyl sulfate in aqueous solution (see Procedure B). The method described here avoids the use of the hazardous chemical dimethyl sulfate and gives comparable yields, employing a simple procedure.

Procedure

The reaction is carried out in a 3-l. three-necked flask equipped with a mechanical stirrer, heating mantle, pressure-equalized dropping funnel, reflux condenser, and nitrogen inlet. To the flask is added 620 ml. of tetrahydrofuran.* Finely divided $B_{10}H_{12}CNH_2C_3H_7$, 312 g. (1.63 mole),† is added slowly with constant stirring to prevent lumping. When homogeneity is obtained, 411 g. (4.89 moles) of sodium hydrogen carbonate and then 1240 ml. of water are added. The dropping funnel is charged with 578 g. (4.07 moles) of iodomethane. The mixture is heated to reflux with stirring, and the iodomethane then is added slowly over a 2-hour period. The reflux and stirring are continued for an additional 5–6 hours or until evolution of gas ceases. The lower layer (water) is removed partially by siphoning, and the remaining liquid is transferred to a 2-l. flask. The tetrahydrofuran is removed by rotary evaporation on a steam bath. The residues are washed from the flask into a 2-l. beaker with 200–300 ml. of water. The mixture is carefully neutralized with concentrated hydrochloric acid. Some foaming occurs during the latter operation. The solid is isolated by filtration, washed with water, and air-dried on the filter. The crude product is further purified by dissolution in boiling acetone, filtration, and then slow addition of methanol to the boiling filtrate until crystallization occurs. The combined yield of $B_{10}H_{12}CN(CH_3)_2C_3H_7$ from three crops of crystals is 268 g. (75% yield based on decaborane used in Procedure A).

Properties

C-(Dimethylpropylamine)carbaundecaborane(12) is a white crystalline solid, m.p. 191–192°. It is very soluble in acetone and tetrahydrofuran, slightly soluble in chloroform and methanol, and insoluble in benzene and water. The infrared spectrum (Nujol and hexachlorobutadiene mulls) contains major absorption bands at 2988(m), 2561(vs), 1481(m), 1472(m), 1414(m), 1130(m), 1035(m), and 934(m) $cm.^{-1}$. The proton nuclear magnetic resonance spectrum (acetone-d_6 solution) exhibits

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* Tetrahydrofuran is freshly distilled over lithium hydroaluminate.

† The crude product from Procedure A is used without further purification.

peaks at 6.44 (triplet, α-CH_2), 6.78 (CH_3), 8.15 (multiplet, β-CH_2), and 8.98 τ (triplet, γ-CH_3).

E. CESIUM TRIDECAHYDROCARBAUNDECABORATE(1-)

$$B_{10}H_{12}CN(CH_3)_3 + 3Na \xrightarrow{THF} Na_3B_{10}H_{10}CH + Me_3N + \tfrac{1}{2}H_2$$
$$Na_3B_{10}H_{10}CH + 2H_2O \rightarrow 2NaOH + NaB_{10}H_{12}CH$$
$$NaB_{10}H_{12}CH + CsCl \rightarrow CsB_{10}H_{12}CH + NaCl$$

Deamination of *C*-(trialkylamine)carbaundecaborane(12) derivatives to the carborane anion $B_{10}H_{12}CH^-$ can be accomplished with sodium metal or sodium hydride in tetrahydrofuran solution. A procedure using sodium metal is described here to illustrate this general reaction. The properties of the cesium and tetramethylammonium salts of the $B_{10}H_{12}CH^-$ anion are given.

Procedure

The reaction is carried out in a 500-ml. three-necked flask equipped with a mechanical stirrer, reflux condenser topped with a nitrogen inlet, ground-glass stopper, and an oil bath. The apparatus is thoroughly dried and flushed with nitrogen. The nitrogen atmosphere is strictly maintained until the reaction is completed.

The *C*-(trimethylamine)carbaundecaborane(12)* (9.57 g., 0.05 mole) is placed in the reaction flask, and 250 ml. of dry tetrahydrofuran† is added. Sodium metal‡ (4.59 g., 0.2 mole) is added to the reaction flask, and after gas evolution has ceased, the oil bath is heated to 75–80° with vigorous stirring of the reaction mixture. A thick white precipitate will develop

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* The preparation and purification of *C*-(trimethylamine)carbaundecaborane(12) is described in Procedure B of this synthesis.

† Tetrahydrofuran is distilled over lithium hydroaluminate in a nitrogen atmosphere.

‡ The sodium metal should be divided into pieces approximately 1 cm. in width and washed under dry hexane. If larger quantities of *C*-(trimethylamine)-carbaundecaborane(12) are used, initial gas evolution may be quite rapid.

over a period of several hours, and the strong odor of trimethylamine can be detected.

The heating is discontinued after 24 hours, and the excess sodium metal is removed mechanically.* After removal of the sodium, 20 ml. of methanol and then 50 ml. of water are added. The tetrahydrofuran and methanol are removed by vacuum rotary evaporation. The remaining aqueous solution is neutralized and gravity-filtered. The filtrate is treated with a saturated solution of cesium or tetramethylammonium chloride. The crude cesium salt is recrystallized as white plates from hot water in 80% yield based on the *C*-(trimethylamine)carbaundecaborane(12). The tetramethylammonium salt is recrystallized from methanol-acetone.

Properties

The cesium and tetramethylammonium salts are white crystalline compounds, air-stable and nonhygroscopic. The cesium salt is soluble in acetone and hot water, insoluble in tetrahydrofuran. The tetramethylammonium salt has partial solubility in acetone or dimethylformamide, but is insoluble in water or methanol. The infrared spectra of the salts (Nujol and hexachlorobutadiene mulls) contain major absorption bands at the indicated frequencies:

$CsB_{10}H_{12}CH$: 3020(vw), 2520(vs), 2000(w), 1149(w), 1129(w), 1094(s), 1066(s), 1019(s), 1004(s), 990(m), 979(w), 13(w), 876(m), 862(m), 834(m), 821(w), 769(w), 749(m), 718(m), 623(m), 518(m) cm.$^{-1}$.

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* Alternatively, the white precipitate is filtered by slowly decanting the mixture through a Schlenk-type filter. The solid is then dried under vacuum on the filter and removed from the apparatus in an oxygen- and water-free box. ■ ***Caution.*** *The dry solid is pyrophoric when exposed to moist air. The precipitate appears to have the composition* $Na_3B_{10}H_{10}CH$ *and is useful for further reactions under anhydrous conditions.*

$(CH_3)_4NB_{10}H_{12}CH$: 3020(w), 2510(vs), 1990(w), 1476(s), 1412(m), 1280(w), 1190(w), 1095(m), 1063(m), 1012(m), 995(m), 980(w), 945(s), 876(w), 850(w), 813(w), 746(w), 702(m), 620(m) cm.$^{-1}$.

The proton nuclear resonance spectrum (acetone-d_6 solution) exhibits a broad C—H resonance at 8.55 τ.

At 300–320° the cesium salt $CsB_{10}H_{12}CH$ loses hydrogen with concurrent disproportionation to form CsB_9H_9CH and $CsB_{11}H_{11}CH$, which are monocarborane analogs of $Cs_2B_{10}H_{10}$ and $Cs_2B_{12}H_{12}$, respectively.[2] Various transition-metal halides have been treated with $B_{10}H_{12}CH^-$ in the presence of bases to form π-bonded sandwich complexes exemplified by $(B_{10}H_{10}CH)_2Fe^{3-}$ and $(B_{10}H_{10}CH)_2Ni^{2-}$.[3,5]

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8. TRANSITION-METAL COMPLEXES OF $B_{10}H_{10}CNH_3^{2-}$ AND $B_{10}H_{10}CH^{3-}$

Submitted by **W. H. KNOTH,* JOHN L. LITTLE,† and LEE J. TODD†**
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The preparation of a series of transition-metal derivatives of monocarbon carborane anions of the type $B_{10}H_{10}CNH_3^{2-}$,

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$B_{10}H_{10}CNH_2R^{2-}$, and $B_{10}H_{10}CH^{3-}$ has been reported.[1,2] The syntheses are based on two general reactions very closely related to the preparative methods recently described for the [3]-1,2-dicarbaundecahydroundecaboranyl ["(3)-1,2-dicarbollyl"] sandwich complexes:[3,4] (1) the reaction of $Na_3B_{10}H_{10}CH$ and an anhydrous metal chloride, and (2) the reaction of $CsB_{10}H_{12}CH$, aqueous sodium hydroxide, and a metal chloride. Complexes of Fe(III), Co(III), and Ni(IV) with the three types of monocarbon carborane anions indicated above can be conveniently prepared by the aqueous route. The preparations of $Cs_2Ni(B_{10}H_{10}CH)_2$ and $(B_{10}H_{10}CNH_3)_2Ni$ by this route are described here.

A. $Cs_2Ni(B_{10}H_{10}CH)_2$

$$4CsB_{10}CH_{13} + 2NiCl_2 + 4OH^- + O_2 \rightarrow 2Cs_2Ni(B_{10}H_{10}CH)_2 + 6H_2O$$

Procedure

To a 250-ml. three-necked flask fitted with a reflux condenser, magnetic stirring bar, and air bubbler is added a solution of 10.84 g. of sodium hydroxide in 100 ml. of water, and then 5.87 g. (0.0221 mole) of solid $CsB_{10}H_{12}CH$.[5] An oil bath maintained at 40° is placed around the flask. Stirring is begun, and 3.2 g. (0.0135 mole) of nickel(II) chloride 6-hydrate in 37 ml. of water is added slowly to the flask from a dropping funnel. Air* is either sucked or blown through the bubbler into the reaction mixture and up through the condenser.

After a 20-hour period,† the products are transferred to a 500-ml. Erlenmeyer flask and neutralized by drop-by-drop addition of concentrated hydrochloric acid. Foaming occurs during this latter step. A saturated solution of cesium chloride is

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* Use of oxygen gas reduces the absorption of carbon dioxide evolved during the subsequent acidification step.

† After 20 hours, the checkers observed a little Ni(III) color remaining; so a trace of iron(III) chloride was added to effect complete conversion to Ni(IV).

added to the ice-cold reaction mixture until precipitation is complete. *The crude $Cs_2Ni(B_{10}H_{10}CH)_2$ is isolated by filtration* and crystallization from hot water. Second and third fractions *are obtained by reducing the volume of solution. The yield* from three fractions is 5.00 g. (78%).

Properties

$Cs_2Ni(B_{10}H_{10}CH)_2$ is an orange crystalline air-stable solid, soluble in acetone, hot water, tetrahydrofuran, dimethylformamide, dimethyl sulfoxide, and methanol. The infrared spectrum (Nujol and hexachlorobutadiene mulls) contains major absorption bands at 2520(vs), 1094(s), 1051(m), 1016(s), 916(m), and 750(m) cm.$^{-1}$. The proton nuclear magnetic resonance spectrum (DMSO-d_6) exhibits a broad peak at 6.58 τ.

B. $(B_{10}H_{10}CNH_3)_2Ni$

$$4B_{10}H_{12}CNH_3 + 2NiCl_2 + 8NaOH + O_2 \rightarrow 2Na_2(B_{10}H_{10}CNH_2)_2Ni + 4NaCl + 10H_2O$$

$$Na_2(B_{10}H_{10}CNH_2)_2Ni + 2CsOH \rightarrow Cs_2(B_{10}H_{10}CNH_2)_2Ni + 2NaOH$$

$$Cs_2(B_{10}H_{10}CNH_2)_2Ni \xrightarrow{H^+\text{-ion exchange}} (B_{10}H_{10}CNH_3)_2Ni$$

Procedure

A solution of 19 g. (0.080 mole) of nickel(II) chloride 6-hydrate in 25 ml. of water is added to a solution of 5 g. (0.0335 mole) of $B_{10}H_{12}CNH_3$ in 20% aqueous sodium hydroxide (50 ml.) in a 300-ml. Erlenmeyer flask. The resulting mixture is stirred for 5 minutes and is then heated on a steam bath for 20 minutes. It is then filtered through diatomaceous earth. Aqueous 50% cesium hydroxide (30 ml.) is added to the filtrate; the mixture is chilled for 10 minutes in an ice-water bath and filtered. The filter cake is recrystallized from 35 ml. of water. Complete oxidation to the Ni(IV) state usually occurs spontaneously during the handling, but completeness of the oxidation generally can be assured by bubbling air at a moderate rate through the recrystallization solution for 30 minutes, while the solution is kept sufficiently warm to prevent crystallization.* The solution is then allowed to cool to room temperature, and is filtered to obtain 6.0 g. of $Cs_2(B_{10}H_{10}CNH_2)_2Ni$. This is dissolved in 100 ml. of water with warming, and the solution is passed through an ion-exchange column packed with 75 ml. of a strongly acidic ion-exchange resin, such as Rexyn 101 (H). The column is rinsed with water until a total of 300 ml. of effluent is collected. This is placed on a steam bath in a porcelain evaporating dish and evaporated to dryness to obtain 3.4 g. (58%) of $(B_{10}H_{10}CNH_3)_2Ni$, which is dried at 100° under vacuum. This product is sufficiently pure for most purposes, but can be further purified by recrystallization from water (3.5 ml. of water per gram of solid) with thorough chilling of the recrystallization mixture in an ice-water bath before recovering the recrystallized product by filtration. The recovery of recrystallized material from 1 g. of the crude product is 0.72 g. (72%), after drying at 100° under vacuum for 16 hours. *Anal.* Calcd. for $(B_{10}H_{10}CNH_3)_2Ni$: B, 61.2; C, 6.8; H, 7.4; Ni, 16.6. Found: B, 60.8; C, 7.0; H, 7.6; Ni, 16.2. The product darkens above 360°, but does not melt below 400°. It can be characterized by its infrared spectrum, which, as determined in a Nujol mull, includes absorption bands at 3150 (doublet, m), 3080(m), 2560(s), 1570(w), 1490(w), 1110(w), 1010(m), 945–920(w), and 750–720(mw) $cm.^{-1}$, disregarding the Nujol regions.

Properties

$(B_{10}H_{10}CNH_3)_2Ni$ is an orange crystalline solid which is stable in air and soluble in water and polar organic solvents. It reacts with nitrous acid to give the $(B_{10}H_{10}COH)_2Ni^{2-}$ anion, with

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* Any Ni(III) remaining after this treatment will be oxidized to Ni(IV) during the following ion-exchange process.

aqueous hydroxide to give the $(B_{10}H_{10}CNH_2)_2Ni^{2-}$ anion, and with dimethyl sulfate in aqueous sodium hydroxide to form $[B_{10}H_{10}CN(CH_3)_2]_2Ni^{2-}$. The last can be isolated as normal salts or as the inner salt $[B_{10}H_{10}CNH(CH_3)_2]_2Ni$.

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Chapter Three

COORDINATION COMPOUNDS

9. LATTICE-STABILIZED COMPLEX IONS

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Compounds containing complex ions (including those not found in appreciable concentrations in solution) can frequently be stabilized in the solid state with counterions of similar size. By application of this principle, the pentachlorocuprate(II) anion has been stabilized in $[Cr(NH_3)_6][CuCl_5]$,[1] the pentacyanonickelate(II) anion in $[Cr(NH_3)_6][Ni(CN)_5]$,[2] and various hexachlorometallates as either $[Co(pn)_3][MCl_6]$ or $[Co(NH_3)_6][MCl_6]$.[3] Similarly, the anions PF_6^- and SiF_6^{2-} are often used to permit the isolation of large univalent and bivalent cations, e.g., $[Mo(CO)_4(C_5H_5)]PF_6$ and $[W(CO)_4(C_5H_5)]PF_6$.[4] Acidoaquo complexes of chromium(III), such as $[Cr(en)_2(H_2O)Cl]ZnCl_4$, have been obtained.[5] The resolution of univalent anionic optically active complexes is often achieved[6] by the use of (+) or

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(−) $[Co(en)_2(NO_2)_2]^+$. As a last resort one can almost always use $(C_6H_5)_4As^+$ and $(C_6H_5)_4B^-$ to isolate salts of large counterions.

The procedures for the preparation of $[Co(NH_3)_6][FeCl_6]$, $[Co(pn)_3][MnCl_6]$, $[Co(pn)_3][FeCl_6]$, $[Co(pn)_3][InCl_6]$, $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$, and $[Cr(NH_3)_6][Ni(CN)_5]\cdot 2H_2O$ are given here.

A. HEXAAMMINECOBALT(III) HEXACHLOROFERRATE(III) AND TRIS(1,2-PROPANEDIAMINE)COBALT(III) HEXACHLOROMETALLATES(III)

$$[Co(pn)_3]^{3+} + M^{3+} + 6Cl^- \rightarrow [Co(pn)_3][MCl_6]$$

Procedures

1. $[Co(NH_3)_6][FeCl_6]$

A solution of hexaamminecobalt(III) chloride (0.43 g., 0.0016 mole) in 70 ml. of 3.4 *M* HCl is heated to 70° on a hot plate. To this solution iron(III) chloride 6-hydrate (1.4 g., 0.005 mole) in 10 ml. of hot water is added. The resulting solution is heated for a few minutes until orange crystals begin to form. After the mixture has been cooled to room temperature, the crystals are collected on a Büchner funnel, washed with alcohol and ether, and dried in an evacuated desiccator over potassium hydroxide or sulfuric acid. A typical yield is 0.42 g. (first crop, 60%) plus 0.10 g. (second crop, 14%). *Anal.* Calcd. for $[Co(NH_3)_6][FeCl_6]$: N, 19.54; H, 4.18; Cl, 49.55. Found: N, 19.52; H, 4.13; Cl, 48.42. (The volumetric chloride analysis is difficult because of the interference of iron with the end point.)

2. $[Co(pn)_3][MnCl_6]$

Hot solutions of manganese(II) sulfate 1-hydrate (1.70 g., 0.010 mole) in 5 ml. of 1:1 hydrochloric acid and tris(1,2-propanediamine)cobalt(III) chloride (3.86 g., 0.010 mole) in 5 ml.

of 1:1 hydrochloric acid are mixed and maintained at 60° on a hot plate. Sodium chlorate (1.07 g., 0.010 mole) is added in small quantities over a period of 5 minutes. On commencing the addition of sodium chlorate, effervescence is observed and chlorine gas is evolved. The color of the solution changes from deep orange to dark brown, and a dark brown solid separates. Five milliliters of concentrated hydrochloric acid is added, and the mixture is heated at 60° for 30 minutes. After the mixture has been cooled, the product is collected on a Büchner funnel, washed with 15-ml. portions of alcohol, acetone, and ether, and dried *in vacuo* over potassium hydroxide. A typical yield is 3.62 g. (66%). *Anal.* Calcd. for $CoC_9H_{30}N_6MnCl_6$: C, 19.70; H, 5.50; N, 15.31; Cl, 38.72. Found: C, 20.18; H, 5.61; N, 15.24; Cl, 38.98.

Concentration of the mother liquor with addition of small quantities of sodium chlorate facilitates the isolation of a second crop of the hexachlorometallate, but the product is subject to increasing contamination by sodium salts.

3. $[Co(pn)_3][FeCl_6]$

A solution of iron(III) chloride 6-hydrate (2.71 g., 0.010 mole) in 5 ml. of hot water is added to a filtered solution of tris(1,2-propanediamine)cobalt(III) chloride (3.87 g., 0.010 mole) in 35 ml. of water at 70°. A small quantity of brown-black precipitate sometimes separates on initial mixing of the reactants. When necessary, this is filtered off, and the dark orange filtrate is reduced in volume to *ca.* 10 ml. by evaporation on the hot plate (care to avoid splashing!). Addition of 5 ml. of concentrated hydrochloric acid results in the immediate separation of the hexachlorometallate as yellow crystals. After cooling, the crystals are collected on a Büchner funnel, washed with 15-ml. portions of alcohol, acetone, and ether, and dried in the air. A typical yield is 2.64 g. (48%). *Anal.* Calcd. for $CoC_9H_{30}N_6$-$FeCl_6$: C, 19.66; H, 5.50; N, 15.28; Cl, 38.69. Found: C, 19.88; H, 5.14; N, 15.46; Cl, 38.65.

4. $[Co(pn)_3][InCl_6]$

A filtered solution of tris(1,2-propanediamine)cobalt(III) chloride (3.87 g., 0.010 mole) in 10 ml. of water at 70° is treated with a solution of indium metal (1.15 g., 0.010 mole) dissolved in 10 ml. of 1:1 hydrochloric acid. [Alternatively, the stoichiometric quantity of indium(III) chloride 4-hydrate dissolved in dilute hydrochloric acid may be used.] A pale orange precipitate of the complex separates immediately. The mixture is heated for 5 minutes, cooled, and then filtered. The product is washed with 15-ml. portions of alcohol, acetone, and ether, and then dried in the air. A typical yield is 4.68 g. (77%). *Anal.* Calcd. for $CoC_9H_{30}N_6InCl_6$: C, 17.76; H, 4.96; N, 13.81; Cl, 34.96. Found: C, 17.68; H, 5.00; N, 13.08; Cl, 35.00.

Properties

The hexachlorometallate salts described here all display similar physical properties, and with the exception of the manganese(III) derivative, the complexes are all stable. $[Co(pn)_3][MnCl_6]$ decomposes slowly, and a slight odor of chlorine persists even after extensive periods of time in an evacuated desiccator. The salts are soluble in water (with decomposition) and insoluble in common organic solvents. Room-temperature magnetic measurements afford values of 4.91 B.M. for the manganese complex and 5.97, 5.86 B.M. for $[Co(NH_3)_6][FeCl_6]$ and $[Co(pn)_3][FeCl_6]$, respectively. These values lie within the accepted range for high-spin octahedral species.

An initial report that the crystal structure of $[Co(NH_3)_6][FeCl_6]$ is isomorphous with that of $[Co(NH_3)_6][TlCl_6]$ has been shown to be incorrect.[7] However, the Mössbauer chemical isomer shifts[8] for $[Co(en)_3][FeCl_6]$ and $[Co(NH_3)_6][FeCl_6]$ of 0.60 ± 0.10 and 0.59 ± 0.10 mm./second, respectively, agree with the values found for other hexacoordinate iron(III) compounds and differ considerably from the value of 0.40 mm./

second found for the $FeCl_4^-$ anion. The Mössbauer results confirm the earlier suggestion[3] that these compounds contain the octahedral $FeCl_6^{3-}$ anion.

B. TRIS(ETHYLENEDIAMINE)CHROMIUM(III) PENTACYANONICKELATE(II) AND HEXAAMMINECHROMIUM(III) PENTACYANONICKELATE(II)

$$[Cr(en)_3]^{3+} + Ni(CN)_5^{3-} + 1.5H_2O \rightarrow [Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$$
$$[Cr(NH_3)_6]^{3+} + Ni(CN)_5^{3-} + 2H_2O \rightarrow [Cr(NH_3)_6][Ni(CN)_5]\cdot 2H_2O$$

Procedures

1. $[Cr(en)_3][Ni(CN)_5]\cdot 1\cdot 5H_2O$

To a solution of $K_2Ni(CN)_4\cdot H_2O$[9] (2.0 g., 0.0078 mole) and potassium cyanide (6.0 g., 0.092 mole) in 10 ml. of water is added, with stirring, a solution of $[Cr(en)_3]Cl_3\cdot 3.5H_2O$[10] (1.8 g., 0.0045 mole) in 10 ml. of water. The beaker containing the resultant deep red solution is thermally insulated and cooled very slowly to 0° in a refrigerator. A convenient method of insulating the beaker is to place it on an asbestos sheet inside one or two larger concentric beakers and wrap these with foil. After about 8 hours, large deep red crystals separate, and these are collected on a coarse sintered-glass filter and dried by suction. Because of the ready dissociation of the $Ni(CN)_5^{3-}$ complex, the product is not washed. The formation of large crystals and rapid suction drying minimize the impurities from the mother liquor. The yield is 1.9 g. (94%). *Anal.* Calcd. for $[Cr(C_2H_8N_2)_3][Ni(CN)_5]\cdot 1.5H_2O$: Ni, 13.1; Cr, 11.6; C, 29.5; H, 6.07; N, 34.4; O, 5.4. Found: Ni, 13.1; Cr, 11.6; C, 28.5; H, 5.95; N, 33.2; O, 6.2 (from weight loss, assuming loss of H_2O). The molecular formula is confirmed by x-ray analysis.[11]

2. $[Cr(NH_3)_6][Ni(CN)_5]\cdot 2H_2O$

This salt is prepared in the same way as that above, except that an even higher concentration of cyanide is used because of the greater solubility of the $[Cr(NH_3)_6]^{3+}$ salt. To a solution of $K_2Ni(CN)_4 \cdot H_2O$[9] (4.0 g., 0.0156 mole) and potassium cyanide (15 g., 0.230 mole) in 20 ml. of water is added, with stirring, a solution containing $[Cr(NH_3)_6]Cl_3 \cdot H_2O$[12] (4.0 g., 0.0144 mole) in 20 ml. of water. The solution is cooled very slowly to about −5° and allowed to stand at that temperature for at least 24 hours. The orange-red crystals that form are collected on a coarse suction filter and dried by suction. The yield is 2.5 g. (45%). *Anal.* Calcd. for $[Cr(NH_3)_6][Ni(CN)_5] \cdot 2H_2O$: Ni, 15.5; Cr, 13.7; C, 15.8; H, 5.85; N, 40.6; O, 8.45. Found: Ni, 15.1; Cr, 14.2; C, 16.0; H, 5.80; N, 41.1; O, 8.1 (from weight loss, assuming loss of H_2O).

Properties

The chromium(III) ammine salts of $Ni(CN)_5^{3-}$ dissolve in water to give dilute solutions containing predominately $Ni(CN)_4^{2-}$ and CN^-. The equilibrium constant for the reaction:

$$Ni(CN)_4^{2-} + CN^- \rightleftarrows Ni(CN)_5^{3-}$$

is 1.08 at 25° and an ionic strength of 4 *M*.[13]

The infrared spectrum of solid $[Cr(NH_3)_6][Ni(CN)_5] \cdot 2H_2O$ in the C—N stretching region has three sharp absorption bands[2] at 2130(m), 2100(vs), and 2070(s) $cm.^{-1}$. The single-crystal x-ray structure[11] of $[Cr(en)_3][Ni(CN)_5] \cdot 1.5H_2O$ has been determined, and it was found that the asymmetric unit contains two cations and two anions. The anions are five-coordinated $Ni(CN)_5^{3-}$, and it is of interest that one of these has a tetragonal pyramidal structure and one is a distorted trigonal bipyramid. This points to the fact that the energy difference between these two structures in five-coordinated systems must be small.[14]

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10. POTASSIUM OCTACYANOMOLYBDATE(IV) 2-HYDRATE

$$MoO_3 + 8KCN + 2N_2H_4 + 6HCl \rightarrow K_4Mo(CN)_8 \cdot 2H_2O + 2NH_4Cl + 4KCl + N_2 + H_2O$$

Submitted by J. VAN DE POEL* and H. M. NEUMANN†
Checked by M. R. OLAZAGASTI‡ and E. L. MUETTERTIES‡

Various methods for the preparation of potassium octacyanomolybdate(IV) 2-hydrate from molybdenum(VI) oxide, molybdic acid, or molybdates have been reported.[1–3] These methods, although in general reliable, have one unfavorable aspect in common: low efficiencies due to conversions of less than 50%.

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This can be explained by the fact that these syntheses all consist of two separate steps. In the first step the molybdenum is reduced in acid medium from the +6 to the +5 oxidation state. In the second step potassium cyanide is introduced, and formation of the molybdenum(IV) cyanide complex takes place in alkaline medium as a result of disproportionation of the molybdenum(V) into the +4 and +6 oxidation states. As a result of the disproportionation, the conversion cannot possibly exceed 50%. One method described in the literature is not subject to this limitation; however, the procedure is rather lengthy and complex.[4]

The synthesis described here is simpler and more efficient because the reduction and complexation are accomplished at the same time in a solution containing Mo(VI) and cyanide. Hydrazine, which is known to reduce Mo(VI) to Mo(V) in acid medium,[2,3,5] is used as the reducing agent. The reaction proceeds on the slow, drop-by-drop addition of concentrated hydrochloric acid in an amount insufficient to make the overall reaction mixture acidic. It appears that the reduction reaction takes place primarily in the locally acid regions that result from this mode of addition.

The reaction occurring is undoubtedly of great complexity. Disproportionation may enter as a step in the reaction mechanism, but this does not lower the yield since sufficient reducing agent is present to react with the Mo(VI) so formed. The equation used in representing the reaction assumes that in its reducing role each hydrazine molecule provides one electron, thus forming NH_4^+ and N_2 in a 2:1 mole ratio.[6] The amount of hydrazine (2.5 moles of N_2H_4 per mole of MoO_3) allows an excess beyond the assumed stoichiometry.

■ *Although very little potassium cyanide is lost in the form of hydrogen cyanide, it is imperative that the reaction be carried out in a well-ventilated hood.* A slight excess of potassium cyanide (10 moles of KCN per mole of MoO_3) is used to safeguard against such loss. The amount of concentrated hydrochloric acid should be limited to prevent the overall reaction mixture from becoming acidic; otherwise precipitation of unwanted by-products occurs, thus causing a considerable decrease in the final yield. A conversion to octacyanomolybdate(IV) of close to 90% can be attained this way.

Procedure

Ten grams (0.070 mole) of molybdenum(VI) oxide and 46 g. (0.70 mole) of potassium cyanide are mixed in a mortar and placed in a 300-ml. Erlenmeyer flask. Seventy-five milliliters of water is added drop by drop over a period of 30 minutes, while the mixture is being stirred and cooled in ice. The solution turns yellow-brown. Eleven grams of an 85% solution of hydrazine monohydrate (0.19 mole) is added, and the ice bath is removed. While the solution is being stirred continuously, 44.5 ml. of concentrated hydrochloric acid is added drop by drop over a period of 45 minutes. (■ *Hood!*) The solution becomes warm, and gas is evolved during the addition of the hydrochloric acid. After all the hydrochloric acid has been added, the solution should still be alkaline ($pH \approx 8$). This may be checked with litmus. The solution is subsequently heated on a steam bath for a period of one hour, and is then cooled to room temperature. At this point, possible dark deposits are removed by filtration and discarded; however, in an ideal run no dark deposits should form. The solution, which by now is yellow-green, is poured into 850 ml. of methanol to precipitate the crude potassium octacyanomolybdate(IV). The crude product is filtered, washed with methanol and acetone, and dissolved in 125 ml. of water. The solution is then heated to boiling with active carbon, filtered, and again poured into methanol. This purification process is repeated two or three times to produce pure potassium octacyanomolybdate(IV) 2-hydrate. The yield is 30 g., which represents 86% based on MoO_3. *Anal.* (reported by checkers). Calcd. for $K_4Mo(CN)_8 \cdot 2H_2O$: K, 31.5; Mo, 19.3; N, 22.6. Found: K, 31.6; Mo, 19.6; N, 22.3.

Properties

The properties of potassium octacyanomolybdate(IV) 2-hydrate have been described in reference 1, where an oxidimetric method of analysis is described. The purity of the compound may be conveniently determined spectrophotometrically, using the absorption band at 367.7 mμ ($\epsilon_{\max}$ = 170).[7]

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11. MANGANATES(VI)

$$4KMnO_4 + 4KOH \rightarrow 4K_2MnO_4 + O_2 + 2H_2O$$

$$8KMnO_4 + KI + 8Ba(OH)_2 \rightarrow KIO_4 + 8BaMnO_4 + 4H_2O + 8KOH$$

Submitted by R. S. NYHOLM* and P. R. WOOLLIAMS*
Checked by D. SHEPARD,† J. GUYER,† and K. COHN†

The preparation of manganate(VI) salts free from contamination with manganese(IV) oxide poses a real problem; indeed, it is very doubtful whether previous investigators have obtained pure specimens from the fusion of manganese(IV) oxide with alkalies. These previous preparations yield products with magnetic susceptibilities higher by 10–100% than that of the pure com-

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pound. The field-strength dependence of the susceptibility of these specimens indicates a ferromagnetic impurity which is undoubtedly manganese(IV) oxide. Even an analytically pure sample (typically, $\approx 0.2\%$ MnO_2) may exhibit a room-temperature moment as high as 1.85 B.M. With the techniques described here, "magnetically pure" products can be obtained with room-temperature moments of 1.75 B.M. that are independent of field strength.

The sparingly soluble potassium manganate(VI) previously has been prepared either by fusion of potassium hydroxide with manganese(IV) oxide and potassium nitrate or by the decomposition of manganate(VII) (permanganate) in strong alkali. The following modification of the method given by Scholder and Waterstadt[1] gives a magnetically pure sample of K_2MnO_4.

The insoluble barium manganate(VI) can be prepared from barium chloride and potassium manganate(VI), but the product always contains MnO_2 and Cl^- ions. Reduction of $Ba(MnO_4)_2$ with peroxide produces a wide variety of oxidation states with much MnO_2. Fusion of barium permanganate, manganese(IV) oxide, and barium carbonate gives mainly manganate(V). Decomposition of permanganate by concentrated barium hydroxide gives mixed manganates.[2] However, pure barium manganate(VI) is precipitated quantitatively by adding a solution of permanganate to a solution containing iodide and excess barium hydroxide.

A. POTASSIUM MANGANATE(VI), K_2MnO_4

Procedure

Because carbonic acid is strong enough to cause immediate disproportionation of the manganate(VI), contamination of solvents by carbon dioxide must be avoided. All water and solvents should be boiled prior to use to remove any dissolved carbon dioxide.

Sixty-five milliliters of water in a 500-ml. Erlenmeyer flask is warmed to 65°, and a mixture of 75 g. (1.35 moles) of potassium hydroxide and 10 g. (0.063 mole) of potassium permanganate is then cautiously added in small increments with stirring. A condenser bearing a soda-lime or Ascarite tube is attached, and the contents of the flask are heated under reflux. After about 15 minutes, the deep purple permanganate color suddenly disappears; the solution (now green) is *immediately* restored to its original volume by the addition of hot (70°) 2 *M* potassium hydroxide solution. The contents of the flask are then cooled quickly to $-80°$ (Dry Ice–acetone bath) and allowed to warm up to $-5°$ over a period of 2 hours. During this time, the crude product crystallizes—a process which is assisted by occasional agitation of the flask. The solution is then cooled until it becomes viscous and almost freezes, and the product is filtered off in a dry atmosphere (to prevent ice from condensing on the precipitate). The dark green crystals are quickly washed, successively, with the following reagents: (1) 50 ml. of 40% KOH (cooled to $-10°$), (2) 50 ml. of CH_3OH + 0.5 g. of KOH (cooled to $-15°$), (3) 100 ml. of dry ether (cooled to $-20°$).

The product is dried over P_2O_5 *in vacuo.* Final yield: 10.5 g. (85%). *Anal.* Calcd. for K_2MnO_4: K, 39.67; Mn, 27.87. Found (ranges for eight samples): K, 39.58–39.7; Mn, 27.8–27.9. If small amounts of MnO_2 are detected by analysis, the product can be recrystallized from 50% KOH and isolated by the above technique.

B. BARIUM MANGANATE(VI), $BaMnO_4$

It is well known that in alkaline solution, strong reducing agents yield manganese(IV) oxide when oxidized by permanganate. Manganese(VI) is known to be a transient intermediate in such reactions, and in the presence of barium ions the MnO_4^{2-} ion is precipitated as $BaMnO_4$. When the titration of iodide with permanganate in barium hydroxide solution is studied potentiometrically, it is found that the iodide is oxidized to IO_4^-. The end point is sharp and can be used for the analysis of iodide or permanganate. In the absence of barium ions, the main product is manganese(V). With strontium ions, an impure $SrMnO_4$ is obtained containing 10% MnO_2 [possibly because $Ba(OH)_2$ is more soluble than $Sr(OH)_2$]. Below room temperature the solubility of $Ba(OH)_2$ is decreased, and other products are formed. At 60° the manganate(VI) appears to decompose before it can be stabilized by precipitation.

Procedure

A solution saturated with potassium permanganate at room temperature is added drop by drop to 100 ml. of a saturated solution of barium hydroxide at 40° containing 5 g. (0.03 mole) of potassium iodide in a closed system. The dark blue-green precipitate is washed by decantation with concentrated $Ba(OH)_2$ solution, and then isolated by filtration and washed with cooled solutions of $Ba(OH)_2$ in water and methanol (as for K_2MnO_4). Such products may be contaminated by potassium salts, but ultrapure samples are obtained if barium permanganate and barium iodide are used. Barium permanganate is conveniently obtained by decomposing a warm suspension of a crude sample of $BaMnO_4$ in a stream of carbon dioxide. To the filtered solution containing the permanganate a slight excess of $Ba(OH)_2$ is added to remove dissolved carbon dioxide. The solution is filtered to remove the barium carbonate, and is used directly. *Anal.* Calcd. for $BaMnO_4$: Ba, 53.59; Mn, 21.44. Found: Ba, 53.6; Mn, 21.4.

Chemical Analyses

Potassium, barium, and manganese can be determined by standard techniques. A quantitative estimate of any MnO_2 impurity can be obtained from the oxidizing power of the samples. The K_2MnO_4 is dissolved in dilute sulfuric acid, causing disproportionation of the MnO_4^{2-} to MnO_4^- and MnO_2. Both the MnO_4^- and MnO_2 are reduced to Mn^{2+} by addition of potassium iodide; the liberated iodine is then titrated with thiosulfate. The procedure is repeated with the same weight of K_2MnO_4, with filtration of the MnO_2 prior to the titration. For pure manganese(VI) the titers will be in the ratio 6:5.

For the barium salt, dilute phosphoric acid should be used. Apparently, previous investigators have obtained misleading results because barium sulfate was deposited on the surface of the manganate(VI).

Absence of residual hydroxide is confirmed by treatment with oxalic acid containing 0.1 *N* sulfuric acid. The remaining sulfuric acid is determined by back titration.

Magnetic Analysis

The magnetic susceptibility of analytically pure samples should be determined over a range of field strengths 1000–8000 gauss. The moment of an impure sample (0.2% MnO_2) varied from 1.77 to 1.83 B.M. from 9700 to 3250 gauss at room temperature. [The susceptibility of $HgCo(CNS)_4$ is independent of field strength in this range and is a convenient calibrant.] Products are acceptable if the susceptibility is constant to 1% (equivalent to 0.05% MnO_2).

Properties

The dark green rhombic crystals of K_2MnO_4 (decomp. 190°) usually resemble ordinary specimens of $KMnO_4$ in appearing violet-brown by reflection, but they are isomorphous with K_2SO_4 and K_2CrO_4. [Pure freshly prepared manganate(VI) is bright green; its more usual appearance is due to a surface film of permanganate that is spontaneously formed.] It disproportionates slowly in alkali and rapidly in dilute acids:

$$2H_2O + 3MnO_4^{2-} \rightarrow 2MnO_4^- + MnO_2 + 4OH^-$$

The manganate(VI) species is stable in very strong alkali only.

The dark green-blue $BaMnO_4$ is isomorphous with $BaSO_4$, and although insoluble in water, it disproportionates on contact with water or dilute acids, forming MnO_2 and $Ba(MnO_4)_2$.

Pure manganate(VI) salts exhibit a magnetic moment of 1.75 B.M. at room temperature. The susceptibility follows the Curie law after small corrections for temperature-independent paramagnetism and diamagnetism of the ligands have been applied.

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12. BIS(DIMETHYLGLYOXIMATO)COBALT COMPLEXES

(*"Cobaloximes"*)

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Bis(dimethylglyoximato)cobalt complexes are of interest as models of vitamin B_{12}.[1] The cobalt atom in the square planar ligand field of the four sp^2-hybridized nitrogen atoms of dimethylglyoxime has a pronounced tendency to form stable organocobalt derivatives, in analogy to the cobalt atom in the

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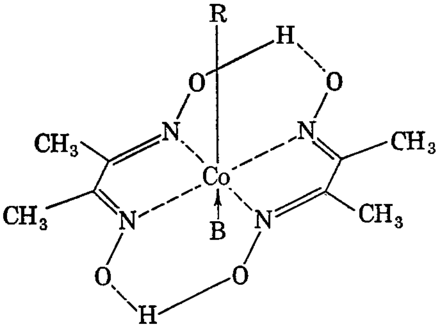
corrins. Many compounds of the type shown below, with direct Co—C bonds, have been characterized.[1–4] To facilitate



R = acid anion, alkyl, or aryl

B = base, e.g., pyridine

the notation we use the name "cobaloxime" for the bis(dimethylglyoximato)cobalt moiety. "Methyl(pyridine)-cobaloxime" thus corresponds to "Co-methyl(pyridine)bis(dimethylglyoximato)-cobalt," CH_3—Co(DH)$_2$py (D = dianion of dimethylglyoxime, $(CH_3)_2C_2N_2O_2^{2-}$, and py = pyridine). Procedures for the preparation of some representative compounds follow.

A. CHLORO(PYRIDINE)COBALOXIME(III)[5]

$$CoCl_2 \cdot 6H_2O + 2DH_2 + 2py + \tfrac{1}{2}O_2 \rightarrow ClCo(DH)_2py + py \cdot HCl + 7H_2O$$

Procedure

To a hot solution of 5.0 g. (0.021 mole) of cobalt(II) chloride 6-hydrate and 5.5 g. (0.047 mole) of dimethylglyoxime in 200 ml. of 95% ethanol, 3.44 g. (0.043 mole) of pyridine is added, using a 1-l. Erlenmeyer flask as the reaction vessel. After cooling to 20°, a stream of air is blown through the solution for 30 minutes. The reaction mixture is then allowed to stand for 60 minutes at 20°, during which period the product crystallizes out of the solution. The brown crystals are collected by filtration on a Büchner funnel, washed successively with 50-ml. portions of water, ethanol, and diethyl ether, and dried at room temperature *in vacuo.* Yield (without work-up of filtrates) 5.9 g. [70% based on cobalt(II) chloride 6-hydrate]. *Anal.* Calcd. for $C_{13}H_{19}N_5O_4$-ClCo: C, 38.67; H, 4.74; N, 17.35. Found: C, 38.52; H, 4.68; N, 17.41.

Preparation of Related Compounds. For the preparation of the complexes $XCo(DH)_2B$, with anions (X) other than chloride or bases (B) other than pyridine, cobalt(II) acetate 4-hydrate is used in place of the chloride, and the calculated amount of an alkali salt of the acid HX is added (X can be, for example, CNO, CN, N_3, SCN, Br, I), whereas the calculated quantity of B (twice the stoichiometric amount of the cobalt, according to the above equation) is added. The method may be varied by adding a 1:1 molar ratio of sodium hydroxide plus one-half of the required amount of base according to the above equation. The amount of base must correspond to the calculated quantity. For instance, if excess pyridine is added, the compound $Co(D_2H)py_2$ is formed.

Properties

Chloro(pyridine)cobaloxime forms yellow-brown crystals which are stable in air and sparingly soluble in most solvents, including water. It is slowly decomposed by acids and bases. With the former, dimethylglyoxime, cobalt salt, and the protonated pyridine are formed. With bases such as potassium hydroxide, derivatives of $Co(D_2H)$ are obtained; the chloride ion is released only slowly in alkaline solution. The compound is not an oxygen carrier, and is not affected by molecular hydrogen. But if a molar equivalent of sodium hydroxide and catalytic amounts of a platinum metal or a reduced cobaloxime are added, hydrogen is rapidly absorbed. The hydrogenation is an autocatalytic reaction. Depending on the pH of the solution, the reduction leads either to the cobaloxime(II) (pH near 7) or the cobaloxime(I) ($pH > 7$). Prolonged interaction with hydrogen causes ligand reduction. Four cathodic waves have been observed in polarography in acetonitrile solution, the $E_{\frac{1}{2}}$ potentials being -0.65, -1.45, -2.42, and -2.92 v. vs. the $Ag/AgNO_3$ electrode. The first three waves correspond to the reduction of the cobalt from +3 to +2, +1, and 0, respectively. The last is due to ligand reduction.[6]

B. DIAQUOCOBALOXIME(II)[4,7]

$$Co(C_2H_3O_2)_2 \cdot 4H_2O + 2DH_2 \rightarrow Co(DH)_2 \cdot 2H_2O + 2C_2H_4O_2 + 2H_2O$$

A 1-l. round-bottomed flask, equipped with a magnetic stirring bar, is filled with 400 ml. of dry methanol. While flushing with dry nitrogen (complete exclusion of air is imperative), 24.9 g. (0.100 mole) of cobalt(II) acetate 4-hydrate and 23.2 g. (0.200 mole) of dimethylglyoxime are added to the methanol. The flask is closed, and the solution stirred for about one hour. The orange crystalline product is collected on a Büchner funnel under a stream of nitrogen. After washing with 100 ml. of cold water, the $Co(DH)_2 \cdot 2H_2O$ is dried at 1 mm. pressure at room temperature. Yield: 26.0 g. (82%, based on dimethylglyoxime). *Anal.* Calcd. for $C_8H_{18}N_4O_6Co$: C, 29.56; H, 5.54; N, 17.23. Found: C, 29.56; H, 5.59; N, 17.28.

Properties

Diaquocobaloxime, $Co(DH)_2 \cdot 2H_2O$, is paramagnetic ($\mu_{\text{eff.}} = 1.80$ B.M.) and on contact with air slowly turns violet-brown. It may be dehydrated by heating to 80° in a vacuum. The resulting violet and insoluble bis(dimethylglyoximato)-cobalt, $Co(DH)_2$, is paramagnetic, mildly hygroscopic, and not isomorphous with $Ni(DH)_2$. It absorbs oxygen. The dihydrate [as well as $Co(DH)_2$] reacts with various donor ligands to produce 1:1 or 1:2 adducts. The 1:1 adducts are diamagnetic and must be formulated as dimers with a Co—Co bond. The 1:2 adducts, on the other hand, are paramagnetic. To obtain the bis adducts one can proceed according to the above method, except that an excess of the base B (twice or three times the calculated amount) is added. The complex with B = triphenylphosphine forms black crystals ($\mu_{\text{eff.}} = 1.82$ B.M.) which are fairly stable in air. This compound may also be prepared from $Cl—Co(DH)_2P(C_6H_5)_3$ by refluxing the latter in methanol in the presence of excess of triphenylphosphine, with hydrazine hydrate as the reducing agent. If the above procedure for the preparation of $Co(DH)_2 \cdot 2H_2O$ is carried out in the presence of a 1:1 equivalent amount of the base component, the dimeric cobaloximes are formed. For instance, $[Co(DH)_2py]_2$ forms black crystals which are more air-sensitive than the compounds with phosphines as the base component.

C. METHYL(PYRIDINE)COBALOXIME[3]

$$CoCl_2 \cdot 6H_2O + 2DH_2 + py + 2OH^- = \tfrac{1}{2}[Co(DH)_2py]_2 + 8H_2O + 2Cl^-$$

$$\tfrac{1}{2}[Co(DH)_2py]_2 + [H]_{eq.} + OH^- = Co^I(DH)_2py^- + H_2O$$

$$Co(DH)_2py^- + (CH_3)_2SO_4 = CH_3Co(DH)_2py + CH_3SO_4^-$$

In this procedure the complex $CH_3Co(DH)_2py$ is prepared from the cobaloxime(I) obtained by reducing the dimeric cobaloxime(II), $[pyCo(DH)_2]_2$, with sodium hydroborate, $NaBH_4$. The dimeric cobaloxime(II) is prepared *in situ* and not isolated. Instead of pyridine, other bases may be used in the following procedure.

Procedure

A suspension of 172 g. (1.5 moles) of dimethylglyoxime and 178 g. (0.75 mole) of cobalt(II) chloride 6-hydrate in 2 l. of methanol is stirred under nitrogen in a 3-l. Erlenmeyer flask until the cobalt(II) salt dissolves (complete dissolution of the dimethylglyoxime is not necessary). There is then added 60 g. (1.5 moles) of sodium hydroxide (in the form of a 50% by weight aqueous solution), plus 60 g. (0.75 mole) of pyridine. A dark precipitate of $[pyCo(D_2H_2)]_2$ forms. The suspension is cooled to −10°, using a Dry Ice–acetone bath, and stirred under nitrogen for 15 minutes. For the reduction of the cobaloxime(II) to the cobaloxime(I), 30 g. of sodium hydroxide (in the form of a 50% by weight solution) is added, followed by 4.0 g. (0.13 mole) of sodium hydroborate in 50 ml. of water. The latter reagent should be added in portions to avoid excessive foaming. The reaction mixture turns dark green as the reduction to the cobalt(I) derivative proceeds. Subsequently, 101 g. (0.8 mole) of dimethyl sulfate is added, and the solution is allowed to warm gradually to 20°. The reaction solution is evaporated to a total volume of 800 ml. by blowing a stream of air through it at room temperature, and the suspension is finally poured into 2 l. of water containing 20 ml. of pyridine. Orange crystals precipitate and are collected. After washing with water, they are dried at 1 mm. pressure at 20–40°. Yield: 284 g. (99%). *Anal.* Calcd. for $C_{14}H_{22}N_5O_4Co$: C, 43.87; H, 5.79; N, 18.28. Found: C, 43.86; H, 5.84; N, 18.76.

Properties

Methyl(pyridine)cobaloxime is soluble in many organic solvents, e.g., in benzene, acetone, methanol, methylene chloride, and tetrahydrofuran. The solutions are stable in the dark, but on light irradiation the Co—C bond is cleaved. In crystalline form the compound is less light-sensitive, but should be stored in tinted bottles. For a detailed description of the properties of alkylcobaloximes see reference 3.

D. METHYLAQUOCOBALOXIME[3]

Methylaquocobaloxime, $CH_3Co(DH)_2OH_2$, is best prepared from $CH_3Co(DH)_2S(CH_3)_2$. It can also be made directly from cobaloxime(II), hydrogen, and methyl iodide in alkaline solution, but isolation is difficult. The following procedure is best for the preparation of moderate amounts of the complex.

Procedure

A suspension of 23.8 g. (0.100 mole) of cobalt(II) chloride 6-hydrate and 23.2 g. (0.200 mole) of dimethylglyoxime in 100 ml. of methanol is stirred in a 500-ml. three-necked flask for 5 minutes. A continuous stream of nitrogen is passed through the vessel at all times. Subsequently, 8.0 g. (0.2 mole) of sodium hydroxide in 150 ml. of water is added. The resulting solution is stirred for 15 minutes and then cooled to −20°. While stirring, 7.0 g. (0.113 mole) of dimethyl sulfide is added, followed, after 5 minutes, by 20.0 g. (0.141 mole) of methyl iodide. Next, a previously prepared solution of 4.0 g. of sodium hydroxide in 20 ml. of water is added over a period of 5 minutes, immediately followed by the addition of a solution of 1.0 g. of sodium hydroxide plus 0.6 g. of sodium hydroborate in 10 ml. of water. The solution is stirred for 15 minutes, while it warms to room temperature, and is then filtered.* The filtrate is freed of excess dimethyl sulfide and methyl iodide in a stream of air, diluted with one volume of water, and set aside for crystallization at −10° for 24 hours. The orange crystals of methyl(dimethyl sulfide)cobaloxime are collected, washed with water, and air-dried. Yield, 15.2 g. (41%). From the filtrate an additional 5.1 g. (13%) of methyl(pyridine)cobaloxime can be obtained by adding 5 ml. of pyridine and subsequently crystallizing by cooling to −10°.

To prepare methylaquocobaloxime, a suspension of 15 g. (0.041 mole) of $CH_3Co(DH)_2 \cdot S(CH_3)_2$ in 75 ml. of water is stirred and heated to boiling for 30 minutes. The operation is best performed under a good hood to avoid the malodorous smell of dimethyl sulfide. The resulting suspension of methylaquocobaloxime is cooled to nearly 0° and, after 24 hours of standing, is filtered to yield 10.5 g. (80%) of dark orange crystals of methyl-

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* It is sometimes observed that some of the dimethyl sufide complex precipitates before filtration.

aquocobaloxime, $CH_3Co(DH)_2OH_2$, which are air-dried. *Anal.* Calcd. for $C_9H_{19}N_4O_5Co$: C, 33.44; H, 5.95; N, 17.39. Found: C, 33.51; H, 6.03; N, 17.48.

Properties

Methylaquocobaloxime forms orange crystals which are stable in air. The solid is somewhat light-sensitive, and should be stored in the dark. In solution, photodecomposition occurs quite readily. Under anaerobic conditions, methane and small amounts of ethane are formed. In the presence of air, the principal photolysis product is formaldehyde. The compound decomposes at 215–220°, producing methane and the decomposition products of dimethylglyoxime (viz., nitrogen, ammonia, and acetonitrile). The compound is somewhat soluble in water and in a variety of organic solvents. The protons of the cobalt-bound methyl group are not acidic and do not undergo acid- or base-catalyzed deuterium exchange. Methylaquocobaloxime may be dehydrated to the deep red, insoluble methylcobaloxime, a compound which is formally isoelectronic with, and in appearance remarkably similar to, bis(dimethylglyoximato)nickel(II). The coordinated water molecule can be displaced by bases such as pyridine, phosphines, and isonitriles. With boron trifluoride ether, a complex of composition $CH_3Co(D_2B_2F_4)\cdot H_2O$ is obtained in which the oxime protons are replaced by bridging BF_2 groups.

E. PHENYL(PYRIDINE)COBALOXIME[1]

$$C_6H_5Br + Mg = C_6H_5MgBr$$
$$C_6H_5MgBr + ClCo(DH)_2py = C_6H_5Co(DH)_2py + MgBrCl$$

The synthesis of organocobaloximes via Grignard reactions is exemplified in the following preparation of phenyl(pyridine)-cobaloxime. Since the cobaloximes contain two acidic oxime protons, the Grignard reagent must be employed in threefold excesses.

Procedure

A solution of phenylmagnesium bromide is prepared by treating 5 g. (0.206 mole) of magnesium with 32.3 g. (0.206 mole) of bromobenzene in dry tetrahydrofuran. The organomagnesium reagent solution is slowly added to a cooled (ice-bath) suspension of 27.6 g. (0.068 mole) of chloro(pyridine)cobaloxime in 150 ml. of tetrahydrofuran, while the system is swept with dry oxygen-free nitrogen. During the addition of the Grignard reagent, the reaction mixture becomes green because of the formation of small amounts of reduced cobaloximes. On stirring, the mixture turns red-brown. To complete the reaction it is preferable to heat the reaction mixture for 15 minutes on a steam bath. The cooled solution is then hydrolyzed with 200 ml. of 10% hydrochloric acid containing ice, and the crude product is extracted with petroleum ether (b.p. 60–80°) to free it from small amounts of biphenyl formed as by-products. After filtration, the product is washed with alcohol and ether and dried. It is purified by Soxhlet extraction with dichloromethane. Yield: 25.6 g. (84%). *Anal.* Calcd. for $C_{19}H_{24}N_5O_4Co$: C, 51.24; H, 5.43; N, 15.73; O, 14.37; Co, 13.23. Found: C, 51.10; H, 5.41; N, 15.54; O, 14.32; Co, 13.50.

Properties

Phenyl(pyridine)cobaloxime is stable in air and only sparingly soluble in most organic solvents. The Co—C bond is remarkably stable and difficult to solvolyze, but may be cleaved to produce benzene under reducing conditions in the presence of a noble metal catalyst.

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13. POTASSIUM μ-OXO-BIS[PENTACHLORORUTHENATE(IV)] 1-HYDRATE

$$\mathrm{Ru} + \mathrm{KClO_3} \xrightarrow[\text{2. HCl}]{\text{1. KOH}} \mathrm{K_4[Ru_2Cl_{10}O]\cdot H_2O}$$

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Methods available for the dissolution of ruthenium metal involve alkali fusion under oxidizing conditions. The absence of complete experimental details makes repetition of these methods difficult. The following procedure is a modification of those of Antony and Lucchesi[1] and of Charonnat[2] and, excluding the period of overnight evaporation, takes about 3 hours. The precise stoichiometry of the fused-salt reaction is not known. All procedures must be carried out in a fume hood since chlorine and some ruthenium tetraoxide are produced.

Procedure

Potassium hydroxide (9 g., 0.16 mole) is fused in a silver crucible, using a Bunsen burner as a source of heat, until the water is lost and a quiescent melt is obtained. Ruthenium powder (1.5 g., 0.015 mole) is mixed, *without grinding*, with 2.3 g. (0.019 mole) of finely ground potassium chlorate. (■ ***Caution.***

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Use a clean mortar, free of organic matter, for the grinding.) The mixture is added to the melt in small portions until scintillations are observed above the surface. This addition takes about 20 minutes, and the color of the melt becomes a deep red-black. The remainder of the ruthenium-potassium chlorate mixture is added over a period of 30 minutes, and the rate of heating is maintained so as to keep the mass molten. When the addition is complete, the crucible is heated a further 30 minutes, the flame being reduced in order to minimize creeping of the contents over the sides of the vessel. The crucible is cooled in air for about 15 minutes and then plunged into 110 ml. of 5 *M* hydrochloric acid, the red solid adhering to the crucible being scraped out with a glass rod. After about 10 seconds the crucible is removed, further scraped, and then replaced in the acid solution. This procedure is repeated until all the solid is transferred. The crucible is then washed with 5 *M* hydrochloric acid, and the washings are combined with the main solution. During the reaction with acid there is much effervescence, and the solution changes from red through brown to black in color, returning to a purple-brown when all the solid has dissolved. The solution is boiled for a few minutes, filtered to remove a small amount of unchanged ruthenium, and the filtrate is evaporated on the steam bath to a volume of 100 ml. The filtrate is allowed to stand overnight, and the product is filtered off and washed with ice water, ethanol, and then acetone. More product is obtained by evaporation of the mother liquor. The total yield is 4.4–5.2 g. (79–94% based on Ru). *Anal.* Calcd. for $K_4[Ru_2Cl_{10}O]\cdot H_2O$: Cl, 47.5; Ru, 27.1. Found: Cl, 48.0; Ru, 27.1. An x-ray diffractometer powder pattern is in complete agreement with ASTM diffraction data card 11-685 for the compound formulated $K_4[Ru_2Cl_{10}O]\cdot H_2O$. The method of Mercer and Buckley[3] is suitable for the ruthenium estimation.

Properties

Potassium μ-oxo-bis[pentachlororuthenate(IV)] 1-hydrate is a deep brown microcrystalline diamagnetic solid, sparingly soluble in water. The solution hydrolyzes readily and deposits a brown-black precipitate. The conductivity of a freshly prepared 7.45×10^{-4} *M* aqueous solution at 25° is 502 ohm^{-1} cm.^2 mole^{-1}. Potassium μ-oxo-bis[pentachlororuthenate(IV)] 1-hydrate is a convenient starting material for many syntheses of ruthenium(II) and ruthenium(III)[4] complexes, and may be reduced with agents such as formaldehyde to give the pentachloroaquoruthenate(III) ion. The diamagnetism of the ruthenium(IV) complex has been accounted for by a simple molecular orbital treatment,[5] and is correlated with the μ-oxo structure established by x-ray studies.[6]

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14. VANADIUM(III), COBALT(II), AND NICKEL(II) β-KETO AMINE COMPLEXES

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Checked by I. L. MADDEN,§ J. M. GROW,§ and L. J. TODD§

The recent and continuing surge of interest in transition-metal complexes of α,β-unsaturated β-keto amines (β-amino ketones),[1] especially with respect to their stereochemical properties,[2–4] has resulted in increased efforts to secure general synthetic procedures for these complexes. Methods of preparation of these complexes have been reviewed recently.[1,5,6] Although most of

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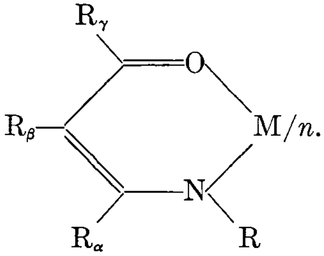
the methods classified in these sources are to some degree useful, none has been shown to be general with respect to alteration in metal-ion or ligand structure. A particular disadvantage in some of these methods (especially direct reaction of metal salt and β-keto amine, direct combination of 1,3-diketone, primary amine, and metal ion, and preparation by amine exchange) is that the reactions are frequently carried out in partially aqueous media. Although some complexes, particularly quadridentate copper(II) and nickel(II) complexes and bischelate derivatives of these metals having aryl-substituted nitrogen substituents, are often stable under these conditions, many other complexes are hydrolyzed or otherwise decomposed. With metal ions such as vanadium(III), cobalt(II), and nickel(II), β-keto amine complexes having alkyl-substituted nitrogen substituents are particularly sensitive to water and are not satisfactorily prepared by the conventional methods mentioned above.

Herein is reported a synthetic procedure for the preparation of β-keto amine complexes of the general structure



The method is applicable to the preparation of bis ($n = 2$) and tris ($n = 3$) complexes with a variety of ring substituents R_α, R_β, R_γ, and metal ions such as V(III),[4] Fe(II),[7] Co(II),[3] Ni(II),[2] and Pd(II).[2] Complexes having $R = H$, alkyl, and aryl are readily prepared. The method is related to the nonaqueous synthesis of tris(β-keto amine)Cr(III) complexes with R = aryl,[8] and is illustrated by the preparation of the Ni(II), Co(II), and V(III) complexes of 4-methylamino-3-penten-2-one ($R = R_\alpha = R_\gamma = CH_3$, $R_\beta = H$). The general procedure involves the reaction in *t*-butyl alcohol of a tetraalkylammonium tetrahalometallate with the appropriate β-keto amine in the presence of potassium *t*-butoxide. The complex metal salt offers a convenient source of the metal ion in an anhydrous, reactive, and slightly soluble form; *t*-butoxide deprotonates the weakly acidic β-keto amine. Slight variations of this same procedure have been successfully applied to the synthesis of other chelates which have the general property of hydrolytic instability and are frequently derived from very weakly acidic organic systems.[9]

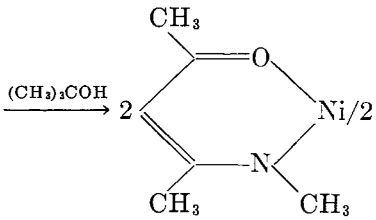
A. 4-METHYLAMINO-3-PENTEN-2-ONE

$$CH_3COCH_2COCH_3 + CH_3NH_2 \rightarrow CH_3COCH{=}C(NHCH_3)CH_3 + H_2O$$

This compound is readily prepared by bubbling dry gaseous methylamine through pure 2,4-pentanedione.[10] The resultant oily product is taken up in ether. The ethereal solution is dried over sodium sulfate for 2 hours and filtered. The solvent is evaporated completely, leaving a residue which crystallizes on cooling to 10°. Recrystallization of this material from petroleum ether (b.p. 40–60°) yields colorless crystals, m.p., 43–45°, (literature,[10] 45°) in 70–80% yield. The compound should be stored in a desiccator or used immediately after purification.

B. BIS(4-METHYLAMINO-3-PENTEN-2-ONATO)NICKEL(II)

$$2CH_3COCH{=}C(NHCH_3)CH_3 + 2KOC(CH_3)_3 + [(C_2H_5)_4N]_2[NiBr_4]$$



$+ 2(C_2H_5)_4NBr + 2KBr$

$+ 2(CH_3)_3COH$

Procedure

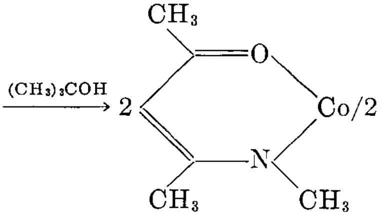
t-Butyl alcohol is dried over anhydrous calcium sulfate, refluxed over freshly cut sodium for several hours, and then distilled. To 150 ml. of this solvent in a 250-ml. standard taper flask is added 1.95 g. (0.050 mole) of freshly cut potassium. (■ **Caution.** *Potassium is a very reactive metal and should be exposed to the atmosphere for only a few seconds.*) The rate of reaction with *t*-butyl alcohol can be increased by initially warming the alcohol to 80°. After the potassium has completely dissolved, 5.65 g. (0.050 mole) of 4-methylamino-3-penten-2-one is added. The solution is stirred magnetically and warmed to about 50° during the next 10 minutes. At the end of this time 18 g. (0.028 mole) of tetraethylammonium tetrabromonickelate (II)[11] is added. The mixture is stirred vigorously at room temperature with protection from atmospheric moisture for 3 hours, during which time a gray-green precipitate forms. The flask containing the reaction mixture is then connected to a vacuum pump equipped with cold traps, and all the solvent is removed by evaporation. Dry *n*-heptane (100 ml.) is added to the residue, and the mixture is boiled and stirred vigorously for about 2 minutes. (Heating the solution for a longer period results in some decomposition of the complex.) The hot mixture is filtered under suction through a coarse glass filter frit. Green crystals of the complex form when the gray filtrate is cooled for several hours at −10°. Two further recrystallizations of this crop from dry *n*-heptane solution produce an analytically pure product. The yield from each recrystallization is considerably improved by reduction in volume of the hot filtrate by removal of solvent *in vacuo.* The pure complex is obtained as green needles (2.7 g.) in 38% yield, based on the ligand. *Anal.* Calcd. for $C_{12}H_{20}N_2O_2Ni$: C, 50.93; H, 7.12; N, 9.90. Found: C, 50.88; H, 7.02; N, 10.04. By checkers: C, 50.90; H, 7.15.

Properties

Bis(4-methylamino-3-penten-2-onato)nickel(II) forms diamagnetic green needlelike crystals which melt at 125°. It is fairly soluble in most weakly polar organic solvents, and especially soluble in chloroform. The proton magnetic resonance spectrum shows small isotropic contact shifts, the analysis of which indicates a 95:5 ratio of planar to tetrahedral stereoisomers at 25° in chloroform solution.[3] In solution the complex is decomposed by small amounts of water.

C. BIS(4-METHYLAMINO-3-PENTEN-2-ONATO)COBALT(II)

$[(C_2H_5)_4N]_2[CoBr_4] + 2CH_3COCH{=}C(NHCH_3)CH_3 + 2(CH_3)_3COK$



$+ 2(C_2H_5)_4NBr + 2KBr$

$+ 2(CH_3)_3COH$

*Procedure**

t-Butyl alcohol is dried as described in Procedure B. One hundred and fifty milliliters of this solvent is placed in a 250-ml. single-necked standard taper flask equipped with a sidearm carrying a vacuum stopcock (flask *A* in Fig. 6). Freshly cut potassium (1.95 g., 0.050 mole) is added. (■ ***Caution.*** *Potassium is a very reactive metal and should be exposed to the atmosphere for only a few seconds.*) After the potassium has completely dissolved, the solution is brought to a boil, and dry

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* The technique of chemical manipulation under a nitrogen atmosphere, using apparatus like that in Fig. 6, is described in reference 12.

high-purity nitrogen, introduced through the neck, is bubbled through the solution while it cools to about 50°. Then 5.65 g. 0.50 mole) of 4-methylamino-3-penten-2-one is added to the solution, and the nitrogen stream is continued for about 10 minutes. At this point a magnetic stirring bar is placed in the flask, the nitrogen source is connected to the sidearm of the flask, and a 20-cm. glass chimney with standard-taper joints is attached to the flask. Tetraethylammonium tetrabromocobaltate(II)[11] 18 g., 0.028 mole) is added through the chimney under a stream of nitrogen admitted through the sidearm. The chimney is closed off at the top, and a slight positive pressure of nitrogen is maintained in the flask.

The mixture is stirred at room temperature for 3 hours, during which time a red-orange precipitate forms. The mixture is then warmed to about 40°; the nitrogen hose is replaced by one connected to a vacuum pump with cold traps, and the *t*-butyl alcohol is completely removed under vacuum. The flask containing the residue is flushed with nitrogen, and 200 ml. of dry oxygen-free *n*-heptane is introduced under nitrogen pressure by means of a right-angle standard-taper glass tube connecting the top of the chimney with the flask containing the *n*-heptane. The right-angle tube and chimney are replaced by the filtering apparatus shown in Fig. 6, flask *A* being at the bottom. Stopcocks *D* and *F* are opened, and the mixture of *n*-heptane and reaction products is stirred vigorously and heated to boiling in the presence of a nitrogen stream admitted through stopcock *C*, thereby purging the apparatus of oxygen. After several minutes of boiling, the source of heat is removed, *C* and *F* are closed, and flask *B* is evacuated through *D*. The glass components of the system are held together during these operations by small steel springs. The whole apparatus is then inverted so that flask *B* is at the bottom. Stopcock *F* is opened, and the hot filtrate is collected in flask *B*. The nitrogen source is connected to the sidearm of this flask, and the flask is removed from the remainder

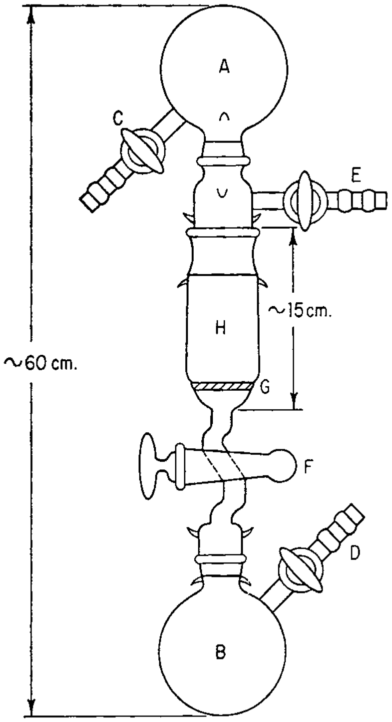


Fig. 6. Sketch of apparatus for the filtration of oxygen-sensitive materials. (A, B), *250-ml. flask equipped with 24/40 joint and 5-mm.-i.d. sidearm;* (C–E), *vacuum stopcocks, 2-mm. bore;* (F), *vacuum stopcock, 6-mm. bore;* (G), *fritted disk filter, coarse, 40-mm.-diam.;* (H), *filtration chamber with 45/50 joint, volume to bottom of joint 100 ml.*

of the apparatus while nitrogen is passed rapidly over the solution. The flask is stoppered under positive nitrogen pressure and cooled at −10° for several hours, during which time orange crystals form. The orange residue remaining on the filter is extracted twice more with *n*-heptane in a similar manner in order to obtain an optimum yield of complex.

The product which crystallizes from the cold *n*-heptane solutions is collected, using the apparatus and techniques just described. The products from the three extractions are combined, and two additional recrystallizations are performed by the indicated procedure. Traces of solvent are removed from the final product by drying it on the filter at room temperature by means of evacuation through *E* with *C* and *F* closed. The final product is obtained as orange crystals (5 g.) in 70% yield, based on the ligand. *Anal.* Calcd. for $C_{12}H_{20}N_2O_2Co$: C, 50.88; H, 7.12; N, 9.89. Found: C, 50.93; H, 7.13; N, 9.92. By checkers: C, 50.96; H, 7.41; N, 9.59.

Properties

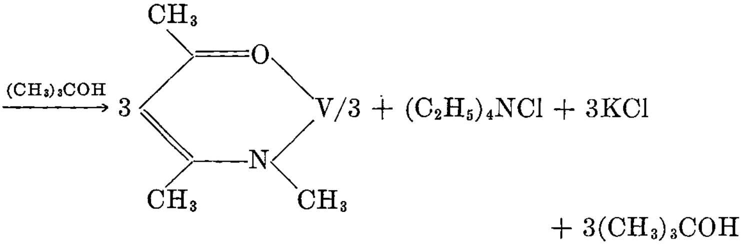
Bis(4-methylamino-3-penten-2-onato)cobalt(II) forms orange crystals which melt at 169–171° and which are stable in air for several hours. The complex is soluble in most organic solvents, but its solutions are susceptible to rapid oxidation by air. Traces of moisture in solution may hydrolyze the complex. Room-temperature magnetic moments of the crystalline solid (4.22 B.M.) and of the complex in toluene solution (4.36 B.M.), together with ligand field spectra, demonstrate a tetrahedral stereochemistry in both phases.[3]

D. TRIS(4-METHYLAMINO-3-PENTEN-2-ONATO)-VANADIUM(III)

$$(C_2H_5)_4NCl + VCl_3 \xrightarrow{CH_3CN} [(C_2H_5)_4N][VCl_4]\cdot 2CH_3CN$$

$$[(C_2H_5)_4N][VCl_4]\cdot 2CH_3CN \xrightarrow{80°/10^{-2}\text{ mm.}} [(C_2H_5)_4N][VCl_4] + 2CH_3CN$$

$$[(C_2H_5)_4N][VCl_4] + 3CH_3COCH{=}C(NHCH_3)CH_3 + 3(CH_3)_3COK$$



*Procedure**

The preparation of tetraethylammonium tetrachlorovanadate(III) has recently been given.[13] The procedure which follows

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* The technique of chemical manipulation under a nitrogen atmosphere, using apparatus like that in Fig. 6, is described in reference 12.

is more explicit and yields a product of the purity necessary for use in the subsequent complexation reaction. A 250-ml. single-necked standard taper flask equipped with a sidearm carrying a vacuum stopcock is charged with 100 ml. of degassed anhydrous acetonitrile under nitrogen. Vanadium(III) chloride* (11.4 g., 0.073 mole) and tetraethylammonium chloride (12.5 g., 0.076 mole) are added, and the slurry is subjected to vigorous magnetic stirring under dry nitrogen for 2 hours. At the end of this time the reaction mixture changes from violet to yellow. The reaction mixture is filtered in the absence of air, using the apparatus and procedure described in Preparation C. A light yellow product, which is the bis(acetonitrile) adduct,[13] is obtained. This material is transferred in the absence of air to a drying pistol and maintained at 80°/10^{-2} mm. for 2 hours. Tetraethylammonium tetrachlorovanadate(III) is obtained as a blue-gray, very air-sensitive powder which must be stored in a dry oxygen-free atmosphere.

A 250-ml. flask of the above type is fitted with a reflux condenser connected to a mercury pressure valve. *t*-Butyl alcohol (150 ml., dried as in Procedure B) is added to the flask, which is then purged with dry high-purity nitrogen introduced through the sidearm. Freshly cut potassium (2.7 g., 0.069 mole) is added, and the solution is gently refluxed until the potassium is completely dissolved. During this time the atmosphere in the flask is displaced four times by nitrogen in order to degas thoroughly the solvent. 4-Methylamino-3-pentene-2-one (7.0 g., 0.062 mole) is added, and the reaction mixture is stirred magnetically while it is maintained at 50–60° for 15 minutes, and then is cooled to room temperature. The reflux condenser is removed; 6.8 g. (0.021 mole) of tetraethylammonium tetrachlorovanadate(III) is added through the glass chimney under a nitrogen stream (see Procedure C). The apparatus is closed off under a slight positive nitrogen pressure, and the reaction mixture is then subjected to vigorous magnetic stirring for 18 hours at room tem-

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* Available from Alfa Inorganics, Inc., Beverly, Mass.

perature. Termination of the reaction is evidenced by a deep red-brown appearance of the reaction mixture. The *t*-butyl alcohol is removed completely *in vacuo* through the sidearm while the flask is maintained at about 40°. To the residue, anhydrous oxygen-free benzene (200 ml.) is added through the chimney under nitrogen pressure. The resultant mixture is stirred vigorously for 5 minutes at 40° and filtered, using the apparatus and method given in Preparation C. The red-brown filtrate in flask *B* is evaporated to dryness *in vacuo*. The product is purified by two sublimations at $170°/10^{-3}$ mm., using a cylindrical sublimation tube without a cold finger to yield the final product as dark red crystals (5.8 g.) in 71% yield, based on the ligand. *Anal.* Calcd. for $C_{18}H_{30}N_3O_3V$: C, 55.83; H, 7.75; N, 10.85; V, 13.15. Found: C, 56.17; H, 8.00; N, 10.74. By checkers: C, 55.76; H, 7.67; V, 13.25.

Properties

Tris(4-methylamino-3-penten-2-onato)vanadium(III) forms dark red crystals which melt at 163–164°. The complex is very soluble in chloroform and dichloromethane, fairly soluble in benzene, and only slightly soluble in saturated hydrocarbons. In the absence of moisture or oxygen the reddish-brown solutions prepared from these solvents are stable, but are rapidly decomposed by exposure to either. The solid is also sensitive to oxygen and water, and should be stored in a dry-nitrogen atmosphere. The crystalline complex has a magnetic moment of 2.83 B.M. at 294°K.[4] The proton magnetic resonance spectrum of the complex in chloroform solution unambiguously demonstrates the trans pseudo-octahedral configuration.[4]

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15. HEXACOORDINATE COMPLEXES OF BIS(2,4-PENTANEDIONATO)COBALT(II)

[*Bis(acetylacetonato)cobalt(II)*]

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Checked by REBECCA J. ALLEN,† ASHIM B. CHATTERJEE,† and DEAN F. MARTIN†

A series of neutral addition compounds of bis(2,4-pentanedionato)cobalt(II), Co(acac)$_2$, can be obtained by adding the desired base to a benzene solution of this compound. The adducts are all less soluble than the starting compound; the yields are high, and most are quite pure without recrystallization. An ionic compound, sodium tris(2,4-pentanedionato)cobaltate(II), is also easily made; it is somewhat less satisfactory as a starting material for the adducts.

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A. BIS(2,4-PENTANEDIONATO)DIAQUOCOBALT(II)

[Bis(acetylacetonato)diaquocobalt(II)]

$$HC_5H_7O_2 + NaOH \rightarrow NaC_5H_7O_2 + H_2O$$
$$2NaC_5H_7O_2 + CoCl_2{\cdot}6H_2O \rightarrow Co(C_5H_7O_2)_2(H_2O)_2 + 2NaCl + 4H_2O$$

Bis(2,4-pentanedionato)diaquocobalt(II) was first obtained by Gach[1] by warming 2,4-pentanedione (acetylacetone) with precipitated cobalt(II) hydroxide. Jones prepared the compound by adding 2,4-pentanedione to an aqueous solution of hexaamminecobalt(II) ion.[2] Recent workers[3-6] have employed the method of Charles and Pawlikowski,[7] which consists of adding sodium acetate solution to a water-methanol solution of cobalt(II) chloride and 2,4-pentanedione, followed by recrystallization from methanol. Bullen[8] grew crystals from dimethylformamide for an x-ray diffraction study.

The following method is rapid, gives a reasonable yield, and gives well-formed pure crystals, even using practical-grade 2,4-pentanedione.

Procedure

2,4-Pentanedione (40 g., 0.4 mole) is added slowly with stirring to a solution of 16 g. (0.4 mole) of sodium hydroxide in 150 ml. of water, keeping the temperature below 40°. Any white solid formed at this point must be dissolved before continuing. The yellow solution is added drop by drop with vigorous stirring during 10 minutes to a solution of 47.6 g. (0.2 mole) of cobalt(II) chloride 6-hydrate in 250 ml. of water. The resulting orange precipitate is filtered in a large Büchner funnel and washed with water until the washings are nearly colorless (about 500 ml.). The moist solid is dissolved in a hot mixture of 390 ml. of 95% ethanol and 260 ml. of chloroform. (Lengthy boiling should be avoided, because it causes partial decomposition and azeotropically dehydrates the compound.) The red solution is allowed to cool slowly to room temperature, then in ice. The orange needles are filtered with suction, washed with cold 95% ethanol, air-dried, and stored in a dark bottle. The yield is 40 g., 68%. *Anal.* Calcd. for $C_{10}H_{18}O_6Co$: C, 40.97; H, 6.18; Co, 20.10. Found: C, 40.37; H, 5.97; Co, 20.11.

Properties

The compound is only slightly soluble in water, but dissolves in methanol and ethanol, from which it can be recrystallized. A saturated chloroform solution at 25° is *ca.* 0.02 *M*. It is only very slightly soluble in cold carbon tetrachloride and benzene. In hot chloroform, carbon tetrachloride, and benzene, it is azeotropically dehydrated, giving solutions of anhydrous bis(2,4-pentanedionato)cobalt(II) (*vide infra*).

The visible spectrum in chloroform consists of a split peak [presumably, $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$[9] at 515 and 493 mμ ($\epsilon \approx 31$) with a shoulder at 468 mμ identical with that obtained for a mixture of it and the dimethanol addition compound].[5] The infrared spectrum is substantially the same as that of the anhydrous compound[10] except for water bands.

An x-ray diffraction study[8] showed the water molecules to be trans.

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

Dehydration of the diaquo complex is accomplished by heating at reduced pressures.[3] Using a temperature of 100° causes some decomposition.[7]

Procedure

The diaquo compound is placed in an Abderhalden drying apparatus with barium oxide as the desiccant. After 14 hours at 57° (or 6 hours at 67°) and pressure of 30 mm. (a water aspirator is adequate), dehydration is complete. The measured loss in weight should agree with the theoretical within about ±1%.

Properties

The compound is sufficiently volatile so that it may be purified by sublimation *in vacuo*.[4] It is quite hygroscopic. It is very soluble in benzene, carbon tetrachloride, and chloroform; the reported low solubility in benzene[11] may refer to the diaquo compound. The anhydrous compound can be precipitated from benzene by ether, probably as an ether addition compound. Solutions air-oxidize at a rate inversely related to the donor properties of the solvent.[3] Magnetic moments ranging from 3.9 to 4.93 B.M. have been found; the high value is probably the most accurate.[3,5]

The compound has been found to be associated in noncoordinating solvents.[5] The structure in the solid state has recently been determined to be octahedrally coordinated and tetrameric.[12]

C. BIS(2,4-PENTANEDIONATO)-2-(AMINOMETHYL)PYRIDINECOBALT(II)

[Bis(acetylacetonato)2-picolylaminecobalt(II)]

A solution of 2.57 g. (0.01 mole) of anhydrous bis(2,4-pentanedionato)cobalt(II) in 40 ml. of benzene is boiled for 5 minutes, after which 2.5 g. (0.023 mole) of 2-(aminomethyl)pyridine-(2-picolylamine) is added. The solution is boiled until the volume has been reduced to 10–15 ml., during which time some reddish crystals appear. The slurry is cooled in ice, and the crystals are filtered with suction, washed with four 5-ml. portions of cold benzene, sucked dry, and air-dried to constant weight (one day). The yield of brick-red platelets is 2.92 g., 80%. The product darkens above 150° and melts with decomposition at 174–175°. *Anal.* Calcd. for $C_{16}H_{22}O_4N_2Co$: C, 52.60; H, 6.03; N, 7.67; Co, 16.16. Found: C, 52.40; H, 6.11; N, 7.75; Co, 16.05.

The analogous ethylenediamine compound, Co(acac)$_2$en, (orange powder) can be prepared by a similar procedure. It precipitates immediately in 85–90% yield upon adding a stoichiometric amount of ligand to a benzene solution of Co(acac)$_2$. The compound carbonizes above 220° to a brown solid which melts at 229–232°.

Properties

The (aminomethyl)pyridine compound is quite soluble in chloroform and somewhat soluble in benzene. The visible spectrum in chloroform consists of a peak at 482 mμ ($\epsilon \approx 50$) with a shoulder at 462 mμ. In the infrared, the N—H stretch occurs at 3255 and 3165 cm.$^{-1}$.

D. BIS(2,4-PENTANEDIONATO)-1,10-PHENANTHROLINECOBALT(II) AND BIS(2,4-PENTANEDIONATO)-2,2′-BIPYRIDINECOBALT(II)

Both of these compounds have been made by treating methanol solutions of NaCo(acac)$_3$ (*vide infra*) with the appropriate base.[13] The following procedure has the advantage that the product is less soluble than the starting substance in the reaction medium.

Procedure

A 1.04-g. (0.004-mole) sample of Co(acac)$_2$ is dissolved in 25 ml. benzene, and the solution is boiled briefly. On adding a 5-ml. benzene or chloroform solution of 0.005 mole of ligand [1,10-phenanthroline or 2,2′-bipyridine(dipyridyl)], the solution turns from purple to dark red. The reaction mixture is then boiled to a volume of 5–10 ml., whereupon tiny orange needles appear. The slurry is cooled in ice, the precipitate is filtered off, washed with two 3-ml. portions of cold benzene, and air-dried.

The yield of the phenanthroline complex is 60%; the complex melts with decomposition at 249–252°. The yield of the bipyridine complex is 85%; the substance melts with decomposition at 249–251° (reported[6] 250–252°). *Anal.* (for the phenanthroline complex). Calcd. for $C_{22}H_{22}O_4N_2Co$: N, 6.41; Co, 13.55. Found: N, 6.69; Co, 13.67.

Properties

The compounds are soluble in chloroform and benzene. They are more stable toward air oxidation than those previously described; the solutions do not darken on standing.

A broad shoulder appears on the charge-transfer band in the spectra of both compounds. For the bipyridine compound, it is at about 390 mμ ($\epsilon \approx 830$); for the phenanthroline compound, about 380 mμ ($\epsilon \approx 1100$). The molar absorbance due to the transition at 390 and 380 mμ is estimated to be ≈250.

E. SODIUM TRIS(2,4-PENTANEDIONATO)COBALTATE(II)

The compound was first obtained in low yield by adding excess aqueous sodium acetylacetonate to a solution of sodium dinitrobis(2,4-pentanedionato)cobaltate(III).[14] The procedure below is similar to that of Dwyer and Sargeson,[13] omitting the rather tedious recrystallization from methanol-ether.

Procedure

A solution of 47.6 g. (0.2 mole) of cobalt(II) chloride 6-hydrate in 270 ml. of methanol is added drop by drop with vigorous stirring over a 25-minute period* to a solution of 24 g. (0.6 mole) of sodium hydroxide and 60 g. (0.6 mole) of 2,4-pentanedione in

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* Too rapid addition contaminates the product with the water and methanol adducts of $Co(acac)_2$. Also, reversing the order of addition gives mainly these compounds.

400 ml. of methanol. The fine reddish precipitate is filtered with suction and washed thoroughly with methanol until the washings are nearly colorless (about 500 ml.). It is then washed with ether, sucked dry, and dried over sulfuric acid at atmospheric pressure to constant weight. The yield is 74 g., 98%. *Anal.* Calcd. for $C_{15}H_{21}O_6NaCo$: C, 47.49; H, 5.58. Found: C, 47.66; H, 5.65.

Properties.

The compound shows no melting or decomposition on heating to 260°. It is sparingly soluble in water and methanol. The separation of the "bis compound," presumably $Co(acac)_2(H_2O)_2$, from aqueous solution has been reported.[13] The dissociation of the anion has been studied.[15,16] One 2,4-pentanedionato group is easily replaced by various nitrogeneous bases.[13]

The visible spectrum of the sodium salt in methanol has the same shape as that of diaquo complex in chloroform: a split peak at 511 and 488.5 mμ ($\epsilon \approx 13$), with a shoulder at 461 mμ. The charge-transfer band is at 278 mμ. The infrared spectrum in the range 4000–650 cm.$^{-1}$ is very similar to that of $Co(acac)_2$,[10] except that all the peaks are much sharper.

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16. METAL DERIVATIVES OF 2,2′-IMINOBIS(ACETAMIDOXIME)

$$2Na + 2C_2H_5OH \rightarrow 2NaOC_2H_5 + H_2$$
$$NaOC_2H_5 + NH_3OHCl \rightarrow NH_2OH + NaCl + C_2H_5OH$$
$$HN(CH_2CN)_2 + 2NH_2OH \rightarrow HN(CH_2CNOHNH_2)_2$$
$$MCl_2 + 2HN(CH_2CNOHNH_2)_2 \rightarrow \{M[HN(CH_2CNOHNH_2)_2]_2\}Cl_2$$

Submitted by **LOWELL P. EDDY,* WARREN W. LEVENHAGEN,*** and **SHARON K. McEWEN***
Checked by **LAWRENCE C. NATHAN†** and **RONALD O. RAGSDALE†**

Amidoximes have been prepared by ten methods, which are described in a review article by Eloy and Lenaers.[1] These methods are as follows:

Method A: Action of hydroxylamine on nitriles
Method B: Action of hydroxylamine on amides or thio amides
Method C: Reduction of nitrosolic and nitrolic acids
Method D: Action of ammonia on hydroximic acid chlorides
Method E: Reduction of oxamidoximes
Method F: Action of hydroxylamine on imino ethers
Method G: Action of hydroxylamine on amidine hydrochlorides
Method H: Action of ammonia on oximino ethers

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Method I: Action of formamidoxime on aromatic aldehydes
Method J: Action of ammonia on glyoxime peroxides

First used by Tiemann,[2] method A, the reaction of hydroxylamine with nitriles, has been the one used most often. Tiemann and Krüger[3] were the first to show the simultaneous presence of the —NH_2 and =NOH groups in an amidoxime, benzamidoxime. Method A is described in this preparation.

Procedures

A. 2,2′-IMINOBIS(ACETAMIDOXIME)

An ethanolic solution of hydroxylamine* is prepared, in a fashion similar to that described by Hurd,[4] as follows: To 300 ml. of absolute ethanol in a 500-ml. Erlenmeyer flask is added 12.5 g. (0.545 mole) of metallic sodium. After completion of the reaction (2–3 hours), the sodium ethoxide solution is added drop by drop to a suspension of 35.0 g. (0.50 mole) of *finely ground* hydroxylammonium chloride in 200 ml. of absolute ethanol which contains about 0.01 g. of phenolphthalein in a 1-l. flask. A magnetic stirrer keeps the mixture stirred while the sodium ethoxide is added; the base is added at such a rate that the mixture does not turn pink. (If the addition of all the base causes the suspension to turn pink, some more solid hydroxylammonium chloride is added to discharge the pink color.) The solid is quickly removed by suction filtration on a 60-ml. medium-porosity sintered-glass funnel; the filtrate is collected in a 2-l. filter flask. The residual sodium chloride is rinsed twice with small portions of absolute ethanol.

To this alcoholic solution of hydroxylamine in the 2-l. filter flask is added an absolute-ethanolic solution of 19.0 g. (0.20 mole) of iminodiacetonitrile,† which has been purified by ether extrac-

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* Reagent-grade chemicals are used throughout.

† Available from Hampshire Chemical Corp., Nashua, N.H.

tion in a Soxhlet apparatus. (About 700 ml. of absolute ethanol is required to dissolve the nitrile. ■ ***Caution.*** *The alcohol should not be heated to speed the dissolution, because some yellowing of the solution may take place. The alcohol and nitrile are stirred with a magnetic stirrer in a 1-l. Erlenmeyer flask; this dissolution process is started at the same time the sodium ethoxide preparation is started.*)

The clear colorless solution is stirred for 48 hours. After a few hours, a white solid begins to separate. After 48 hours, the solid is separated by filtration on a 60-ml. medium-porosity sintered-glass funnel, rinsed twice with absolute ether, and air-dried. The yield is 25.2 g. (76%, based on the iminodiacetonitrile). *Anal.* Calcd. for $C_4H_{11}N_5O_2$: C, 29.81; H, 6.88; N, 43.45. Found: C, 29.96; H, 7.01; N, 43.23.

B. BIS[2,2′-IMINOBIS(ACETAMIDOXIME)]NICKEL(II) CHLORIDE

The ligand, 3.22 g. (0.020 mole) of 2,2′-iminobis(acetamidoxime), is dissolved in the minimum amount of water at room temperature in a 50-ml. beaker. To this solution is added a concentrated aqueous solution of 2.38 g. (0.010 mole) of nickel(II) chloride 6-hydrate. Violet crystals form almost immediately, and are filtered off after about 7 hours, using a 30-ml. medium-porosity sintered-glass crucible. The crystals are washed once with ice-cold water, twice with absolute ethanol, twice with dry ether, and air-dried. The yield is 3.80 g. [84%, based on the nickel(II) chloride]. *Anal.* Calcd. for $Ni(C_8H_{22}N_{10}O_4)Cl_2$: Ni, 13.00; C, 21.28; H, 4.92; N, 31.14; Cl, 15.70. Found: Ni, 12.94; C, 21.91; H, 4.55; N, 31.75; Cl, 16.72.

C. BIS[2,2′-IMINOBIS(ACETAMIDOXIME)]MANGANESE(II) CHLORIDE

A 0.62-g. (0.0031-mole) quantity of manganese(II) chloride 4-hydrate is dissolved in 6 ml. of absolute ethanol. This solution is added drop by drop with stirring to an aqueous solution of the ligand, 1.00 g. (0.0062 mole) in 10 ml. of water. A tan precipitate forms immediately, and is filtered off at once as above. The tan precipitate is washed with three portions of absolute ethanol, one portion of acetone, and one portion of dry ether, and then it is air-dried. The yield is 1.07 g. [76%, based on the manganese(II) chloride]. *Anal.* Calcd. for $Mn(C_8H_{22}N_{10}O_4)Cl_2$: Mn, 12.26; C, 21.44; H, 4.95; N, 31.25; Cl, 15.82. Found: Mn, 12.46; C, 21.60; H, 5.10; N, 31.09; Cl, 15.91.

D. BIS[2,2′-IMINOBIS(ACETAMIDOXIME)]COPPER(II) CHLORIDE

A 1.06-g. (0.00622 mole) quantity of copper(II) chloride 2-hydrate is dissolved in 5 ml. of absolute ethanol. This solution is added drop by drop with stirring to an aqueous solution of the ligand, 2.00 g. (0.0124 mole) in 25 ml. of water. As the copper solution is added to the ligand solution, a deep blue color develops. After 3½ hours, large crystals form, and after 24 hours, the deep blue crystals are filtered off, using a 30-ml. medium-porosity funnel. The crystals are washed on the crucible with two portions of acetone, two portions of dry ether, and are air-dried. The yield is 1.73 g. [61%, based on the copper(II) chloride]. *Anal.* Calcd. for $Cu(C_8H_{22}N_{10}O_4)Cl_2$: Cu, 13.91; C, 21.04; H, 4.85; N, 30.66; Cl, 15.52. Found: Cu, 13.75; C, 20.99; H, 4.70; N, 30.90; Cl, 15.79.

Properties

The 2,2′-iminobis(acetamidoxime) is a white solid which melts with decomposition at 126–127°. It is soluble in water and dimethylformamide and insoluble in absolute ethanol, acetone, and ether.

The metal complexes are slightly soluble in water and insoluble in alcohol, acetone, and ether. Conductivity measurements on 10^{-3} M solutions suggest three ions for each of the complexes $[NiL_2]Cl_2$, $[MnL_2]Cl_2$, and $[CuL_2]Cl_2$, where L is 2,2′-iminobis-(acetamidoxime). Aqueous solutions of the complexes show absorption peaks at the following wavelengths: Ni complex, 910 mμ ($\epsilon = 25$) and 532 mμ ($\epsilon = 21$); Cu complex, 620 mμ ($\epsilon = 144$); Mn complex, 670 mμ ($\epsilon \approx 4$). The complexes do not exhibit melting points; they darken and then decompose in the neighborhood of 200°.

The ligand is tridentate; in the case of nickel, coordination occurs through the imine and the two oxime nitrogen atoms. The coordination polyhedron of the nickel ion involves two ligand molecules and is a centrosymmetric, slightly distorted NiN_6 octahedron. The two imine nitrogens are trans, and the three nitrogens from one ligand are on a face of the octahedron. The chloride ions and the water molecules are not coordinated to the nickel ion. The nickel-nitrogen bond distances are Ni—N(imine) 2.116 A. and Ni—N (oxime) 2.068 and 2.078 A. The bond distances within the ligand are normal. The crystals of the bis-chelate nickel complex are monoclinic with space group $P_{21/a}$ (point group C_{2h}) and a cell of dimensions $a = 10.050$, $b = 12.366$, $c = 8.206$ A., $\beta = 103.45°$, containing two molecules of $[Ni(C_4H_{11}N_5O_2)_2]Cl_2 \cdot 2H_2O$. The structure has been determined by single-crystal x-ray work performed by Lingafelter and Cullen.[5]

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17. VOLATILE RARE-EARTH CHELATES OF 2,2,6,6-TETRAMETHYLHEPTANE-3,5-DIONE

$$Ln_2O_3 + 6HNO_3{\cdot}aq \xrightarrow{\Delta} 2Ln(NO_3)_3{\cdot}xH_2O$$
$$HC_{11}H_{19}O_2 + NaOH \rightarrow NaC_{11}H_{19}O_2 + H_2O$$
$$Ln(NO_3)_3{\cdot}xH_2O + 3NaC_{11}H_{19}O_2 \rightarrow Ln(C_{11}H_{19}O_2)_3 + 3NaNO_3 + xH_2O$$

Submitted by KENT J. EISENTRAUT* and ROBERT E. SIEVERS*
Checked by D. COUCOUVANIS† and JOHN P. FACKLER, JR.†

Rare-earth tris chelates of 2,2,6,6-tetramethylheptane-3,5-dione, Ln(thd)$_3$, are of considerable interest because they are the first examples of chelates of the rare earths that are thermally and solvolytically stable and are volatile at moderately low temperatures (*ca.* 100–200°).[1]

An earlier method[2] describing the syntheses of four of these compounds was found to yield dimethylformamide adducts instead of the pure tris chelates[3] as originally claimed.[2] The synthesis described here is a general one, and can be used to prepare the pure tris chelates of Sc(III), Y(III), and the trivalent lanthanides with 2,2,6,6-tetramethylheptane-3,5-dione, hereafter abbreviated H(thd), in yields greater than 90%. The general synthesis is described here, using as an example the preparation of tris(2,2,6,6-tetramethylheptane-3,5-dionato)-ytterbium(III), Yb(thd)$_3$.

Procedure

To 3.94 g. (0.010 mole) of 99.9% ytterbium(III) oxide‡ in a 600-ml. beaker is added 50 ml. of 15.4 *M* nitric acid (an excess).

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‡ Michigan Chemical Corp., Saint Louis, Mich. 48880.

The solution is heated on a steam bath in a fume hood until the solution is clear and until the excess nitric acid is removed (an air line can be used in combination with heating on the steam bath in order to decrease the time required for removal of the excess nitric acid, or a rotary evaporator can be used when a much speedier process is desired). White crystals of hydrated ytterbium(III) nitrate are obtained.

A solution of 11.06 g. (0.060 mole) of H(thd)* in 30 ml. of 95% ethanol is added to a 500-ml. round-bottomed flask with 24/40 standard-taper joint. The solution is stirred at a moderately fast rate with a Teflon-covered magnetic stirring bar for the remainder of the synthesis. A solution of 2.40 g. (0.060 mole) of reagent-grade sodium hydroxide in 50 ml. of 50% ethanol is added to the reaction flask. The solution turns from colorless to yellow upon addition of the base. Next, 0.020 mole of $Yb(NO_3)_3 \cdot xH_2O$, formed in the previous step, is dissolved in 50 ml. of 50% ethanol, and is added to the reaction flask. Immediately, a 24/40 joint (with stopcock and connection to a vacuum line through a Dry Ice trap) is attached to the flask, and the head space is evacuated. The stopcock is then opened completely, and the volume of the solution is decreased by 50%. The time required to decrease the volume of the solution by 50% is approximately 3 hours. The reaction flask is opened, and, with rapid stirring, 350 ml. of distilled water is added. The amount of white solid that begins to precipitate during the vacuum removal of solvent is further increased by the addition of the distilled water.† The $Yb(thd)_3$ is isolated by suction filtration of the solution through a medium-porosity sintered-glass funnel. An additional 100 ml. of distilled water is used to rinse all the white precipitate from the reaction flask

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† The checker obtained a solid precipitate with Yb(III), but he obtained oils with Y(III) and Er(III). These oils were extracted with chloroform, dried with sodium sulfate, and crystallized by evaporation of the solvent. The crude products were then recrystallized as indicated above for Yb(III).

into the sintered-glass funnel.* The $Yb(thd)_3$ is air-dried, and the particles are ground to a small size with a porcelain spatula. The crude product is vacuum-dried at 95° at 0.1 mm. Hg or lower for 1 hour and is then vacuum-sublimed† at 180° at 0.1 mm. Hg or lower. Yield: 13.3 g. of sublimed $Yb(thd)_3$ (92.2%). The melting point of the sublimed $Yb(thd)_3$ is 167–169°. The molecular weight measured in ethyl acetate is 720 (calculated, 722.9) *Anal.* Calcd. for $Yb(thd)_3$: C, 54.83; H, 7.95; Yb, 23.94. Found: C, 54.79; H, 8.10; Yb, 23.81. Elemental analyses of the other complexes are reported in reference 1.

Properties

The melting points of the volatile rare-earth–thd complexes are summarized in Table I. The proton n.m.r. spectra of the diamagnetic rare-earth–thd chelates measured in carbon tetra-

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* Extraction of the aqueous layer with *n*-hexane yielded an additional quantity of product.

† As an alternative to vacuum sublimation as a purification method for the rare-earth–thd chelates, the chelates can be recrystallized from hot methylcyclohexane.

TABLE I Melting Points of the Rare-earth–thd Complexes

Complex	M.P., °C.	Complex	M.P., °C.
$Sc(thd)_3$	152–155	$Tb(thd)_3$	177–180
$Y(thd)_3$	169–172.5	$Dy(thd)_3$	180–183.5
$La(thd)_3$	238–248*	$Ho(thd)_3$	180–182.5
$Pr(thd)_3$	222–224*	$Er(thd)_3$	179–181
$Nd(thd)_3$	215–218*	$Tm(thd)_3$	171.5–173.5
$Sm(thd)_3$	195.5–198.5	$Yb(thd)_3$	167–169
$Eu(thd)_3$	187–189	$Lu(thd)_3$	172–174
$Gd(thd)_3$	182–184		

* Melting point taken in a sealed evacuated capillary.

TABLE II

Solubility of Yb(thd)$_3$, g./ml.	Temperature, °C.	Solvent
0.19	21	Methylcyclohexane
0.20	23.5	Benzene
0.42	24	Chloroform
0.16	24.5	Methanol
0.70	24	Ethyl acetate
0.51	24	Ethanol (anhyd.)
0.36	23	Carbon tetrachloride
0.12	22	*n*-Hexane
Insoluble	23	Water

chloride solution show signals attributable to CH_3 and CH protons at 1.12 and 5.78 p.p.m. for Sc(thd)$_3$, at 1.12 and 5.74 p.p.m. for Y(thd)$_3$, at 1.08 and 5.68 p.p.m. for La(thd)$_3$, and at 1.16 and 5.79 p.p.m. for Lu(thd)$_3$, respectively, relative to internal tetramethylsilane.[1] The solubilities of Yb(thd)$_3$ in some common solvents* are presented in Table II. The infrared spectrum of Er(thd)$_3$ in carbon tetrachloride, as measured on a Perkin-Elmer Model 521 infrared grating spectrophotometer from 4000–600 cm.$^{-1}$, exhibits the following absorptions: 2965(s), 2958(sh), 2932(sh), 2905(m), 2868(m), 1596(s), 1577(sh), 1571(s), 1567(sh), 1561(sh), 1555(sh), 1550(s), 1546(sh), 1537(sh), 1530(sh), 1522(sh), 1517(sh), 1509(s), 1502(s), 1493(sh), 1479(m), 1460(m), 1449(s), 1419(sh), 1406(s), 1401(s), 1388(s), 1357(s), 1300(sh), 1288(w), 1247(m), 1225(s), 1196(w), 1177(m), 1141(s), 1023(w), 961(w), 933(w), 929(w), 870(s), 611(m) cm.$^{-1}$. Since carbon tetrachloride was used in a matched cell placed in the reference beam, and because of the C—Cl absorption, the pen was not responsive in the approximate range 860–620 cm.$^{-1}$.

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* The solubility of the rare-earth chelates in common organic solvents increases as the ionic radius of the metal ion decreases.

A mineral-oil mull of $Er(thd)_3$ indicated absorption bands at 819(w), 796(s), 765(s), 736(m), 731(m), 720(sh) $cm.^{-1}$ in this region. The other rare-earth–thd chelates give infrared spectra similar to the above.

The rare-earth–thd chelates are unsolvated compounds that are volatile and thermally and solvolytically stable, and they are monomeric in organic solvents. Mixtures of the rare-earth–thd chelates can be separated and eluted from gas chromatography columns at 100–200°.

The chelates can be purified, and mixtures of the complexes can be separated by fractional sublimation and distillation. In the gas phase, in solution, and in the solid state, $Tb(thd)_3$ emits a brilliant green fluorescence when irradiated at 3660 A. with an ultraviolet lamp.[1,4] Fluorescence is also exhibited by $Eu(thd)_3$, $Dy(thd)_3$, and $Sm(thd)_3$.[4] The praseodymium complex is thermally stable in the gas phase when heated for prolonged periods of time. Vapor pressure measurements on this complex showed no increase in pressure when the sample was heated at 250° for 6 hours.[5] Thermogravimetric analyses[6] and discussions of trends in volatility[7] of the rare-earth–thd chelates have been published.

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18. *trans*-CHLOROCARBONYLBIS(TRIPHENYLPHOSPHINE)RHODIUM AND RELATED COMPLEXES

$$RhCl_3{\cdot}3H_2O + 2PPh_3 \xrightarrow{HCHO} RhCl(CO)(PPh_3)_2{}^*$$

Submitted by D. EVANS,† J. A. OSBORN,† and G. WILKINSON†
Checked by ROBERT PAINE, JR.,‡ and R. W. PARRY‡

Chlorocarbonylbis(triphenylphosphine)rhodium and related compounds with substituted phosphine or arsine ligands have been made by interaction of the ligand with rhodium carbonyl chloride.[1] Alternative procedures starting with solutions of rhodium(III) chloride and the ligand and using carbon monoxide in hot alcohols, methanolic pentene, or ethanol and potassium hydroxide as reducing agents and sources of carbon monoxide are useful but slow, the reactions often taking several hours.[2,3] During studies of the rapid decarbonylation of aldehydes by chlorotris(triphenylphosphine)rhodium(I),[4] it was found that aqueous formaldehyde could be used for the preparation of the carbonyl complex directly from rhodium(III) chloride and that the method was also rapid and efficient when other phosphines and arsines were employed. With ortho-substituted aryl phosphines, bivalent rhodium species may be stabilized.[5]

Procedure

Rhodium(III) chloride 3-hydrate (2 g., 0.0076 mole) in 70 ml. of absolute ethanol is slowly added to 300 ml. of boiling absolute

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* The stoichiometry of the reaction is uncertain.

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ethanol containing about a twofold excess* of triphenylphosphine (7.2 g., 0.0275 mole). The solution, which may be turbid, becomes clear in about 2 minutes. Then sufficient (10–20 ml.) 37% formaldehyde solution is added to cause the red solution to become pale yellow in about 1 minute, and yellow microcrystals to precipitate. After cooling, the collected crystals are washed with ethanol and ethyl ether and dried in air or vacuum. They can be recrystallized from the minimum of hot benzene. Yield: 4.5 g. (85% based on $RhCl_3 \cdot 3H_2O$). The triphenylarsine complex can be prepared in an analogous manner.

Properties

The properties of *trans*-$RhCl(CO)(PPh_3)_2$ (m.p. 195–197°) and *trans*-$RhCl(CO)(AsPh_3)_2$ (m.p. 242–244°) have been given.[1] The chlorides can be rapidly converted to the corresponding bromides, iodides, or thiocyanates by the interaction[3] in acetone solutions at room temperature with lithium bromide, sodium iodide, or potassium thiocyanate, respectively. Alternatively, rhodium(III) chloride can first be converted to the bromide or iodide by boiling the ethanolic solution with a *ca.* fivefold excess of lithium bromide or iodide.

The complex *trans*-$RhCl(CO)(PPh_3)_2$ has recently been shown to act as a catalyst for the hydroformylation of olefins and acetylenes under mild conditions,[6] and for decarbonylation of aldehydes[7] and of acyl and aroyl halides.[8]

The properties of other complexes made in the above way and in yields exceeding 80%, together with original literature references, are as follows (R for PR_3 given): p-$CH_3C_6H_4$,[9] m.p. 195°, ν_{CO} 1965 cm.$^{-1}$; o-$CH_3C_6H_4$,[10] m.p. 230°, ν_{CO} 1962 cm.$^{-1}$; p-FC_6H_4,[10] m.p. 175–180°, ν_{CO} 1984 cm.$^{-1}$. (Melting points uncorrected on

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* If a stoichiometric quantity is used, the product is contaminated and in low yield.

Köfler hot stage.) Infrared spectra were taken in Nujol mulls on a grating spectrophotometer.

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19. *trans*-CHLOROCARBONYLBIS(TRIPHENYLPHOSPHINE)IRIDIUM

Submitted by K. VRIEZE* (Method A) and J. P. COLLMAN,† C. T. SEARS, JR.,† and M. KUBOTA† (Method B)
Checked by ALAN DAVISON‡ and E. T. SHAWL‡

Vaska and DiLuzio[1] prepared $(Ph_3P)_2(CO)IrCl$ from $IrCl_3(H_2O)_x$ or $(NH_4)_2IrCl_6$ and triphenylphosphine in various solvents such as aqueous 2-(2-methoxyethoxy)ethanol, ethylene glycol, diethylene glycol, triethylene glycol, with yields varying between 75 and 86%. Collman and Kang[2] have described a preparation which involves refluxing $IrCl_3(H_2O)_x$ and triphenylphosphine in dimethylformamide under nitrogen for 12 hours. Upon cooling and adding excess methanol, yields of 85–90% are obtained.

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Under Method A is described an improved procedure based on the method of Vaska and DiLuzio.[1] Under Method B, the details of the Collman procedure are given.[2] Both methods have been found to be useful.

METHOD A

$$(NH_4)_2IrCl_6 + Ph_3P \xrightarrow[H_2O]{\text{diethylene glycol}} (Ph_3P)_2(CO)IrCl$$

Procedure

In a 1-l. two-necked round-bottomed flask, 3 g. (0.0068 mole) of ammonium hexachloroiridate(IV) is dissolved in 50 ml. of water; subsequently 600 ml. of diethylene glycol and 20 g. (0.076 mole) of triphenylphosphine are added. The flask is fitted with a nitrogen inlet and a distillation unit. The mixture is slowly heated to reflux under a slow stream of nitrogen. The water is distilled off in about half an hour, thus ensuring a slow increase in the required reaction temperature. When, after evaporation of the water, the color of the solution has changed from light yellow to dark brown, the distillation condenser is removed, and a reflux condenser is attached to the flask. The solution is then vigorously refluxed for 2 hours, after which it is slowly cooled to 50–70° in about 2 hours by putting the flask in an insulating material. The yellow-green crystalline material thus obtained is filtered off, thoroughly washed with hot ethanol, and dried under vacuum (yield 70–80%). *If the solution is allowed to stand longer than about 3 hours, other lighter-colored compounds with infrared bands characteristic of Ir—H bonds*[3] *crystallize out.* *Anal.* Calcd. for $IrClP_2C_{37}H_{30}O$: Cl, 4.5; P, 7.9; C, 57.0; H, 3.9. Found: Cl, 4.50; P, 7.5; C, 58.0; H, 4.08.

METHOD B

$$IrCl_3{\cdot}3H_2O + Ph_3P \xrightarrow{\text{dimethylformamide}} (Ph_3P)_2(CO)IrCl$$

Procedure

A mixture of 3.52 g. (0.010 mole) of iridium(III) chloride 3-hydrate, 13.1 g. (0.05 mole) of triphenylphosphine, and 150 ml. of dimethylformamide is heated at vigorous reflux for 12 hours in a 250-ml. round-bottomed flask. The resulting red-brown solution is filtered while hot; 300 ml. of warm methanol is rapidly added with stirring. After cooling the mixture in an ice bath, the yellow crystals are collected on a filter and washed with 50 ml. of cold methanol. Yield: 6.8–7.0 g. of product (87–90% yield). The purity of the compound can be ascertained by examining its infrared spectrum. An absorption band at 2000 cm.$^{-1}$ indicates the presence of some oxygen adduct. The pure complex may be regenerated from the oxygen adduct by heating the solid overnight at 100° *in vacuo.* The isostructural rhodium complex[3] may be prepared by this method,[4] except that the required heating time is only 2–3 hours. The bromide and iodide complexes of iridium and rhodium may also be prepared by a similar procedure, except that oxygen must be excluded in their syntheses.

Properties

trans-Chlorocarbonylbis(triphenylphosphine)iridium is a bright yellow crystalline solid (ν_{CO} = 1961 cm.$^{-1}$ in Nujol mull), which is stable in air, but takes up oxygen in solution. The compound is soluble in benzene and chloroform but is insoluble in alcohols. The compound was first prepared by Angoletta,[5] but it was correctly formulated by Vaska,[1] who first described its addition reactions. It is often referred to as "Vaska's compound."

This complex forms adducts with H_2,[6] O_2,[6] SO_2,[7] CO,[8] HCl,[6] HgX_2 and Hg_2X_2 (X = halide, acetate),[9] CH_3I,[10,11] allyl iodide,[10] benzyl chloride,[10] methyl iodoacetate,[10] acetyl chloride,[12] sulfonyl chlorides,[13] trichlorosilane,[14] olefins,[2,15–17] and electronegatively substituted acetylenes.[2,17] It catalyzes the hydrogenation of olefins.[15] Treatment with organic azides affords the molecular nitrogen complex $Ir(Ph_3P)_2N_2Cl$;[18] whereas reaction with sodium amalgam in tetrahydrofuran under carbon monoxide pressure gives an intermediate, $Na[Ir(CO)_3Ph_3P]$, from which compounds with metal-metal bonds can be prepared.[19] The chloride ion in $Ir(Ph_3P)_2COCl$ can be replaced by other halides,[11] and the triphenylphosphine can be displaced by alkyl(phenyl)-phosphines,[12] but not by triphenylarsine. Treatment with 1,2-diphenylphosphinoethane (DPE) yields $(DPE)_2IrCl$.[20]

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20. TRIS- AND TETRAKIS(TRIPHENYLPHOSPHINE)PLATINUM(0)

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Checked by JOSEPH J. MROWCA†

Tris- and tetrakis(triphenylphosphine) derivatives of zerovalent platinum can be obtained by reduction of platinum(II) triphenylphosphine compounds by alcoholic potassium hydroxide or hydrazine.[1] The tris(triphenylphosphine) derivative is easily obtained from the tetrakis derivative by treatment with hot ethanol.‡

Tris- and tetrakis(triphenylphosphine)platinum(0) are the source of many platinum compounds. They react with carbon monoxide,[1,2] acids,[3] methyl iodide,[4] fluoroalkyl derivatives,[5] carbon disulfide,[6] oxygen,[7] chloro,[8] fluoro,[5] and activated olefins,[9,10] hydrogen sulfide and selenide,[11] and sulfur dioxide,[12] yielding many platinum(II) or platinum(0) compounds which cannot be obtained easily by other routes.

A. TETRAKIS(TRIPHENYLPHOSPHINE)PLATINUM(0)

$$K_2PtCl_4 + 2KOH + 4PPh_3 + C_2H_5OH \rightarrow Pt(PPh_3)_4 + 4KCl + CH_3CHO + 2H_2O$$

Procedure

Triphenylphosphine (15.4 g., 0.0588 mole) is dissolved in 200 ml. of absolute ethanol at 65°. When the solution is clear,

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‡ The contributors are indebted to Professor G. Wilkinson (Imperial College, London S.W.7) for suggesting this simple method.

a solution of 1.4 g. of potassium hydroxide in a mixture of 32 ml. of ethanol and 8 ml. of water is added. Then 5.24 g. (0.0126 mole) of potassium tetrachloroplatinate(II) dissolved in 50 ml. of water (0.0126 mole) is slowly added to the alkaline triphenylphosphine solution while stirring at 65°. The addition should be completed in about 20 minutes. A pale yellow compound begins to separate within a few minutes of the first addition. After cooling, the compound is recovered by filtration, washed with 150 ml. of warm ethanol, then with 60 ml. of cold water, and again with 50 ml. of cold ethanol. The resulting pale yellow powder is dried *in vacuo* for 2 hours. Yield 12.4 g., 79%. The compound must be stored under pure nitrogen. *Anal.* Calcd. for $C_{72}H_{60}P_4Pt$: C, 69.50; H, 4.86; P, 9.96. Found: C, 69.32; H, 4.74; P, 10.0. Found by checker: C, 69.33; H, 4.99; P, 9.69.

Properties

Tetrakis(triphenylphosphine)platinum(0) is a pale yellow powder which decomposes in the air to a red liquid at 118–120° and melts *in vacuo* (1 mm.) to a yellow liquid at 159–160°. The infrared spectrum in Nujol shows absorption maxima at 700(vs), 737(vs), 837(w), 992(s), 1022(s), 1077(vs), 1147(m), 1162(m), 1302(w), and 1432(vs) cm.$^{-1}$. The compound is soluble in benzene with dissociation;[1] by leaving the benzene solution in the air, a white powder [the carbonatobis(triphenylphosphine)-platinum(II) formed by action of oxygen and carbon dioxide] separates slowly.[13] The compound reacts with carbon tetrachloride, giving *cis*-dichlorobis(triphenylphosphine)platinum(II).[1]

B. TRIS(TRIPHENYLPHOSPHINE)PLATINUM(0)

$$Pt(PPh_3)_4 \rightarrow Pt(PPh_3)_3 + PPh_3$$

Procedure

Tetrakis(triphenylphosphine)platinum(0) (5.8 g., 0.00467 mole) is suspended in 250 ml. of absolute ethanol under a nitrogen atmosphere and boiled, with stirring, for 2 hours. The hot suspension is filtered, and the precipitate is washed with 30 ml. of cold ethanol. The resulting yellow crystals are dried *in vacuo* for 2 hours. Yield, 3.0 g., 66%. The compound must be stored under pure nitrogen. *Anal.* Calcd. for $C_{54}H_{45}P_3Pt$: C, 66.0; H, 4.59; P, 9.48. Found: C, 65.90; H, 4.69; P, 9.55.

Properties

Tris(triphenylphosphine)platinum(0) is a yellow compound which can be crystallized from acetone in a nitrogen atmosphere. It decomposes in the air to a red liquid at 125–135° and melts *in vacuo* (1 mm.) to a red liquid at 205–206°. The infrared spectrum in Nujol shows absorption maxima at 700(vs), 742(vs), 840(w), 997(s), 1023(s), 1075(vs), 1150(m), 1177(m), 1300(w), 1430(vs) cm.$^{-1}$.

The compound dissolves in benzene, with dissociation. By leaving the benzene solution in the air, carbonatobis(triphenylphosphine)platinum(II) separates slowly.[13] It reacts easily with carbon tetrachloride giving *cis*-dichlorobis(triphenylphosphine)platinum(II).[1] The complex is tricoordinated in the solid state, and shows a nearly pure sp^2 hybridization of the platinum atom.[14]

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21. SQUARE PLANAR DICHLOROPALLADIUM(II) COMPLEXES WITH ORGANOPHOSPHORUS LIGANDS

Submitted by J. M. JENKINS* and J. G. VERKADE*
Checked by JOHN GODDARD† and FRED BASOLO†

Trialkyl phosphines and phosphites generally form with palladium(II) chloride well-defined square planar complexes of the type [$PdCl_2L_2$], which exist as either cis or trans isomers.

The trialkyl phosphine complexes are usually prepared by reaction of the phosphine with sodium tetrachloropalladate(II) in alcohol, with hydrated palladium(II) chloride in ethanol, or with a suspension of anhydrous palladium(II) chloride in benzene.[1] However, these methods cannot be extended to include ligands, or their derived complexes, which undergo solvolysis or which do not react with anhydrous palladium(II) chloride suspensions.[2] Although trialkyl phosphite complexes have been

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synthesized by reaction of the phosphorus trichloride complex $[PdCl_2(PCl_3)_2]$ with alcohols, the method has only limited applicability.

A convenient route for synthesizing complexes of easily solvolyzed ligands utilizes a metathetical reaction with *trans*-dichlorobis(benzonitrile)palladium(II), *trans*-$[PdCl_2(PhCN)_2]$. A typical example is the preparation of *trans*-dichlorobis[tris-(dimethylamino)phosphine]palladium(II), *trans*-$[PdCl_2(tdp)_2]$ [tdp = tris(dimethylamino)phosphine, $P(N(CH_3)_2)_3$]. Attempts to prepare this complex via sodium tetrachloropalladate(II) in methanol[3] or anhydrous palladium(II) chloride suspended in benzene[4] give uncharacterizable products. In contrast, the reaction of tdp with $[PdCl_2(PhCN)_2]$ in benzene readily gives the desired complex.

Burmeister[5] has recently shown that this metathetical reaction is a convenient method for the preparation of some palladium(II) complexes which cannot be synthesized by direct reaction of the ligand with tetrachloropalladate(II) ion. By this method he has prepared dichloro(diphenylphosphinoethane)palladium(II), as well as complexes containing ligands other than those of the organophosphorus type, for example, dichlorobis(thiourea)-palladium(II), $[PdCl_2\{(NH_2)_2CS\}_2]$, and dichlorobis(2,3,5,6-tetraphenylpyridine)palladium(II), $[PdCl_2(C_5NHPh_4)_2]$.[5]

Although the complex $[PdCl_2(PhCN)_2]$ has the trans configuration,[6] the configuration of the product from the metathesis depends upon the substituting ligand. In the case of the reaction with trimethyl phosphite, *cis*-dichlorobis(trimethyl phosphite)palladium(II), *cis*-$[PdCl_2(P(OCH_3)_3)_2]$, is formed in 96% yield. Similarly, the solvolytically unstable caged ligands $P(CH_2O)_3CCH_3$[7] and $P(NCH_3CH_2)_3CCH_3$[8] give *cis*-$[PdCl_2\{P(CH_2O)_3CCH_3\}_2]$ and *cis*-$[PdCl_2\{P(NCH_3CH_2)_3CCH_3\}_2]$ in 80 and 64% yields, respectively, using this procedure. The detailed preparation of *trans*-$[PdCl_2(tdp)_2]$ is given as an example. The other complexes are prepared in an analogous manner.

A. *trans*-DICHLOROBIS(tdp)PALLADIUM(II)

$$trans\text{-}[PdCl_2(PhCN)_2] + 2tdp \rightarrow trans\text{-}[PdCl_2(tdp)_2] + 2PhCN$$

Procedure

Tris(dimethylamino)phosphine (tdp) is prepared by the method of Burg and Slota.[9] The benzonitrile complex, *trans*-$[PdCl_2(PhCN)_2]$, is prepared by Kharasch's method.[10] The benzene is dried over Linde 4-A molecular sieve.

With a syringe, 0.92 ml. (0.00505 mole) of tdp is added quickly to a magnetically stirred suspension of 0.965 g. (0.00250 mole) *trans*-$[PdCl_2(PhCN)_2]$ in 15 ml. of dry benzene under nitrogen. The solution immediately changes from a dark red color to pale yellow, and a yellow crystalline precipitate begins to form. After the suspension has been stirred for 30 minutes, 10 ml. of *n*-pentane is added to the solution, causing further precipitation.* The yellow solid is then filtered under nitrogen and washed three times with *n*-pentane. Any residual solvent is removed under vacuum at room temperature. The crude yield is 1.05 g. (83%). The complex can be recrystallized from boiling dry benzene to give orange-yellow prisms.

Properties

The complex decomposes slowly when exposed to the atmosphere, but rapidly in chloroform and ethanol solutions. An indication of the configuration of the complexes of this type, the elemental analyses of which are shown in the table below, stems from their solubility characteristics in benzene. Thus the orange-yellow *trans*-$[PdCl_2(tdp)_2]$ is quite soluble, whereas the colorless *cis*-$[PdCl_2\{P(OCH_3)_3\}_2]$ and remaining pale yellow cis

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* Although $[PdCl_2P(OCH_3)_2]$ is not soluble in benzene, *n*-pentane is needed to bring it out in good yield from the reaction mixture. This procedure is not necessary in the preparation of the complexes of $P(CH_2O)_3CCH_3$ and $P\{N(CH_3)\text{-}CH_2\}_3CCH_3$.

complexes are not. A more complete characterization of these compounds appears elsewhere.[4] All the complexes are unstable in moist air and polar solvents.

Analytical Data

Compound	C		H		X	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
trans-$[PdCl_2(tdp)_2]$[a]	28.63	29.01	7.21	7.20	14.10	14.23[b]
	28.63	28.74[c]	7.20	7.37[c]	16.68	16.49[c,d]
cis-$[PdCl_2\{P(OCH_3)_3\}_2]$[e]	16.94	17.05	4.26	4.14	16.69	16.80[b]
cis-$[PdCl_2\{P(CH_2O)_3CCH_3\}_2]$[f]	25.38	25.35	3.84	3.65	14.95	14.99[b]
cis-$[PdCl_2\{P(NCH_3CH_2)_3CCH_3\}_2]$[g]	34.83	34.69	6.58	6.32	11.23	11.22[h]
					15.23	14.93[d]

[a] Recrystallized from benzene.
[b] X = Cl.
[c] Checkers' analysis.
[d] X = N.
[e] Recrystallized from a dichloromethane-*n*-hexane mixture.
[f] Recrystallized rapidly from acetonitrile.
[g] Recrystallized from a large volume of benzene.
[h] X = P.

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Chapter Four

THE DEPROTONATION OF WEAK ACIDS WITH POTASSIUM HYDROXIDE: APPLICATIONS TO THE SYNTHESIS OF ORGANOMETALLIC COMPOUNDS

WILLIAM L. JOLLY*

Potassium hydroxide may be used to deprotonate extremely weak† acids if hydroxylic solvents such as water and alcohols are avoided.[1] The following syntheses illustrate the general applicability of this procedure to organometallic syntheses.

The methylcyclopentadienylmolybdenum tricarbonyl synthesis illustrates how a cyclopentadienylpotassium solution can be prepared and then used to prepare a typical transition metal-cyclopentadienyl complex. By analogous procedures, one can prepare a wide variety of metal complexes of the anions of cyclopentadiene, indene, etc. The ferrocene and nickelocene syntheses illustrate how the procedure can be adapted to the

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† Although it has been calculated that KOH should only be able to deprotonate acids having aqueous pK values less than 31, it has been observed that even triphenylmethane (pK $\approx$ 32.5) is at least 95% deprotonated using dimethyl sulfoxide as the solvent for the triphenylmethane and its salt.[1]

simultaneous deprotonation of cyclopentadiene and the dehydration of a transition-metal salt.

The methylphosphine and dimethylphosphine* syntheses show how alkyl derivatives of a volatile hydride can be prepared in amounts as great as 0.05 mole. The methylgermane synthesis shows a somewhat simpler procedure applicable to amounts less than 0.005 mole.

General Deprotonation Procedure

Potassium hydroxide which is to be used for deprotonation of a weak acid must be finely pulverized. For this purpose, pellets of reagent-grade potassium hydroxide (85% KOH) are quickly ground to a powder with a mortar and pestle and transferred for temporary storage to a tared widemouthed bottle which can be capped to prevent absorption of moisture by the potassium hydroxide. The potassium hydroxide should be ground sufficiently fine so that the largest particles are less than 0.5 mm. in diameter. It is very difficult to pulverize a large quantity of potassium hydroxide at one time; therefore it is recommended that the pulverization be done in batches whenever more than 15 g. of powdered KOH is required. The pulverization can be very easily carried out using a Waring Blendor.† For example, 60 g. of KOH in 120 ml. of diglyme (the dimethyl ether of diethylene glycol) is completely pulverized in 3 minutes in the Blendor. The resulting slurry of potassium hydroxide can then be transferred through a wide-necked funnel into a suitable reaction vessel. However, some deprotonations can be conveniently carried out right in the Waring Blendor. By using a variable transformer, the stirring speed of the blender may be conveniently adjusted.

The amount of KOH used is generally determined by the

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* Larger amounts of dimethylphosphine can be prepared by the procedure on p. 157.

† Dr. John Tanaka suggested this technique.

amount of acid to be deprotonated. Good results are usually obtained when the KOH powder is used in the proportion of 25 g./0.1 mole of acid; however, very weak acids, with aqueous pK values greater than 25, may require a KOH/acid ratio two or three times as great in order to obtain complete deprotonation in a reasonable time. The KOH serves as a drying agent for the solvent, as well; consequently, no less than 10 g. of KOH powder should be used per 100 ml. of solvent unless the solvent is carefully dried beforehand.

The amount of solvent used is generally dictated by the solubility of the potassium salt. But even in the case of highly soluble potassium salts, the ratio of KOH to solvent should not be allowed to exceed 80 g. to 100 ml.; otherwise the slurry will be too difficult to stir, and too large a fraction of the solution will be held back during subsequent filtration.

The reaction is conveniently carried out in a round-bottomed flask having a capacity about double the volume of the solvent. If less than 80 g. of KOH is used, a magnetic stirring bar is adequate; however, larger amounts of KOH require a paddle stirrer. Often the anion of the weak acid is susceptible to autooxidation, requiring that the reaction flask be sealed and that oxygen be eliminated. With liquid and solid acids, this is best accomplished by providing a nitrogen atmosphere. It is convenient to use a three-necked ground-glass flask, with one of the side necks connected to a source of nitrogen. The tubing leading to the source of nitrogen should be connected via a T-connection to a mercury bubbler set to maintain a pressure differential of 5–10 mm. With gaseous acids, the use of a vacuum line is most convenient.

In the case of a relatively strong acid such as cyclopentadiene, the solution of the acid is vigorously stirred with the KOH for about one hour. Weaker acids, such as fluorene and triphenylmethane, require 10–15 hours, or even longer, to effect complete deprotonation. The reaction times are not appreciably reduced by increasing the temperature. The rate and, in some cases, the extent of deprotonation are somewhat controllable by the choice of solvent. For example, it has been observed that some deprotonations proceed much more readily in dimethyl sulfoxide than in 1,2-dimethoxyethane. However, dimethyl sulfoxide can sometimes be disadvantageous because of its high viscosity, its low volatility, or its oxidizing power.

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22. σ-METHYL-π-CYCLOPENTADIENYLMOLYBDENUM TRICARBONYL

$$2KOH + C_5H_6 \rightarrow K^+ + C_5H_5^- + KOH\cdot H_2O$$
$$Mo(CO)_6 + C_5H_5^- \rightarrow Mo(CO)_3C_5H_5^- + 3CO$$
$$CH_3I + Mo(CO)_3C_5H_5^- \rightarrow CH_3Mo(CO)_3C_5H_5 + I^-$$

Submitted by **WILLIAM L. JOLLY***
Checked by **N. A. D. CAREY†** and **H. C. CLARK†**

The anion $Mo(CO)_3C_5H_5^-$ has been prepared by the reaction of the cyclopentadienyl anion with molybdenum hexacarbonyl[1,2] and by the reaction of dicyclopentadiene with molybdenum hexacarbonyl to form $[C_5H_5Mo(CO)_3]_2$, followed by reduction of the latter compound with sodium amalgam.[3] In view of the simplicity of preparing cyclopentadienylpotassium (by deprotonation of cyclopentadiene with potassium hydroxide), the former method is preferable, and is described below. The $Mo(CO)_3C_5H_5^-$ anion may be converted to the hydride HMo-

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$(CO)_3C_5H_5$[1,2,4] or to any of a series of alkyl derivatives, $RMo(CO)_3C_5H_5$.[1] The preparation of the methyl compound is described here. Many other cyclopentadienylmolybdenum tricarbonyl derivatives are known; synthetic methods for some of these are discussed by Pruett.[5]

Procedure

A 300-ml. three-necked flask, equipped with a magnetic stirring bar and a connection from one side neck to a source of nitrogen, is charged with 150 ml. of 1,2-dimethoxyethane and 50 g. of potassium hydroxide powder. As the mixture is slowly stirred and the flask flushed with a stream of nitrogen, 16.4 ml. (0.20 mole) of cyclopentadiene* is added. The other side neck and the main neck of the flask are loosely stoppered, and when it is judged that 99% of the air has been flushed from the flask, the flask is tightly stoppered. The stirring rate is then increased as much as possible without causing undue splashing.

After one hour, the stopper in the side neck is removed and replaced with a coarse-porosity filter tube leading to the side neck of another 300-ml. three-necked flask. (See Fig. 7.) The main neck of the receiver flask should be stoppered, and the other side neck should be closed with a stopper having a stopcock permitting evacuation of the flask. The filtering apparatus is flushed with nitrogen, and the apparatus is slowly tipped so as to decant the red solution through the filter into the receiver flask. Occasional application of a vacuum through this stopcock will hasten the filtration. When about 130 ml. of the solution has collected in the receiver flask, the first flask is righted, and about 25 ml. of dry 1,2-dimethoxyethane is added to wash the

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* Cyclopentadiene is obtained by the thermal cracking of dicyclopentadiene (3*a*,4,7,7*a*-tetrahydro-4,7-methanoindene). Dicyclopentadiene is slowly distilled through a short fractionating column, collecting only that which refluxes below 44°. (Cyclopentadiene boils at 42.5°, dicyclopentadiene at 170°.) This cyclopentadiene must be used within 2 or 3 hours or stored at −78° until use, because slow dimerization occurs at room temperature.

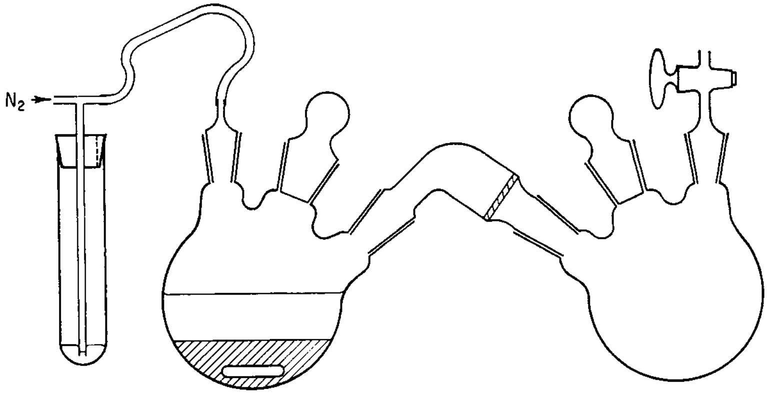

Fig. 7. Apparatus for filtering under nitrogen atmosphere.

remaining potassium hydroxide. After another 30 ml. of filtrate is collected, the washing procedure is repeated. About 190 ml. of solution should be obtained.

In a fume hood, the main stopper of the flask containing the filtrate is removed, and while the flask is flushed with nitrogen, 45 g. (0.17 mole) of molybdenum hexacarbonyl is added. (■ **Caution.** *Molybdenum hexacarbonyl is somewhat volatile and extremely toxic.*) The main neck of the flask is then fitted with a water-cooled reflux condenser. After the condenser has been flushed with nitrogen, the top of the condenser is connected to the source of nitrogen, and the side necks of the flask are stoppered. The mixture is refluxed, using a heating mantle, for at least 12 hours. Carbon monoxide is evolved during this time, and it will escape through the mercury bubbler.

The resulting solution of $KMo(CO)_3C_5H_5$ is cooled to room temperature, the reflux condenser is replaced with a dropping funnel containing 12.5 ml. (0.20 mole) of methyl iodide, and a magnetic stirring bar is placed in the flask. During a 5-minute period, the methyl iodide is added drop by drop to the stirred solution. Stirring is continued for 5 hours. Two necks of the flask are then stoppered, and the third is fitted with a stopcock leading to a large Dry Ice–cooled trap and a vacuum pump. While the solution is being stirred, the solvent is removed *in vacuo* at room temperature. (About 3–4 hours is required.)

After complete removal of the solvent, the stopcock is closed and the flask is placed in a nitrogen-flushed dry bag. The flask is opened, and the solid contents are scraped out and transferred to a large vacuum sublimation apparatus. (If a sufficiently large sublimation apparatus is not available, the sublimation may be accomplished batchwise using a smaller apparatus.) With circulated ice water in the condenser of the sublimation apparatus, the $CH_3Mo(CO)_3C_5H_5$ is sublimed using a bath temperature of 80–90° and a pressure less than 0.1 mm. The vacuum is broken with nitrogen, inasmuch as the residue is usually pyrophoric. The residue is discarded in a place where it may safely burn. Yield: 33–35.5 g. (75–80%) of yellow $CH_3Mo(CO)_3C_5H_5$, melting at 121–124° (decomp.).

Properties

In σ-methyl-π-cyclopentadienylmolybdenum tricarbonyl, the methyl group is attached to the molybdenum by a metal-to-carbon σ-bond, and the cyclopentadienyl group is attached by π-type bonding, as in sandwich compounds. The material forms yellow crystals, m.p. 124° (decomp.), that are soluble in organic solvents and slowly oxidized by air. Purification is readily effected by vacuum sublimation. The infrared and n.m.r. spectra have been described.[1]

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23. BIS(CYCLOPENTADIENYL)IRON

(*Ferrocene*)

$$8KOH + 2C_5H_6 + FeCl_2{\cdot}4H_2O \rightarrow Fe(C_5H_5)_2 + 2KCl + 6KOH{\cdot}H_2O$$

Submitted by WILLIAM L. JOLLY*
Checked by N. A. D. CAREY† and H. C. CLARK†

Of the wide variety of methods which have been used for the preparation of ferrocene,[1] one of the most straightforward is the reaction of an alkali metal cyclopentadienyl derivative with iron(II) chloride.[2] The present procedure, although analogous in principle, is superior because of the simplified method of deprotonating cyclopentadiene and because ordinary hydrated iron(II) chloride may be used. The potassium hydroxide serves not only as a deprotonating agent, but also as a dehydrating agent.

Procedure

A 300-ml. three-necked flask, equipped with a magnetic stirring bar and a connection from one side neck to a source of nitrogen, is charged with 120 ml. of 1,2-dimethoxyethane and 50 g. of potassium hydroxide powder. While the mixture is slowly stirred, and while the flask is flushed with a stream of nitrogen, 11.0 ml. (0.134 mole) of cyclopentadiene is added. The other side neck is stoppered, and the main neck is fitted with a 100-ml. dropping funnel with its stopcock open. When it is judged that 99% of the air has been flushed from the flask, the stopcock is closed, and a solution of 13.0 g. (0.065 mole) of

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iron(II) chloride 4-hydrate* in 50 ml. of dimethyl sulfoxide† is placed in the dropping funnel. The vent tube in the mercury bubbler is lifted above the mercury surface so that the pressure within the reaction vessel is atmospheric. The mixture is stirred vigorously. After about 10 minutes of vigorous stirring, drop-by-drop addition of the iron(II) chloride solution is begun. The rate of addition is adjusted so that the entire solution is added in 45 minutes. At this point, the stopcock of the dropping funnel is closed, and the stirring is continued for another 30 minutes. Then the flow of nitrogen is stopped, and the mixture is added to a mixture of 180 ml. of 6 *M* hydrochloric acid and approximately 200 g. of ice. Some of the resulting slurry may be used to wash the residual material out of the flask. After the slurry has been stirred for about 15 minutes, the precipitate is collected on a coarse sintered-glass funnel and washed with four 25-ml. portions of water.‡ The product is spread out on a large watch glass and allowed to air-dry overnight. Yield: 11.0–11.9 g. (89–98%) of ferrocene melting at 173–174°. Material prepared in this manner is quite satisfactory as an intermediate for subsequent syntheses. If an extremely pure product is desired, this material should be sublimed.

Properties

Ferrocene forms orange crystals (m.p. 173–174°) which are soluble in most organic solvents but essentially insoluble in

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* The iron(II) chloride should be pulverized in a mortar and pestle in order to aid dissolution.

† Dimethyl sulfoxide should not be allowed to contact the skin because it is absorbed very rapidly. Vigorous stirring for about an hour is required to effect dissolution of the salt.

‡ Sometimes the filtrate is deep blue because of formation of the ferricinium ion. If desired, the latter may be reduced to a relatively impure form of ferrocene by the addition of tin(II) chloride. However, this recovery is seldom worthwhile, because the amount of ferricinium ion seldom accounts for more than 4% of the total yield of ferrocene.

water. The compound readily sublimes at temperatures above 100°. The infrared spectrum has been recorded and interpreted.[3] The ultraviolet spectrum in ethanol or hexane shows maxima at 325 mμ ($\epsilon = 50$) and 440 mμ ($\epsilon = 87$), and rising short-wavelength absorption ($\epsilon = 5250$ at 225 mμ).[4]

References

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24. BIS(CYCLOPENTADIENYL)NICKEL

(*Nickelocene*)

$$10KOH + 2C_5H_6 + NiCl_2{\cdot}6H_2O \rightarrow Ni(C_5H_5)_2 + 2KCl + 8KOH{\cdot}H_2O$$

Submitted by WILLIAM L. JOLLY* and DAVID J. CHAZAN*
Checked by N. A. D. CAREY† and H. C. CLARK†

Most of the published methods for preparing nickelocene[1] are analogous to methods used for preparing ferrocene. The following procedure is analogous to the preceding ferrocene procedure, except that some extra precautions are necessary in order to avoid oxidation of the product.

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Many derivatives of nickelocene can be prepared.[1] A particularly useful reaction is that between nickelocene and nickel tetracarbonyl, leading to $[C_5H_5NiCO]_2$ and $(C_5H_5)_3Ni_3(CO)_2$.[2]

Procedure

The procedure is identical with that described under the ferrocene procedure except for the following changes. Only 8.5 ml. (0.104 mole) of cyclopentadiene is used, and a solution of 11.9 g. (0.05 mole) of nickel(II) chloride 6-hydrate in 65 ml. of dimethyl sulfoxide* is used instead of the iron(II) chloride solution. The 6 *M* hydrochloric acid used in the precipitation step and the wash water are deaerated with a stream of nitrogen before use. The product is collected on a sintered-glass funnel (in a nitrogen-filled glove bag), washed, and then dried overnight *in vacuo* (<0.1 mm. pressure). Yield: 5.2–5.4 g. (55–57%) of nickelocene melting† at 173–174°.

Properties

Nickelocene forms dark green crystals (m.p. 173–174°) which are soluble in most organic solvents but essentially insoluble in water. The microcrystalline material formed in the above synthesis undergoes oxidation on standing in air and should be kept in an inert atmosphere. Purification can be effected by vacuum sublimation at 100°.

References

1. R. B. King, *Organometallic Syn.*, **1,** 71 (1965).
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* Dimethyl sulfoxide should not be allowed to contact the skin because it is absorbed very rapidly. Vigorous stirring for about an hour is required to effect dissolution of the salt.

† The melting point should be determined using a sample under a nitrogen atmosphere in a sealed capillary.

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25. METHYLPHOSPHINE

$$2KOH + PH_3 \rightarrow K^+ + PH_2^- + KOH{\cdot}H_2O$$
$$CH_3I + PH_2^- \rightarrow CH_3PH_2 + I^-$$

Submitted by **WILLIAM L. JOLLY***
Checked by **ROBERT PAINE, JR.**†

Both methylphosphine (this synthesis) and dimethylphosphine (the following synthesis) are considerably stronger Lewis bases than phosphine, and their reactions with various Lewis acids,[1] including boranes,[2,3] have been the subject of recent studies. Both methylphosphine and dimethylphosphine are readily oxidized by air, and thus can serve as sources of methylphosphonous (methylphosphinic) acid, $CH_3PHO(OH)$, and dimethylphosphinic acid, $(CH_3)_2PO(OH)$.[1]

A commonly used synthetic method for these substituted phosphines involves the deprotonation of phosphine[2,4] (or methylphosphine[2]) by a sodium-ammonia solution, followed by treatment with a methyl halide. More recently,[3] methylphosphine has been produced by the reduction of methyldichlorophosphine (unfortunately, not a readily available compound) by lithium hydroaluminate. The present method is essentially the deprotonation-methylation procedure, but instead of sodium-ammonia solutions, relatively easily handled KOH–dimethyl sulfoxide suspensions are used.

Procedure

■ **Caution.** *Phosphine and methylphosphine are toxic materials which must be handled with great care, using vacuum-line manipulation. Dimethyl sulfoxide should not be allowed to contact the skin because it is absorbed very rapidly.*

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A magnetic stirring bar, 30 g. of potassium hydroxide powder, and 40 ml. of dimethyl sulfoxide are placed in a 200-ml. three-necked round-bottomed flask with standard-taper joints. One side neck is stoppered, the other is fitted with a small dropping funnel, and the main neck is fitted with an adapter connected to a 0- to 760-mm. manometer and a stopcock leading to a vacuum line. The joints are greased with Dow-Corning silicone grease. The flask is thoroughly evacuated while the mixture is stirred, and the stopcock is then closed. About 0.012 mole of pure phosphine[5] is transferred to a 300-ml. bulb connected to the vacuum line just beyond the stopcock, and the stopcock is opened so as to allow the phosphine to be absorbed by the stirred potassium hydroxide suspension. The dimethyl sulfoxide becomes yellow because of the formation of the PH_2^- ion. When the manometer indicates that about 99% of the phosphine has been absorbed (after about 25 minutes), the system is again thoroughly evacuated. The stopcock is closed, a solution of 1.0 ml. (0.016 mole) of methyl iodide in 10 ml. of dimethyl sulfoxide is placed in the dropping funnel, and a trap between the stopcock and the vacuum pump is immersed in liquid nitrogen.

About 2 ml. of the methyl iodide solution is added to the stirred mixture, and after about 10 seconds, the stopcock is opened for a minute. This process is repeated until the dimethyl sulfoxide solution is colorless. The crude methylphosphine which collects in the liquid-nitrogen-cooled trap is then purified by fractional condensation in traps cooled to −112° (CS_2 slush), −130° (*n*-pentane slush), and −196° (liquid nitrogen). The material which collects in the −112 and −196° traps is discarded. About 0.009 mole (75% yield) of purified methylphosphine collects in the −130° trap.

Properties

Methylphosphine is an evil-smelling material which is probably very poisonous. The vapor pressure may be represented[4] by the equation $\log P(\text{mm.}) = 7.402 - 1158/T$, where $T = {}^\circ\text{K}$.

The extrapolated boiling point is −17.1°, and the vapor pressures at −78.5° (28 mm.), −63.5° (73 mm.), and −45.2° (210 mm.) may be used as criteria of purity. The infrared spectrum of the gas has been reported;[6] the appearance of a band at 1252 $cm.^{-1}$ indicates the presence of methyl iodide, and the appearance of a band at 1170 $cm.^{-1}$ indicates the presence of dimethyl ether.

The methylphosphine prepared by this procedure has a vapor pressure at −78.5° (Dry Ice slush) of 29 mm. The principal impurity is dimethyl ether, estimated by mass spectrometry and infrared spectrometry to amount to less than 1%.

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26. DIMETHYLPHOSPHINE

$$2KOH + PH_3 \rightarrow K^+ + PH_2^- + KOH{\cdot}H_2O$$
$$CH_3I + PH_2^- \rightarrow CH_3PH_2 + I^-$$
$$2KOH + CH_3PH_2 \rightarrow K^+ + CH_3PH^- + KOH{\cdot}H_2O$$
$$CH_3I + CH_3PH^- \rightarrow (CH_3)_2PH + I^-$$

Submitted by WILLIAM L. JOLLY*
Checked by LESLIE HODGES†

The following procedure is adaptable to the synthesis of 0.05 mole, or less, of dimethylphosphine. The procedure described on p. 157 may be used for the synthesis of larger quantities.

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† University of Michigan, Ann Arbor, Mich.

Procedure

■ **Caution.** *Phosphine and the methylphosphines are toxic materials which must be handled with great care, using vacuum-line manipulation. Dimethyl sulfoxide should not be allowed to contact the skin because it is absorbed very rapidly.*

The procedure is the same as that used for the preparation of methylphosphine up to the point where the methyl iodide solution is added. A solution of 1.5 ml. (0.024 mole) of methyl iodide in 10 ml. of dimethyl sulfoxide is placed in the dropping funnel, and the stopcock connecting the system to the vacuum line is closed. Sufficient methyl iodide solution is added, during a period less than 1 minute, to decolorize the solution. If, during the addition, the pressure in the flask exceeds 600 mm., the volume of the system should be increased by opening the stopcock to an evacuated volume of several hundred milliliters so as to keep the pressure below 600 mm. However, the volume of the system should not be unduly expanded, or the deprotonation of the methylphosphine will proceed too slowly. The slurry is vigorously stirred for an hour, during which time the pressure of methylphosphine should markedly decrease. Then the remainder of the methyl iodide solution is added (leaving a drop of solution to ensure that air does not enter the flask), and stirring is continued for another half-hour. The volatile material is collected in a liquid-nitrogen-cooled trap and is then fractionally condensed in traps cooled to −78° (Dry Ice slush), −112° (CS_2 slush), and −196° (liquid nitrogen). The material which collects in the −78 and −196° traps is discarded. The dimethylphosphine in the −112° trap usually contains an appreciable amount of methyl iodide as an impurity. However, this impurity may be readily eliminated by simply allowing the mixture to stand in the liquid state at 0° for about one hour, during which time the methyl iodide is converted to the relatively nonvolatile salt, $(CH_3)_3PHI$. About 0.0078 mole (65% yield) of purified dimethylphosphine remains.

Properties

Like methylphosphine, dimethylphosphine has a disgusting odor and is probably very poisonous. The vapor pressure may be represented[1] by the equation $\log P(\text{mm.}) = 7.539 - 1370/T$, where $T = °\text{K}$. The extrapolated boiling point is 21.1°, and the vapor pressure at 0° (338 mm.) may be used as a criterion of purity. Dimethylphosphine prepared by this procedure has a vapor pressure at 0° of 339 mm.

Dimethylphosphine can be converted to trimethylphosphine by treatment with excess methyl iodide at 0° to form $(CH_3)_3PHI$, followed by reaction with potassium hydroxide to liberate the trimethylphosphine. The latter step is readily accomplished by adding a dimethyl sulfoxide solution of $(CH_3)_3PHI$ to a slurry of potassium hydroxide in dimethyl sulfoxide *in vacuo*.

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27. METHYLGERMANE

$$2KOH + GeH_4 \rightarrow K^+ + GeH_3^- + KOH \cdot H_2O$$
$$CH_3I + GeH_3^- \rightarrow CH_3GeH_3 + I^-$$

Submitted by DOUGLAS S. RUSTAD,* THOMAS BIRCHALL,* and WILLIAM L. JOLLY*
Checked by GERST A. GIBBON† and CHARLES H. VAN DYKE†

As in the case of alkylphosphines (see the preceding two syntheses), alkylgermanes are generally prepared by either of two methods: a method based on the deprotonation and subsequent

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alkylation of germane,[1] and a method based on the reduction of germanium-halogen bonds with lithium hydroaluminate or with hydroborates.[2,3] In view of the ease of preparation of germane[4] and the simple potassium hydroxide deprotonation procedure, the deprotonation-alkylation method is believed to be superior, and is described here for the synthesis of methylgermane. In this procedure, 1,2-dimethoxyethane is used as solvent, but in analogous procedures, dimethyl sulfoxide has been used in the preparation of dimethylgermane,[5] and liquid ammonia has been used in the preparation of 2-butylgermane and methylethylgermane.[6]

Procedure

Potassium hydroxide powder (2.8 g.) and 10 ml. of 1,2-dimethoxyethane are placed in a 50-ml. round-bottomed flask with a standard-taper neck. The flask is fitted with an adapter having a stopcock for connecting to the vacuum line. With the flask in a −78° bath (Dry Ice slush), the mixture is degassed by pumping for about 5 minutes. Then the −78° bath is replaced with a −196° bath (liquid nitrogen), and the reactor is thoroughly evacuated. About 0.002 mole of pure germane is condensed into the reactor, and the stopcock is closed. The reactor is warmed in air to room temperature and is shaken for a half-hour. The shaking should be very vigorous in order to increase the surface area of the solution as much as possible. The reactor is then placed in a −196° bath, and the very small amount of hydrogen gas (from the slow decomposition of germylpotassium) is pumped out. Approximately 0.003 mole of methyl iodide is condensed into the reactor. The reactor is allowed to warm up to about 15° in air, while shaking occasionally, whereupon a white precipitate forms.* Then the reactor is immediately quenched in a −78° bath. If the reaction mixture is allowed to stand after formation of the precipitate,

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* This precipitate is difficult to see in the presence of the potassium hydroxide.

secondary reactions yielding dimethylgermane and dimethyl ether occur. With the reactor in series with −78 and −196° traps, it is allowed to warm in air. Half or more of the 1,2-dimethoxyethane is allowed to distill into the −78° trap. The crude methylgermane which collects in the −196° trap is purified by fractional condensation in traps cooled to −130° (*n*-pentane slush), −160° (isopentane slush), and −196°. The material which collects in the −160° trap is pure methylgermane. A yield of about 0.0016 mole (80%) is obtained.

Properties

The vapor pressure of methylgermane may be represented[2] by the equation

$$\log P(\text{mm.}) = 3.9624 - 0.003034T + 1.75 \log T - 1080.3/T$$

from which one calculates a boiling point of −34.1°. The vapor pressures at −83.9° (ethyl acetate slush), −78.5° (Dry Ice slush), and −63.8° (chloroform slush) are 46.3, 67.7, and 169.4 mm., respectively. The infrared spectrum of the gas has been reported.[7] Although toxicity data are unavailable, methylgermane should probably be handled as if it were a very toxic gas.

The methylgermane prepared by this procedure has vapor pressures of 46 mm. at the ethyl acetate slush temperature and 168 mm. at the chloroform slush temperature.

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Chapter Five

FLUORINE COMPOUNDS

28. THIONYL TETRAFLUORIDE AND PENTAFLUOROSULFUR HYPOFLUORITE

$$SOF_2 + F_2 \rightarrow SOF_4$$
$$SOF_2 + 2F_2 \xrightarrow{CsF} SF_5OF$$

Submitted by **JOHN K. RUFF***
Checked by **RALPH CZEREPINSKI†**

Thionyl tetrafluoride and pentafluorosulfur hypofluorite can be prepared by the fluorination of thionyl fluoride. The product distribution obtained upon fluorination appears to be dependent not only upon the reaction conditions, but on whether a source of fluoride ion is present. Fluorination of thionyl fluoride over a hot platinum gauze[1] or in a Monel pressure reactor[2] produces thionyl tetrafluoride, whereas fluorination in the presence of cesium fluoride[2] or a silver fluoride catalyst[3] yields pentafluorosulfur hypofluorite. The role of the fluoride ion in the fluorination has not been conclusively established; however, the avail-

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able evidence suggests that it combines with thionyl tetrafluoride to form the ionic intermediate SF_5O^-. It is this species which is converted to pentafluorosulfur hypofluorite by the action of fluorine.

Although thionyl tetrafluoride and pentafluorosulfur hypofluorite can be prepared by fluorination in a flow reactor, the procedures described here are performed in a static system. This method offers several advantages. The metal equipment needed is commercially available, and the ability to closely control the stoichiometry of the reactions results in the formation of the products in high purity. However, the amount of material that can be prepared in one run is limited. Thionyl tetrafluoride may also be prepared in good yield by the oxidation of sulfur tetrafluoride.[4] This method is also easy to carry out if the requisite high-pressure equipment is available.

General Procedure

The procedures for the preparation of thionyl tetrafluoride and pentafluorosulfur hypofluorite are essentially the same, with one important difference: the use of a catalyst. The apparatus employed in the preparations consists of several Monel pressure vessels* (which have been prefluorinated at 150–200°), a standard glass vacuum line equipped with several large calibrated storage bulbs (1- or 2-l.), a partial fractionation train, and several ball-joint connections on the main manifold. All the joints and stopcocks on the vacuum line are lubricated with Kel-F-90† grease, and all mercury manometers are covered with Kel-F-10 oil,† which has been well outgassed. The vacuum line is connected to a fluorine metering system and a water

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* Hoke, Inc., 148 Dean Street, Englewood, N.J.; valves No. M327 were obtained from the same supplier.

† Trademark of the Minnesota Mining and Manufacturing Company. These fluorocarbon lubricants should be well outgassed before use.

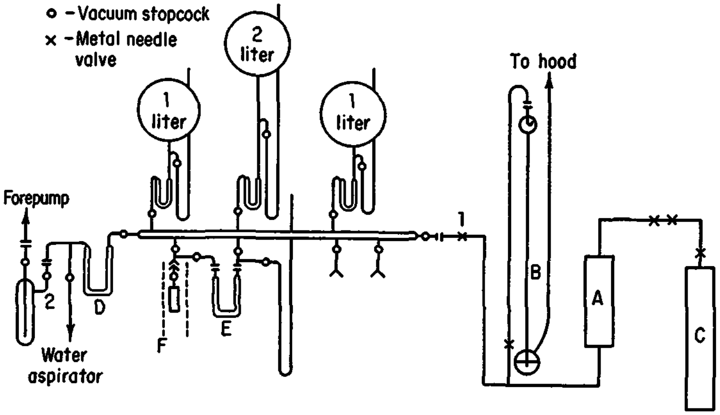

Fig. 8. Schematic diagram of the fluorination system.

aspirator, in addition to the usual vacuum pump. Figure 8 shows a schematic diagram of the fluorine metering system and vacuum line.

The fluorine metering system is designed for use with high-pressure fluorine.* Alternatively, fluorine may be prepared; a small electrolytic cell is commercially available for this purpose.*† The use of tank fluorine, although more convenient, presents additional safety hazards, because equipment failure may result in the escape of large amounts of fluorine. Therefore it is good practice to enclose the fluorine cylinder in a tight steel housing which is vented either to an efficient hood or to the outside. Extension handles should be used on the control valves so that there is no need to open the steel enclosure during operation. The fluorine metering system is constructed of $\frac{1}{4}$-in. copper tubing. All joints are silver-soldered where possible (flare or compression fittings may be used). The needle valves may be obtained from the fluorine supplier, although the needle

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* The Matheson Company, Inc., East Rutherford, N.J.

† General Chemical Division, Allied Chemical Company, New York, N.Y.

valves used on the pressure reactors are satisfactory. The blowout manometer *B* is approximately 2 m. long and is constructed of glass. It uses Kel-F-10 oil as a working fluid and should exit to a well-ventilated hood. The large sodium fluoride scrubber *A* (45 × 13 cm.) is used to remove traces of hydrogen fluoride from the tank fluorine. After a new tank of fluorine *C* is connected, most of the air may be flushed out of the metal system by allowing the fluorine to escape slowly out of the blowout manometer for approximately 15 minutes. However, some air remains trapped between the flowout manometer and needle valve 1. A liquid-nitrogen bath then is placed around trap *D* on the vacuum line, and the forepump is isolated by closing stopcock 2. The metal fluorine-handling system is partially evacuated (to approximately 550 mm.) using the water aspirator and then pressurized with fluorine. This procedure of alternately filling the metal system with fluorine and evacuating it is repeated several times in order to remove the residual air in the system. The completeness of the air removal can be checked either by mass-spectral analysis or by allowing a known amount of the fluorine obtained from the metal system to react with an acidified solution of potassium iodide. Once the fluorine system is air-free, it is kept closed and pressurized with a slight overpressure of fluorine when not in use.

In the procedures described below, high pressures of fluorine are employed in the reactors. Therefore adequate shielding is necessary from the time of loading the reactor until the time of product removal. This is accomplished by placing a 60-cm. length of 12-in.-diam. water pipe around the Monel cylinder while it is attached to the vacuum line (see *F*). A Dewar flask, which can be raised or lowered by means of a hydraulic jack, is placed inside the water pipe, around the Monel cylinder. Manipulation of the valve on the Monel cylinder is best accomplished with an extension rod, approximately 30 cm. long. If the necessary shielding is not available, both of the procedures described below may be run using subatmospheric pressures of fluorine. The yields are equally good, and the product purity is slightly better.

A. THIONYL TETRAFLUORIDE

A storage cylinder containing thionyl fluoride[5] is attached to the manifold of the vacuum line by means of a ball joint, and the thionyl fluoride is allowed to expand into one of the calibrated storage bulbs. After 0.021 mole of thionyl fluoride is collected in the bulb, the excess in the manifold is recondensed into the storage vessel with liquid nitrogen. The measured volume of thionyl fluoride is condensed into the shielded 300-ml. Monel pressure reactor, which is attached to the vacuum line at *F*. The reactor is then closed and kept at −196°.

The vacuum line is isolated from the forepump, and a liquid-nitrogen bath is put around trap *D*. The fluorine metering system is partially evacuated with the water aspirator, as discussed above. Then the vacuum line is completely evacuated with the forepump. Fluorine is allowed to expand slowly into the metal system by means of the needle valve 3. As the pressure increases above atmospheric, some fluorine is allowed to bleed into the vacuum line and storage bulbs until a pressure of 650–700 mm. is reached. First needle valve 1 on the metal system and then the fluorine control valve 3 are quickly closed. (Some fluorine may escape from the blowout manometer during this operation.) Approximately a 10% excess of fluorine (0.023 mole in this case) is condensed into the metal pressure reactor containing the thionyl fluoride. The amount of fluorine used is measured by the pressure drop in a calibrated volume in the pressure range of approximately 700–400 mm., since fluorine has a vapor pressure of approximately 400 mm. at −196°.

The reactor is closed with the extension rod, and the Dewar flask is lowered. After the reactor has stood for at least 30 hours at ambient temperature, it is cooled to −196°. Liquid-nitrogen cold baths are also placed on trap *D* and on the U-tube trap *E* adjacent to the reactor. The reactor is opened slowly, allowing the noncondensable gases to expand into the line, and into the storage bulbs if necessary, to keep the pressure below 200 mm. The excess fluorine is removed by means of the water aspirator. After aspiration for 10 minutes, the line is pumped down with the forepump. Then the reactor is allowed to warm, and the product is condensed into trap *E*. About 0.021 mole (essentially quantitative yield) of crude product is obtained. Mass-spectral analysis shows the material to contain about 1% each of SF_6 and SO_2F_2 as impurities. The product may be stored in a metal pressure reactor at room temperature.

B. PENTAFLUOROSULFUR HYPOFLUORITE

A 10-g. sample of cesium fluoride* (dried under vacuum at 150–175° for 12 hours) and 20- to 30 $\frac{3}{8}$-in. stainless-steel balls† are loaded into a 150-ml. Monel pressure reactor in a nitrogen-filled dry box. The reactor is removed, resealed, and then evacuated on the vacuum line. It is then shaken on a wrist-action shaker overnight to complete the grinding of the cesium fluoride. The reactor is then attached to the vacuum line at *F* and shielded with the 12-in. water pipe. A 0.025-mole sample of thionyl fluoride is measured out and condensed into the reactor with liquid nitrogen. Fluorine (0.051 mole) is added to the reactor as described above. The reactor is warmed to room temperature and allowed to stand for 24 hours. Work-up of the product in the manner described above yields about 0.025 mole of crude product which contains 2–5% SOF_4 and a little SF_5OOSF_5. Subsequent runs using the same cesium fluoride catalyst are essentially quantitative, with only traces of SF_6, SO_2F_2, and SOF_4 in the product. The catalyst improves with use. Although the product can be stored in the gas phase in a

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* Alfa Inorganics, 2 Congress St., Beverly, Mass.

† McMaster Carr Supply Company, 640 West Lake St., Chicago, Ill.

metal container, it is best stored in the condensed phase in a long glass tube at −196°.

Properties

Thionyl tetrafluoride is a gas (m.p. −99.6°, b.p. −49°) which is hydrolyzed by water to sulfuryl fluoride and hydrogen fluoride. It may be handled in glass provided the system is dry, and it is readily identified by its infrared spectrum, which contains strong bands at 1383, 928, and 821 cm.$^{-1}$.[3]

Pentafluorosulfur hypofluorite is also a gas, m.p. −86.0°, b.p. −35.1°. It is stable in glass, and can be easily identified by its infrared spectrum, which contains strong bands at 935 and 888 cm.$^{-1}$.[3] Pentafluorosulfur hypofluorite liberates 1 mole of iodine from an acidified potassium iodide solution per mole of hypofluorite added. It also reacts with water to liberate oxygen.

Although detailed information on the toxicity of SF_4O and SF_5OF is not available, they should both be handled as if highly toxic. The former is a ready source of hydrogen fluoride (produced by hydrolysis). The latter, being a hypofluorite, may be similar to oxygen difluoride in toxicity. (Oxygen difluoride is considerably more toxic than fluorine.) While SF_5OF is not known to be an explosive substance, it should be regarded as potentially explosive to form SF_6 and O_2. Large quantities should not be used or stored until safe procedures have been established.

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29. IMIDODISULFURYL FLUORIDE, CESIUM IMIDODISULFURYL FLUORIDE, AND FLUOROIMIDODISULFURYL FLUORIDE

[*Imidobis(sulfuryl fluoride), Cesium Imidobis(sulfuryl fluoride), and Fluoroimidobis(sulfuryl fluoride)*]

Submitted by JOHN K. RUFF* and MAX LUSTIG*
Checked by A. E. PAVLATH† and J. P. GUERTIN†

Imidodisulfuryl fluoride is a useful intermediate for the preparation of a number of compounds containing the $N(SO_2F)_2$ group.[1,2] It was first prepared by the reaction of fluorosulfuric acid with urea.[3] This method gives inconsistent yields and is sometimes difficult to control. A more convenient procedure involves a halide exchange reaction between arsenic(III) fluoride and imidodisulfuryl chloride.

Neutralization of imidodisulfuryl fluoride with the alkali-metal carbonates results in the formation of the corresponding alkali metal imidodisulfuryl fluoride salts.[1] Fluorination of imidodisulfuryl fluoride at ambient temperature produces fluoroimidodisulfuryl fluoride in high yield.[4]

A. IMIDODISULFURYL FLUORIDE

$$3HN(SO_2Cl)_2 + 2AsF_3 \rightarrow 3HN(SO_2F)_2 + 2AsCl_3$$

Procedure

Imidodisulfuryl chloride[5]‡ (100 g., 0.47 mole) is placed in a 500-ml. polyethylene bottle. Then 200 ml. (4.04 moles) of

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* Redstone Research Laboratories, Rohm and Haas Company, Huntsville, Ala. 35807. This work was carried out under the sponsorship of the U.S. Army Missile Command, Redstone Arsenal, Ala., under Contract No. DA-01-021 AMC-11536 (Z).

† Western Research Center, Stauffer Chemical Co., Richmond, Calif. 94804.

‡ Imidodisulfuryl chloride should be carefully fractionated and handled in a moisture-free atmosphere; otherwise it will contain chlorosulfuric acid. The latter is fluorinated by AsF_3 to give fluorosulfuric acid, which is difficult to separate.

arsenic(III) fluoride,* which has been distilled from sodium fluoride, is added. [■ **Caution.** *The toxicity of arsenic*(III) *fluoride is similar to that of other inorganic fluorinating agents. However, it is particularly dangerous because it is a liquid of high vapor pressure. It hydrolyzes easily; therefore it is a vesicant like hydrogen fluoride. Care must be taken to avoid breathing or contact with skin. This operation, as well as subsequent operations, should be performed in an efficient hood.*] A reflux condenser is fitted to the top of the bottle by friction, and the bottle is flushed with nitrogen. The mixture is refluxed for 2 hours by means of a water bath and is then allowed to cool. The reflux condenser is replaced by a small distillation head, and the excess arsenic(III) fluoride is distilled off at 55 to 65°. The residue is transferred to a round-bottomed flask and distilled through a 60-cm. spinning-band column under a reduced pressure of 25 mm. Arsenic(III) chloride distills near room temperature; therefore a Dry Ice trap between the column and vacuum pump is necessary. Imidodisulfuryl fluoride boils at 82–84° at 25 mm. Fluorosulfuric acid (if present from the hydrolysis of imidodisulfuryl fluoride) boils at 78–80° at 25 mm. and is thus difficult to separate from the product. The yield of crude imidodisulfuryl fluoride is 72 g. (85%). Removal of small amounts of fluorosulfuric acid from imidodisulfuryl fluoride is best accomplished by allowing the imidodisulfuryl fluoride to react with a suspension of sodium chloride in dichloromethane at ambient temperature. For example, 50 g. of crude imidodisulfuryl fluoride and 25 g. of sodium chloride are stirred together for 2 hours in 300 ml. of dichloromethane.† The solution is filtered, and the dichloromethane is removed at a pressure of 10 mm. The residue is then distilled at reduced pressure as described above. The yield is 34 g.

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* Available from Alfa Inorganics, 8 Congress St., Beverly, Mass.

† The yield of imidodisulfuryl fluoride will decrease with additional time, because NaCl slowly reacts with it. Therefore care should be taken to minimize the formation of FSO_3H.

This purification process is particularly important if the imidodisulfuryl fluoride is to be used in the preparation of fluoroimidodisulfuryl fluoride since the fluorination of imidodisulfuryl fluoride which contains small amounts of fluorosulfuric acid does not occur under the conditions to be described. However, if imidodisulfuryl fluoride is to be converted to one of the alkali metal salts, this purification step is not necessary.

Properties

Imidodisulfuryl fluoride is a colorless liquid, b.p. 170°, m.p. 17°. It behaves as a weak acid in water, in which it is stable, and undergoes slow hydrolysis in alkaline solution. The infrared spectrum of imidodisulfuryl fluoride obtained using silver chloride plates (it reacts with sodium chloride) contains bands at 3311(m), 1471(vs), 1337(w), 1248(w), 1217(vs), 923(s), 893(m), and 832(s) cm.$^{-1}$. The ^{19}F n.m.r. spectrum of imidodisulfuryl fluoride consists of a single band at -58.5 p.p.m. (from CCl_3F), and the proton spectrum consists of a single band at -8.60 p.p.m. (from TMS).

B. CESIUM IMIDODISULFURYL FLUORIDE

$$2HN(SO_2F)_2 + Cs_2CO_3 \rightarrow 2CsN(SO_2F)_2 + CO_2 + H_2O$$

Procedure

A 7.7-g. sample of imidodisulfuryl fluoride is placed in a 300 ml. round-bottomed flask and cooled to $-78°$. Then 50 ml. of ice water is slowly added, and the mixture is allowed to warm to ambient temperature. The solution is just neutralized with cesium carbonate* (approximately 7.5 g.). The neutralization can be followed with pH paper. The mixture is evaporated to

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* Available from Alfa Inorganics, Beverly, Mass.

dryness under vacuum, and the residue is taken up in 125 ml. of absolute ethanol. The hot ethanolic solution is filtered and concentrated to 50 ml. Upon cooling, crystalline cesium imidodisulfuryl fluoride forms. After filtering off the crystals and drying under vacuum, a yield of 11.4 g. (85%) is obtained. *Anal.* Calcd. for $CsN(SO_2F)_2$: Cs, 42.5; N, 4.47; F, 12.1. Found: Cs, 42.3; N, 4.48; F, 12.0.

Properties

Cesium imidodisulfuryl fluoride is a white crystalline solid with a remarkably low melting point for an alkali metal salt, m.p. 115–117°. Differential thermal analysis shows that it is stable up to 300°. Cesium imidodisulfuryl fluoride behaves as a 1:1 electrolyte in nitromethane. The infrared spectrum of cesium imidodisulfuryl fluoride contains bands at 1940(vw), 1836(vw), 1379(vs), 1222(w), 1179(vs), 1101(s), 843(s), 820(sh), 763(vs), and 729(vs) $cm.^{-1}$.

C. FLUOROIMIDODISULFURYL FLUORIDE

$$HN(SO_2F)_2 + F_2 \rightarrow FN(SO_2F)_2 + HF$$

Procedure

■ **Caution.** *The use of fluorine requires that this procedure be carried out in an efficiently hooded area. If fluorine contained in a tank is employed, the tank should be enclosed in a steel box and equipped with extension rods so that the box need not be opened during the operation. Furthermore, protective shielding should be used in front of the vacuum line during fluorination. Further scale-up of this reaction should not be attempted without adequate facilities. Although no hazard has been experienced in handling fluoroimidodisulfuryl fluoride, other nitrogen fluoride derivatives are known to be dangerous to handle.*

A standard Pyrex vacuum apparatus is employed in this preparation. The system includes a fractionation train consisting of four U-tube traps, attached with ball joints, a mercury manometer, and several ball-joint connections on the manifold. The mercury in the manometer is covered with outgassed Kel-F-10 oil,* and the stopcocks and ball joints are lubricated with Kel-F-90 grease.* The fluorine metering system consists of a fluorine tank properly shielded and vented, a sodium fluoride scrubber (45 × 13 cm.), two calibrated rotameters for measuring flow rate and fluorine concentration, and a helium source, and is constructed of $\frac{1}{4}$-in. copper tubing.

Imidodisulfuryl fluoride,† 18.5 g. (0.102 mole), is loaded into a Pyrex U-tube containing a small magnetic stirring bar. The U-tube is attached to the fractionation train on the vacuum line, and the train is flushed with helium. The two adjacent U-tubes are cooled to −78°, and the last U-tube is cooled to −196°. The two −78° traps should be packed with Pyrex helices to ensure efficient trapping. The fluorine tank is opened, and the concentration of fluorine is adjusted to approximately 30%. The helium-diluted fluorine is passed over the surface of the imidodisulfuryl fluoride at ambient temperature and at a flow rate of 150–175 ml./minute for approximately $2\frac{1}{2}$ hours or until most of the imidodisulfuryl fluoride has disappeared from the U-tube. After the fluorination is finished, the system is flushed for 15 minutes with helium and then evacuated. The contents of the two −78° traps [crude $FN(SO_2F)_2$] are combined. Final purification is achieved by slow fractionation through U-tubes maintained at −33° (bromobenzene slush) and −78°. The former trap retains approximately 1 g. of imidodisulfuryl fluoride; the −78° trap collects 15.3 g. (75% yield) of fluoroimidodisulfuryl fluoride. *Anal.* Calcd. for $FN(SO_2F)_2$: N, 7.03; S, 32.3; F, 28.6. Found: N, 7.11; S, 32.7; F, 28.8.

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* Minnesota Mining and Manufacturing Company, Minneapolis, Minn.

† Imidodisulfuryl fluoride should be freed from FSO_3H and handled in a moisture-free atmosphere. The yield is diminished by the presence of FSO_3H.

Properties

Fluoroimidodisulfuryl fluoride melts at −79.9 ± 0.3° and boils at 60.8 ± 1.0°. The liquid-vapor equilibrium pressure above 80 mm. is given by the Clausius-Clapeyron equation, $\log P(\text{mm.}) = 7.980 - 1703/T$. Its Trouton constant (e.u.) and latent heat of vaporization (kcal./mole) are 23.3 and 7.80, respectively. Its vapor-density molecular weight has been measured to be 203 (calcd.: 199). The infrared spectrum shows absorptions at 1495(vs), 1247(vs), 1020(m), 997(vs), 849(vs), 660(m), and 562(vs) cm.^{-1}. The ^{19}F n.m.r. absorptions for $FN(SO_2F)_2$ are located at −44.9 and 28.5 p.p.m. (from CCl_3F). When in contact with dilute aqueous base, $FN(SO_2F)_2$ hydrolyzes substantially in the following way:

$$3FN(SO_2F)_2 + 12OH^- \rightarrow 2NH_2SO_3^- + NO_2^- + 5F^- + 4SO_3F^- + 4H_2O$$

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30. BIS(FLUOROXY)DIFLUOROMETHANE

$$CO_2 + 2F_2 \xrightarrow[-78°]{CsF} CF_2(OF)_2$$

Submitted by FREDERICK A. HOHORST* and JEAN'NE M. SHREEVE*
Checked by STANLEY M. WILLIAMSON†

Bis(fluoroxy)difluoromethane is prepared in essentially stoichiometric amounts by the fluorination of carbon dioxide with an

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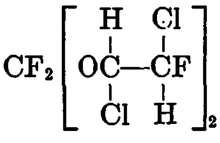
excess of fluorine in the presence of anhydrous cesium fluoride.[1] The reaction proceeds readily at −78° and is complete within 6 hours.

■ **Caution.** *Fluorine is highly oxidizing and can best be contained and handled in copper or nickel equipment. Any apparatus used should be thoroughly cleaned and degreased, and then prefluorinated prior to use. Organic materials, such as rubber tubing and organic solvents, should be absent. As in any laboratory, safety glasses are required. These should be supplemented with Neoprene gloves, a face shield of preferably transparent, highly fluorinated polymeric material, and a laboratory coat.*[2] *Fluorine is condensed to a liquid with about 300 mm. vapor pressure when liquid nitrogen is used as a coolant. Fluorine is a toxic gas and should be disposed of in a well-drawing hood away from combustible material or by pumping through a soda-lime trap.*[3]

Although the procedure described utilizes metal vessels for ease of treating the cesium fluoride and to avoid the formation of large amounts of silicon tetrafluoride, glass may be used. This procedure has been used for preparation of up to 0.015 mole of $CF_2(OF)_2$ at a time with the aid of liquid nitrogen to condense excess fluorine into the vessel. The method is analogous to that used in the preparation of pentafluorosulfur hypofluorite by the static, catalytic fluorination of thionyl fluoride in the presence of cesium fluoride.[4]

This method is in general applicable to the conversion of compounds containing the $-\overset{|}{C}=O$ function to the corresponding hypofluorite.[5,6] Bis(fluoroxy)difluoromethane is useful as a reactant in the preparations of poly(fluoro diethers),[7] e.g., with tetrafluoroethylene to give perfluorodiethoxymethane or with *trans*-1,2-dichloroethylene to yield the several isomers of



$$CF_2\left[O\overset{H}{\underset{Cl}{C}}-\overset{Cl}{\underset{H}{C}}F\right]_2$$

Procedure

A charge of 3.04 g. (0.020 mole) of cesium fluoride (99%) and several 7-mm. steel balls are placed in a 75-ml. stainless-steel cylinder. A polyfluorocarbon-packed stainless-steel needle valve equipped with a brass 10/30 standard-taper inner joint is attached. The steel balls help to powder the cesium fluoride. The cesium fluoride is then dried by subjecting it to continued pumping at 190° in a vacuum oven for about 4 hours.

Commercial fluorine is passed through a sodium fluoride scrubber and a −184° cold trap before use to remove hydrogen fluoride and condensable materials, respectively. The reaction vessel is treated with an excess of fluorine at 190° for 4 hours before use. The excess fluorine is then destroyed by pumping through a soda-lime trap.

With the vessel so conditioned, 0.001 mole of carbon dioxide is condensed into the vessel, followed by 0.009 mole of fluorine. The valve is closed, and the vessel is placed in a −78° slush bath, which is allowed to warm slowly toward room temperature. (It is not necessary to maintain this temperature throughout the entire reaction period, but it is advisable to run below 25° to preclude formation of CF_3OF and OF_2.) After 6 hours, the vessel is cooled to −184°, and excess fluorine is pumped through a 1.5 × 50 cm. tube packed with 10-mesh soda-lime, which is placed between the vessel and the pump to remove the fluorine and prevent damage to the pump.

The vessel and a suitable storage tube are attached to a standard vacuum line and evacuated. The vessel is allowed to warm, and the product is condensed into the storage tube at −184°. Nearly quantitative (av. 99.7%) conversion of carbon dioxide to bis(fluoroxy)difluoromethane is realized under these conditions. *Anal.* Calcd. for CF_4O_2: F, 63.3. Found: F, 62.3.

Incomplete conversion of carbon dioxide may occur if the reaction vessel is not properly fluorinated, if a deficiency of fluorine is used, or if the reaction time is too short. Bis(fluoroxy)difluoromethane can be separated from most impurities

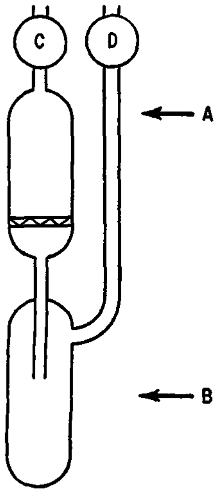


Fig. 9. Apparatus for filtration of $CF_2(OF)_2$.

by filtering the mixture at −184° in the apparatus pictured in Fig. 9. A Dewar of liquid oxygen is raised to level *A*, and the impure mixture is condensed above the fritted plate through stopcock *C* and is permitted to remain there until the liquid phase drips into the lower chamber. Several hundred millimeters pressure of dry nitrogen above the liquid is often helpful. The Dewar is then lowered until the oxygen level is at *B*. Stopcock *C* is opened to a vacuum, and simultaneously, dry nitrogen is admitted slowly through stopcock *D*. The impurities are transferred out of the vessel through *C*, leaving the essentially pure $CF_2(OF)_2$ behind. This process is rapid, and produces product pure enough (99%) for many applications.

Properties

Bis(fluoroxy)difluoromethane is a faintly yellow liquid at −184°; it boils at −65°. When permitted to contact acidic iodide solution, it exhibits an experimental equivalent weight of 30.3 (theoretical, 30.0). It reacts readily with mercury at room temperature and with glass at elevated temperature. The molecular weight as calculated from the vapor pressure, using a precision dial manometer, is experimentally 119 (theoretical, 120). Its infrared spectrum consists of the following peaks: 658(w), 690(w), 900–940(w, complex), 1200(vs), 1245(s), 1270(s), 1370(vw) cm.$^{-1}$. The n.m.r. spectrum shows two 1:2:1 triplets at -155.7 and $+81.7$ p.p.m. relative to trichlorofluoromethane as the internal reference. These are of equal area, and are assigned to the OF and the CF fluorines, respectively.

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31. XENON DIFLUORIDE

$$Xe + F_2 \rightarrow XeF_2$$

Submitted by STANLEY M. WILLIAMSON*
Checked by FRIEDRICH O. SLADKY† and NEIL BARTLETT†

Xenon difluoride, the most easily handled of the xenon fluorides, was first prepared by a complicated, low-pressure, ultraviolet-irradiated reaction between xenon and fluorine.[1] Hypofluorites have been used to produce the difluoride from xenon by means

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of straightforward thermal reactions.[2] The recognition that ordinary sunlight filtered by Pyrex glass[3] was adequate to cause xenon and fluorine at pressures near atmospheric to combine to produce xenon difluoride provided a great simplification for the synthesis. Since the handling of fluorine and xenon fluorides can be dangerous, considerable care should be given to potentially hazardous steps. This atmospheric-pressure photochemical synthesis seems to be the safest one to date.

Procedure

A convenient reaction vessel that requires only minimal glassblowing is a 1-l. Pyrex round-bottomed flask with a short (3 cm.) length of 8-mm. tubing blown into the exact bottom of the flask. The regular neck of the flask should then be sealed and rounded off to a length of 13–15 cm. to serve as a condensation cold finger. To the 8-mm. tubulation, a copper- or Kovar-to-glass seal is attached. A Hoke No. 413 silver-soldered diaphragm needle valve* is attached to the metal tubulation from the flask with lead or silver solder. Minimum distance should be maintained between the flask and the valve for maximum strength. After the vessel has been cleaned of all organic material and dried thoroughly by flaming under vacuum, it should be treated once or twice with fluorine at about 100 mm. pressure in sunlight for about an hour.

The gases can be introduced into the vessel by the use of an all-metal system[4] or a Kel-F lubricated-glass vacuum system equipped with a fluorine-resistant pressure gage† and a soda-lime trap to protect the vacuum pump. The author's preference for an overall system is the all-metal transfer line and the reaction

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* This particular valve is most satisfactory because it is packless, can be baked at moderate temperatures, and can be left out-of-doors without worry. Available from Hoke, Inc., 1 Tenakill Park, Cresskill, N.J.

† Gages with Monel or stainless-steel Bourdon tubes are satisfactory. Available from the Matheson Co., Inc., P.O. Box 85, East Rutherford, N.J.

vessel with a Hoke No. 413 valve.* This system eliminates the handling of fluorine and xenon difluoride through greased stopcocks. Care should be taken not to construct a system that will require the sealing off of a tubulation while the vessel contains fluorine or any of the xenon fluorides. (Silica will burn in fluorine if hot enough.)

■ ***Caution.*** *Fluorine must be handled with great care, using special apparatus. See the preceding syntheses for descriptions of the apparatus and precautions required when withdrawing fluorine from a cylinder.*

A suitable quantity of material for a preparation in the 1-l. vessel is about 300 mm. pressure of each gas. The xenon gas is introduced first to a pressure of 300 mm. and condensed with liquid nitrogen. It is desirable to use a slight deficiency of fluorine, and the measuring out of the gas is conveniently achieved by admitting† it to the vessel to a pressure of about 280 mm.‡ through a trap cooled to −196°. As soon as this pressure is reached, the valve to the fluorine supply must be closed, or else liquid fluorine will collect in the trap. To facilitate the pressure measurements the gage is located between the reaction vessel and the liquid-nitrogen-cooled trap. Alternatively, liquid oxygen may be used as the refrigerant. With this refrigerant, higher pressures of the two gases can be used. Commercially available fluorine and xenon are both suitable without further purification except that the fluorine should be passed through a U-trap cooled by Dry Ice to remove any hydrogen

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* A Monel Whitey valve (Whitey Research Tool Co., Emeryville, Calif. 94608) may be substituted for the Hoke No. 413. The valve, furthermore, may be joined to the Pyrex glass vessel by way of a compression fitting such as a Swagelock union (Crawford Fitting Co., Solon, Ohio 44139). Copper-to-glass seals are fragile at the junction, and Kovar seals are susceptible to attack at the glass-to-metal junction, which leads to eventual weakening of this joint.

† All the precautions appropriate for handling fluorine gas, recommended by the supplier, should be followed. It is important that the glass vessel and other apparatus should be free of readily combustible material, particularly hydrocarbons. The fluorine gas pressure in the line immediately before the 1-l. vessel should be controllable to ~1 atmosphere by a series of suitable valves.

‡ The vapor pressure of liquid fluorine at −196° is about 290 mm.

fluoride. The filled closed vessel should be placed for direct exposure to the sky. After 2 or 3 hours crystals should form on the upper hemisphere of the flask (the top is cooler). Within a day, the reaction is at least 60% complete. With exposures longer than 1 day, small amounts of xenon tetrafluoride may form. The latter substance is dangerous because it can hydrolyze to the explosive xenon trioxide.[5] (See cautions under the syntheses of XeF_4[6] and XeO_3 solution.[7]) Exposure on cloudy, rainy days will also produce reaction. Although the vessel becomes frosted and scaly with use, no decline in its effectiveness has been observed. There is no need to clean the vessel for the gas-phase reactions other than by thorough pumping.

An initial 1:1 F_2:Xe mixture will leave some unreacted xenon because of loss of fluorine to the glass, but pure XeF_2 is produced in this way. F_2:Xe ratios greater than 1 or additional increments of fluorine to the xenon difluoride produce xenon tetrafluoride. (*Care must be taken in handling xenon tetrafluoride because xenon trioxide can be produced from it.*[5])

The xenon difluoride can be removed from the vessel by pumping the gas through the U-trap in the vacuum line. A trap temperature of −40 to −78° is satisfactory because the silicon tetrafluoride and oxygen contaminants will pass through. *Anal.** Calcd. for XeF_2: F, 22.45. Found: F, 21.45.

Properties

Xenon difluoride[1,8] is a dense, white, waxy solid with a vapor pressure of 3.8 mm. at 25°. It can be trapped from a gas stream very effectively in a trap held at −30°. The compound dissolves smoothly in cool water to form a strongly oxidizing solution that can be about 0.1 *M* in XeF_2. The aqueous species is primarily molecular XeF_2, and it slowly oxidizes water at 0°.

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* The XeF_2 sample was sublimed into a nickel weighing bottle containing mercury, and the vessel was shaken overnight to effect complete reaction, $XeF_2 + Hg \rightarrow Xe + HgF_2$. (Analysis performed by checkers.)

Even though the aqueous solution is not too stable, it is a very strong homogeneous oxidizing agent. Xenon difluoride may be identified by its strong infrared absorption band (a P,R doublet) at 550, 566 cm.$^{-1}$.

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32. DISULFURYL FLUORIDE

(*Pyrosulfuryl Fluoride*)

$$6HOSO_2F + (NCCl)_3 \rightarrow 3S_2O_5F_2 + (HNCO)_3 + 3HCl$$

Submitted by S. KONGPRICHA,* W. C. PREUSSE,† and R. SCHWARER*
Checked by JOHN K. RUFF‡

Disulfuryl fluoride has been prepared by the following methods: (1) by heating sulfur trioxide under pressure with such fluoride

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salts as sodium fluoride[1] and calcium fluoride,[2] or at atmospheric pressure with antimony pentafluoride,[3] iodine pentafluoride,[4] and vanadium pentafluoride;[5] (2) by treating disulfuryl chloride under reflux with benzoyl fluoride;[6] (3) by treating fluorosulfuric acid with arsenic pentoxide[7] under reflux or with cyanogen chloride[8] at 100–105°; and (4) by treating sulfur dioxide with fluorine fluorosulfate[9] at 195°. We describe here Appel's method,[8] modified by using cyanuric chloride in place of cyanogen chloride to react with fluorosulfuric acid. The method is simple and gives a good yield of disulfuryl fluoride.

Procedure

■ **Caution.** *Because disulfuryl fluoride is extremely toxic, the experiment should be carried out in a well-ventilated hood. Several of the reagents involved in the synthesis (fluorosulfuric acid, cyanuric chloride, and sulfuric acid) are poisonous and extremely reactive with the skin. It is recommended that protective gloves be worn when these materials are being handled.*

The apparatus consists of a 500-ml. round-bottomed flask equipped with a thermometer and a 45-cm. Vigreux column connected at the top to a distillation tube with a distillation receiver (Fig. 10). Kel-F-90 grease* is recommended as a lubricant for the ground-glass joints. The exit of the system is connected to a trap kept at ice temperature in order to collect the product escaping from the receiver. A drying tube containing anhydrous calcium sulfate is placed at the end of this trap in order to prevent the moisture from entering the system. Four hundred grams (4 moles) of fluorosulfuric acid† is carefully added to 61.5 g. (0.33 mole) of cyanuric chloride‡ in the reaction vessel with occasional stirring. The reaction mixture is observed to warm up slightly at this point because of the heat of

* Minnesota Mining and Manufacturing Company, Minneapolis, Minn.

† Available as "fluorosulfonic acid" from K and K Laboratories, Inc., Plainview, N.Y.

‡ Matheson Coleman and Bell, Norwood, Ohio.

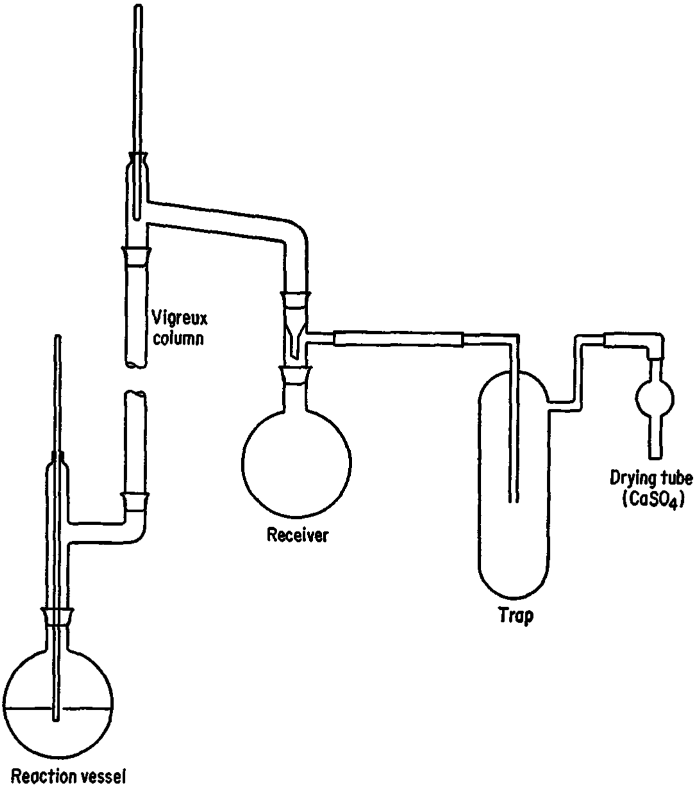

Fig. 10

the solution. The fuming of the fluorosulfuric acid when exposed to air and the heat of the solution will be diminished somewhat if the acid is cooled first to 5–0° before mixing. The reaction is started by slowly and gradually raising the temperature of the reaction mixture, using a heating mantle with a variable transformer, to about 158–160°, at which point the first drops of the distillate, together with the hydrogen chloride gas, are removed at a vapor temperature of 24° (or room temperature). In order to obtain a high yield of disulfuryl fluoride, the mole ratio of 12:1 between fluorosulfuric acid and cyanuric chloride must be strictly adhered to, and it is essential to raise the temperature of the reaction to 158–160° slowly and gradually (45–60 minutes) and to remove the crude product slowly from the very gently boiling reaction mixture. Rapid heating and vigorous boiling of the reaction mixture will result in a reduced yield due to a side reaction to form disulfuryl chloride fluoride (b.p. 100–100.5°). With occasional adjustment of the variable transformer setting, the temperature of the reaction mixture is gradually raised to 186–190° during a period of 19–21 hours, while, as a result, that of the vapor is raised to 35–40°. At this point the main portion of the product has already distilled over into the receiver. The last trace of the product is then removed from the reaction vessel by distilling it at a vapor temperature as high as 50°. The reaction is then terminated, and the combined crude product (201 g.) is cooled to 0° before it is washed with 100 ml. of ice-cold 98% sulfuric acid. The washed material is further purified by fractional distillation to give 166.5 g. of disulfuryl fluoride having a boiling-point range of 50–52°. The yield is 97.5%. *Anal.* Calcd. for $S_2O_5F_2$: S, 35.1; F, 20.9. Found: S, 34.9; F, 20.5.

Properties

Disulfuryl fluoride is a clear colorless liquid with a boiling point of 51°. Its vapor pressure[5] over the temperature range -28 to 43° follows the equation $\log_{10} P(\text{mm.}) = 8.015 - 1662/T$. It has an inhalation toxicity of the same order as that of phosgene, and should be handled only in a well-ventilated area. Its thermal decomposition[2] to sulfur trioxide and sulfuryl fluoride is not very appreciable below 200° but is rapid at 400–500°. In the presence of metal fluorides[10,11] such as cesium or sodium fluoride, however, its decomposition point is considerably lower. It hydrolyzes rather slowly to give fluorosulfuric acid. It is not very soluble in cold concentrated sulfuric acid or fluorosulfuric acid, but is soluble in acetonitrile, ethyl ether, carbon tetrachloride, monofluorotrichloromethane, and benzene.

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33. PEROXYDISULFURYL DIFLUORIDE

(*A Note of Warning*)

Submitted by GEORGE H. CADY*

The synthesis of peroxydisulfuryl difluoride by the fluorination of sulfur trioxide [described by J. M. Shreeve and G. H. Cady, *Inorganic Syntheses*, **7**, 124 (1963)] involves the production of an explosive by-product which should not be collected in large amounts unless adequate protection is provided. The procedure calls for collecting the desired product in a trap at −78° and then passing the stream of gases through a second trap at −183°, where the by-product (largely fluorine fluorosulfate, SO_3F_2) condenses. It is now known that the by-product can explode. While the process is in operation, the second trap should be held at −183° only when tests for fluorine in the product gases are being made. This modification of the procedure causes the fluorine fluorosulfate to be discarded, except for the rather small amount condensed with peroxydisulfuryl difluoride in the trap at −78°. When the main product is

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being refined by pumping out the most volatile portion, the material so removed should be discarded by setting the trap in a hood to allow evaporation of the liquid as the trap becomes warm. While no difficulty has been encountered in this stage of the process, it would seem wise to consider the material in this trap to be possibly explosive.

A hot electric spark in liquid or gaseous peroxydisulfuryl difluoride does not cause the material to explode. There is no evidence that this substance, when alone, is explosive. Since it is a very strong oxidizing agent, it should be capable of forming explosive mixtures.

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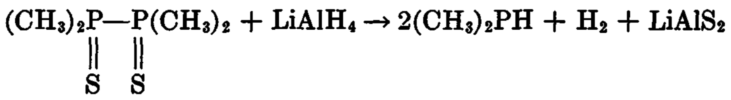
Chapter Six

MISCELLANEOUS NONMETALLIC COMPOUNDS

34. DIMETHYLPHOSPHINE



$$(CH_3)_2\underset{\overset{\|}{S}}{P}-\underset{\overset{\|}{S}}{P}(CH_3)_2 + LiAlH_4 \rightarrow 2(CH_3)_2PH + H_2 + LiAlS_2$$

Submitted by G. W. PARSHALL[*]
Checked by A. H. COWLEY[†] **and L. F. CENTOFANTI**[‡]

Dimethylphosphine has been prepared by alkylation of phosphonium iodide with methyl iodide[1] and by reductive cleavage of phosphorus sulfides with methylmagnesium bromide.[2] Diethyl-, dibutyl-, and dicyclohexylphosphines have been prepared by reduction of the corresponding tetraalkyldiphosphine disulfides with lithium hydroaluminate in ether.[3] This latter method gives dialkylphosphines uncontaminated by mono- and trialkylphosphines.

The present procedure (which, using the stated amounts of

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reagents, yields approximately 0.4 mole of dimethylphosphine) is designed for the synthesis of fairly large quantities of dimethylphosphine. The vacuum-line procedure given on p. 126 is applicable to the preparation of relatively small amounts (less than 0.05 mole).

Procedure

■ ***Caution.*** *This reaction should be carried out in a good hood because dimethylphosphine is extremely toxic and spontaneously flammable in air.*

A carefully dried 1-l. three-necked round-bottomed flask equipped with a thermometer, addition funnel, and magnetic stirrer is fitted to a distillation column 25 cm. long and 15 mm. i.d. packed with glass helices. The still is equipped with reflux control and a condenser which can be cooled to at least −20° by circulation of a refrigerated liquid. Provision is made for collecting the product in glass ampules (total capacity of at least 40 ml.) or in stainless-steel cylinders. If conventional stopcocks are used, they should be lubricated with fluorocarbon or silicone grease. The vent of the still is connected with Tygon tubing to a T-tube (dimethylphosphine attacks rubber tubing). One leg of the T-tube is connected to a source of dry-nitrogen gas, and the other leg to a 1-m. length of 5-mm. glass tubing. The lower end of the tube is immersed at least 5 mm. in mercury contained in a 125-ml. Erlenmeyer flask.

The distillation flask is charged with 49.0 g. (0.26 mole) of tetramethyldiphosphine disulfide[4] and 10.3 g. (0.27 mole) of lithium hydroaluminate, and the flask is flushed with nitrogen.* Four hundred milliliters of anhydrous dioxane (distilled from sodium) is added all at once through the addition funnel. The distillation column is adjusted to provide total reflux of the dimethylphosphine, and the reaction mixture is stirred for 4 hours. Moderately rapid hydrogen evolution occurs, and the

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* One checker observed that dimethylphosphine evolution began even before the addition of the dioxane.

temperature of the reaction mixture slowly rises to 45°. Brief application of an ice bath lowers the temperature to 38°, and thereafter it slowly decreases to room temperature. The mixture is distilled, and the product boiling at 20–22° is collected in the ampules or cylinders; yield 22.5–26 g. (70–81%). (The ampules are chilled in solid carbon dioxide when the necks are sealed.)

The distillation flask is cooled to room temperature and thoroughly flushed with nitrogen. The excess lithium hydroaluminate is decomposed by careful drop-by-drop addition of water to the stirred and cooled reaction mixture until hydrogen evolution ceases. The mixture is then diluted with 500 ml. of water, and the residual traces of dimethylphosphine are destroyed by addition of sodium hypochlorite solution. (A commercial bleaching agent such as Clorox is satisfactory.)

Properties

The properties of dimethylphosphine are discussed on p. 128.

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35. BROMOSILANE, IODOSILANE, AND TRISILYLAMINE

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Checked by ARLAN D. NORMAN,† S. K. GONDAL,‡ and A. G. MacDIARMID‡

The halosilanes, particularly bromo- and iodosilane, are classical synthetic sources of the silyl group, SiH_3. These halosilanes

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have usually been prepared by the aluminum halide-catalyzed gas-phase reaction between silane and the corresponding anhydrous hydrogen halide.[1,2] This synthetic procedure is complicated by the fact that silyl halides disproportionate at room temperature in the presence of the aluminum halide catalyst, and it is difficult to effect the complete removal of the catalyst, traces of which co-distil with the silyl halides under the usual conditions of vacuum-line purification. Bromosilane has also been prepared in high yield through the low temperature (−40 to −50°) reaction between solid bromine and silane.[3] Unfortunately, silane is a rather hazardous reactant and is expensive.

The silyl halides can now be prepared in high purity and high yield by the facile hydrogen halide cleavage of the carbon-silicon bond in arylsilanes.[4–6] No catalyst is required, and the use of the hazardous intermediate reagent, silane, is avoided. Bromosilane is prepared by the reaction of hydrogen bromide and phenylsilane.[4,5] The latter is obtained by lithium hydroaluminate reduction of the commercially available phenyltrichlorosilane.[7] Iodosilane can be prepared in a similar fashion; however, mixtures of iodosilane and benzene are difficult to separate. The preferred alternative procedure described below utilizes an isomeric mixture of 2-, 3-, and 4-chlorophenylsilanes as the intermediate.[6] This intermediate is obtained by the chlorination of phenyltrichlorosilane,[8] and is then reduced to the hydride.

It is believed that the rate and the point of cleavage in the above reactions are sensitive to the presence of trace amounts of catalysts, and that for consistent results the syntheses should be carried out in a clean vacuum system. The checkers found that hydrogen iodide cleaved $ClC_6H_4SiH_3$ to give $ClC_6H_4SiH_2I$ and hydrogen when the reaction was carried out in a vacuum line which previously had been used for handling cobalt carbonyl compounds.

The use of the halosilanes as synthetic sources of the silyl group is illustrated by the preparation of trisilylamine from bromosilane and ammonia.[1,3,9] Iodosilane and bromosilane can be converted to the other halosilanes and pseudohalosilanes (e.g., SiH_3Cl, SiH_3F, SiH_3NCO, and SiH_3NCS) by passing the vapors through a tube packed with the appropriate silver salt. (See the "silver salt conversion[10] series.") Disilyl sulfide (disilthiane) has been prepared from red mercury(II) sulfide and halosilanes.[11]

■ **Caution.** *The silyl compounds described in the following preparations react with oxygen and water vapor. Bromosilane is particularly hazardous because it will inflame upon exposure to air. All manipulations of these materials require either an inert atmosphere or, preferably, the use of a vacuum system.*

Anhydrous diethyl ether, freshly obtained from a commercial supplier, is preferred for the reactions involving lithium hydroaluminate. The ether must be peroxide-free. Carbon dioxide must be rigorously excluded from these reaction systems. Explosions have been observed during evaporation of solutions of aluminum hydride and related compounds when carbon dioxide is present as an impurity.[12] *If it is necessary to concentrate ether solutions of lithium hydroaluminate by distillation, the following precautions must be observed.*[13] *A large fluid volume must be maintained in the distillation flask; such solutions should never be concentrated so far that very little ether remains in the reaction flask. Distillations must be effected in a protective atmosphere. Cyclic ethers, and especially tetrahydropyran solutions of lithium hydroaluminate, present a far greater explosion risk than diethyl ether solutions.*

A. BROMOSILANE[4,5,7]

$$C_6H_5SiCl_3 \xrightarrow[Et_2O]{LiAlH_4} C_6H_5SiH_3 \xrightarrow[-78°]{HBr} C_6H_6 + SiH_3Br$$

Procedure

A solution of fresh lump lithium hydroaluminate in diethyl ether is prepared by stirring 75 g. (1.98 moles, 25% excess) of the former with 1000 ml. of refluxing ether for 5 days. The resultant clear supernatant liquid is transferred under nitrogen to a thoroughly dry 3-l. three-necked flask equipped with a dry-nitrogen inlet, blade mechanical stirrer, double-surface reflux condenser (cooled to 0°), and a pressure-equalized dropping funnel. Phenyltrichlorosilane* (445 g., 2.1 moles), diluted with an equal volume of anhydrous ether, is added slowly to the stirred ethereal solution of lithium hydroaluminate over a 1.5-hour period. The reaction mixture is refluxed for an additional 2 hours after the complete addition of the phenyltrichlorosilane. Most of the ether is then removed by distillation at atmospheric pressure. The remaining ether, together with the desired reaction product, is separated from the lithium chloride, aluminum chloride, and excess lithium tetrahydroaluminate by distillation under reduced pressure, in a nitrogen atmosphere (about 40°/7 mm.) with vigorous mechanical stirring,† and is collected in a receiver cooled in a slush bath of Dry Ice and isopropyl alcohol. The ether is removed from the distillate, and the phenylsilane is purified by distillation under nitrogen at atmospheric pressure to yield 184 g. (81%) of product b.p. 119°/754 mm., n_D^{25} 1.5088 (literature,[7] 120°/760 mm., n_D^{25} 1.5125).

Into a Pyrex tube, 44 × 275 mm., equipped with a standard-taper 29/42 joint, is condensed 100 g. (1.25 moles) of anhydrous hydrogen bromide.‡ To this, under an atmosphere of nitrogen, is added 60 g. (0.555 mole) phenylsilane, b.p. 119°/754 mm. The reaction tube (with its contents at −196°) is fitted with a vacuum-stopcock adapter (which is wired firmly into position)

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* A satisfactory grade of phenyltrichlorosilane, b.p. 195–205°, is obtainable from Union Carbide, Product No. A152, Silicones Division, Crescent Valley Road and Route 38, Moorestown, N.J. The reported boiling point of pure phenyltrichlorosilane is 201°/760 mm.[7]

† A heated oil bath, with a thermometer, is the safest source of heat at this step. The residues must *not* be heated to dryness since phenylsilane and aluminum chloride will react at elevated temperatures (80–100°) to form silane, which will inflame upon contact with air. Phenylsilane is not spontaneously flammable.

‡ Obtainable from Air Products and Chemicals, Inc., Allentown, Pa., or the Matheson Company, Inc., East Rutherford, N.J. It also may be synthesized.[14]

and is then evacuated. The reaction tube is stored for a week at −78° in a slush bath of isopropyl alcohol and powdered Dry Ice.*

At the conclusion of the reaction period, the reaction tube, still at −78°, is connected to the vacuum line,† and the components which are volatile at −78° (all the hydrogen bromide and some of the bromosilane) are condensed, with occasional pumping, in two −196° traps in series. By occasionally raising the liquid-nitrogen Dewar, hydrogen bromide will be prevented from condensing, solidifying, and possibly blocking the entrance limb of the first trap. When the distillation of the excess hydrogen bromide into the −196° trap appears to be complete, the products which remain in the reaction tube at −78° are temporarily set aside. The products in the −196° traps are combined, and then distilled at −96° (toluene slush) through a trap at −126° (methylcyclohexane slush) into a trap at −196°. The −126° trap collects semipure bromosilane; the liquid-nitrogen trap collects the unused hydrogen bromide.

The products which remained at −78° in the reaction tube are now permitted to warm slowly to room temperature while being distilled through a −96° trap and a −126° trap into a −196° trap. This distillation is prolonged in order to minimize the amount of bromosilane retained in the −96° trap. The products which remain in the −96° traps are combined and subjected to a brief (2–4 minutes) distillation from a trap at room temperature through a −126° trap into a −196° trap. Finally, the material which collects in the latter −196° trap is again fractionally distilled through a −126° trap and a −196° trap. These steps are summarized in the "distillation shorthand" diagram of Figure 11. The asterisked fractions (semipure bromosilane) are combined. The yield of semipure bromosilane

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* Periods ranging from 7 to 30 days at −78° make little difference to the yield of bromosilane. The conversion of phenylsilane was not complete in 5 hours, after which time a 28% yield of bromosilane was obtained.

† A suitable vacuum line is depicted in *Inorganic Syntheses*, **7**, 35 (1963). For a discussion of general vacuum technique, see reference 15.

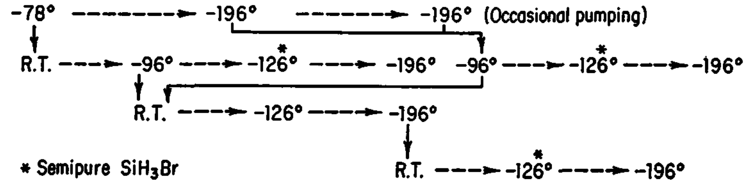

Fig. 11

is 44.7 g. (72.5%). The hydrogen bromide recovered amounts to 48 g., and because it contains some bromosilane, it is saved for subsequent preparations. (If desired, the hydrogen bromide may be disposed of by evaporation in a good hood.)

Bromosilane is purified in 10- to 15-g. portions by slow distillation through a simple low-temperature column* held at $-78°$ through a $-126°$ trap and into a $-196°$ trap (no pumping). Bromosilane condenses in the $-126°$ trap. The bromosilane has a vapor pressure of 706.0 mm. at 0° (literature,[2,3] 710 mm.). The infrared spectrum of the vapor is identical with those spectra published[4,16] for bromosilane.

The less volatile residues should be quite free of bromosilane. However, as a precaution, nitrogen is admitted into the reaction tube, the adapter is removed, and the contents of the tube are poured over pulverized Dry Ice contained in a sink in a hood. Water is then allowed to run over the Dry Ice. The recovered hydrogen bromide can be stored at room temperature after first being condensed at $-196°$ into a 150-ml. stainless-steel cylinder fitted with a stainless-steel needle valve. It is important to

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* A suitable column is easily fabricated from a 30-ml. bulb fused to an 18-in. length of 1-cm.-o.d. glass tubing, in turn connected to the vacuum line. Approximately 12 in. of the 1-cm.-o.d. tube is surrounded with an open-ended jacket, the lower end of which is stoppered, and through which stopper the glass column passes. A slush of Dry Ice–isopropyl alcohol surrounds the center column. The 30-ml. bulb, exposed to the room temperature, contains a $\frac{1}{4} \times \frac{1}{4}$-in. Teflon-covered magnetic stirring bar [available from the Cole Parmer Instrument and Equipment Company (Cat. No. 8549), 224 W. Illinois St., Chicago, Ill. 60610]. Stirring magnetically greatly assists the distillation of the bromosilane.

check that a good vacuum is maintained in the cylinder when it is held at −196°, because of the danger of air being admitted through an accidental leak. It is necessary to exclude moisture rigorously, or the hydrogen bromide will attack the stainless-steel cylinder.

Properties

Bromosilane is a spontaneously flammable liquid with a freezing point of −94° and a boiling point of 1.9°. It is best stored in a stainless-steel cylinder with a stainless-steel needle valve, but alternatively, it may be stored as a liquid at −78° in a glass vessel. Bromosilane, unlike the iodo analog, does not attack mercury or stopcock grease.

B. IODOSILANE[6,8]

$$C_6H_5SiCl_3 \xrightarrow[Fe]{Cl_2} ClC_6H_4SiCl_3 \xrightarrow[Et_2O]{LiAlH_4} ClC_6H_4SiH_3 \xrightarrow{HI} C_6H_5Cl + SiH_3I$$

Procedure

Commercial phenyltrichlorosilane, b.p. 195–205° (1072 g., 5.07 moles), and 1.0 g. of iron powder are placed in a 1-l. three-necked flask equipped with a magnetic stirrer,* a thermometer, and a gas inlet tube 1.0 cm. in diameter, which extends well beneath the level of the liquid in the flask. A vigorous stream of chlorine is admitted through the gas inlet tube.† The temperature of the reaction mixture, initially at room temperature, rises spontaneously, and the flow of chlorine is adjusted so as to maintain the reaction mixture at 65–70°. No external application of heat is required. The chlorination is continued for approximately 6.5 hours, after which time the reaction mixture will have gained 190–200 g. in weight. The crude product is

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* An egg-shaped Teflon-covered stirrer bar provides good stirring.

† This reaction must be conducted in an efficient hood.

distilled at reduced pressure,* and about 1128 g. of material boiling at 90–130°/3 mm. is collected. About 152 g. of material (b.p. > 130°/3 mm.) will remain in the still pot. The distillate is redistilled at reduced pressure through a column 45 × 2.5 cm. packed with $\frac{3}{16}$-in. Fenske helices. About 213 g. of forerun boiling at 85–115°/20 mm. (mainly phenyltrichlorosilane), about 709 g. (82.5%) of middle fraction (mixture of 2-, 3-, and 4-chlorophenyltrichlorosilanes) boiling at 119°/20 mm., and 206 g. of a residue (b.p. > 122°/20 mm.) are obtained.

A solution of lithium hydroaluminate in anhydrous diethyl ether is prepared by stirring 45 g. (1.18 moles, 11% excess) of lithium hydroaluminate with 600 ml. of refluxing ether for 5 days. The resultant clear supernatant liquid is transferred under nitrogen to a thoroughly dry, 3-l. three-necked flask equipped with a nitrogen inlet, blade mechanical stirrer, double-surface reflux condenser (cooled to 0°), and a pressure-equalized dropping funnel. A total of 330 g. (1.34 moles) of chlorophenyltrichlorosilane (b.p. 117–119°/20 mm.) diluted with an equal volume of anhydrous ether is added drop by drop to the stirred ethereal solution of lithium hydroaluminate over a 50-minute period. The reaction mixture is then heated at reflux for 3 hours, after which time the bulk of the ether is removed by distillation at atmospheric pressure. The remaining ether, together with the desired reaction product, is separated from the lithium chloride, aluminum chloride, and excess lithium hydroaluminate by distillation under reduced pressure (40–60°/3 mm.) with rapid mechanical stirring; the distillate is collected in a receiver cooled in a slush bath of Dry Ice and isopropyl alcohol. The residues are not to be heated to dryness. Redistillation at atmospheric pressure under nitrogen of this latter distillate affords 178 g. (93%) of (chlorophenyl)silane, b.p. 165–166°/759 mm., n_D^{25} 1.5367.

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* Considerable quantities of dissolved chlorine will be released during this procedure. A trap at −78° will be necessary to protect the oil pump, if one is used for this operation.

Into a heavy-walled polymer tube (2.4 cm. o.d. × 25 cm., with a wall thickness of 2.5 mm. and a capacity of about 80 ml.) is placed 28.0 g. (0.196 mole) of chlorophenylsilane (b.p. 165–166°/759 mm., n_D^{25} 1.5367). The tube is attached to the vacuum line, cooled to −196°, and then evacuated. Into this tube is then condensed 32 g. (0.25 mole) of anhydrous hydrogen iodide.* The reaction tube is sealed and then, *with explosion-proof protective shielding*, it is stored at −78° until the contents have melted and mixed. (Several hours are required.) Finally, it is permitted to warm slowly (during 1–2 hours) to room temperature, at which temperature it is kept for 24–36 hours. After this time it is cooled to −126°, opened to the atmosphere, and attached to the vacuum line. The reaction tube is now immersed in a −96° slush bath, and the excess hydrogen iodide is distilled into a −196° trap. The contents of the reaction tube are then permitted to warm to room temperature while being distilled through a −23° trap (carbon tetrachloride slush) and a −96° trap into a −196° trap, with pumping. The material which collects in the −196° trap is then distilled at room temperature through a −46° trap† (chlorobenzene slush) and a −96° trap into a −196° trap, with intermittent pumping. The products which condense in the two −96° traps and the −46° trap are combined and distilled at −46° through a −96° trap into a −196° trap, but with no pumping (i.e., the system which is initially completely evacuated is shut off from the pump during this final distillation process). Almost pure iodosilane condenses in the −96° trap, and the unused hydrogen iodide collects in the −196° trap. These steps are summarized in the "distillation shorthand" diagram, Fig. 12.

Iodosilane (20.2 g., 65%) is finally purified by distilling from a −46° trap through a −96° trap into a −196° trap (no pump-

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* Obtainable from Air Products and Chemicals, Inc., Allentown, Pa., or the Matheson Company, Inc., East Rutherford, N.J. It also may be synthesized.[14]

† The possibility of the inlet limb of the −96° trap becoming blocked with solid materials nonvolatile at −46° is avoided with the use of the first −46° trap.

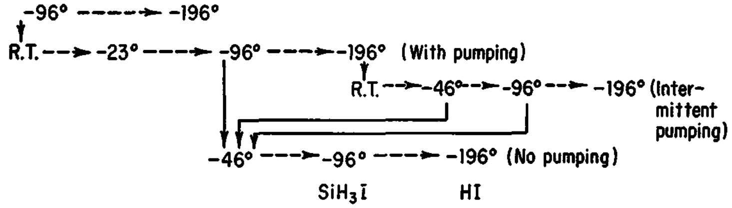

Fig. 12

ing). It is recovered from the −96° trap. The vapor pressure of iodosilane, prepared by this procedure, is 126 mm. at 0° (literature,[2] 123.9 mm.). The unreacted hydrogen iodide is recovered from the −196° trap and saved for subsequent reuse. If desired, the hydrogen iodide may be disposed of by evaporation in a good hood.

Properties

Iodosilane is a colorless liquid, freezing at −56.5° and boiling at 45°, which fumes vigorously upon exposure to the atmosphere. Since the vapor of iodosilane slowly attacks stopcock grease and reacts with mercury, it is best stored in a stainless-steel cylinder with a stainless-steel needle valve. The infrared spectrum of iodosilane is described in the literature.[17,18]

C. TRISILYLAMINE[3,9]

$$3SiH_3Br + 4NH_3 \rightarrow (SiH_3)_3N + 3NH_4Br$$

Procedure

Into a reaction tube (5 × 18 cm.) attached to the vacuum line and containing bromosilane (7.35 g., 0.0662 mole) is condensed a stoichiometric quantity of anhydrous ammonia (1.492 g., 0.0877 mole).* After warming the reaction mixture to room

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* Excess ammonia should be avoided, inasmuch as it catalyzes condensation of the $(SiH_3)_3N$ to SiH_4, etc.

temperature (while occasionally shaking) to complete the reaction, the trisilylamine is isolated by distilling the volatiles from the reaction tube at room temperature into a −196° trap (with pumping, to remove traces of hydrogen and silane). The contents of the −196° trap are then warmed slowly to room temperature while distilling through a −78° trap and a −126° trap into a −196° trap, but this time with no pumping. The trisilylamine (1.84 g., 78%) is recovered from the −78° trap.* The vapor pressure at 0° is 109 mm. (literature,[3,4,9] 110 mm.).

Properties

Trisilylamine is a colorless liquid with a freezing point of −106° and a boiling point of 52°. This silyl derivative is decomposed upon exposure to the atmosphere. The infrared spectrum of the vapor is described by Ebsworth et al.[19]

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* The checker found it necessary to use a low-temperature distillation column in order to remove the last traces of SiH_3Br from the product.

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36. SILANE, STANNANE, SILANE-d_4, GERMANE-d_4, AND STANNANE-d_4

Submitted by ARLAN D. NORMAN,*† JOHN R. WEBSTER,* and WILLIAM L. JOLLY*
Checked by R. A. GORSE,‡ W. R. BORNHORST,‡ and M. A. RING‡

Silane, germane, and stannane can be synthesized by the reduction of a variety of silicon, germanium, or tin compounds with active metal hydrides.[1,2] The general method described below, involving the lithium hydroaluminate ($LiAlH_4$) reduction of silicon tetrachloride and tin(IV) chloride, is convenient for the efficient preparation of 1–50 mmoles of silane and stannane. The method is easily adapted to the synthesis of the deuterio compounds, i.e., silane-d_4, germane-d_4, and stannane-d_4, by

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substituting lithium hydroaluminate-d_4 for lithium hydroaluminate in the appropriate reactions. Silane-d_4 and germane-d_4 are useful in structural and mechanistic studies, and undoubtedly stannane-d_4 will have similar applications.

Normal germane (GeH_4) can also be prepared by reduction of germanium tetrachloride, although the previously reported reduction of germanate ion by potassium hydroborate in aqueous media gives significantly higher yields.[3] Because this latter method involves the use of relatively large quantities of water, acid, and a large excess of potassium hydroborate, it is not economically feasible to adapt it to the preparation of deuterated germane.

Stannane yields considerably higher than those reported here have been reported by Kettle,[4] using a procedure similar to that we have outlined for the preparation of SnD_4. Although Kettle's method gives a higher yield, the procedure described below is preferable for the preparation of SnH_4. The latter method provides for a slow addition of reactants, and thus precludes the possibility of the reaction getting out of control if it should warm up too quickly. It is believed that controlling the reaction by the portional addition of reactants is safer than mixing the stoichiometric amounts of reactants at the outset and relying on temperature control to keep the reaction at a moderate rate.

However, the temperature-control method is used for the preparation of the deuterated compounds. Although the other method is safer, there are two reasons which justify using the temperature-control method in this case. First, special care must be taken to maintain isotopic purity in the preparation of the deuterated compounds. Hence the reactants must be free of water, and this is better accomplished if the solvent is dried and handled in the vacuum line, where it cannot come into contact with atmospheric water. Second, because the reaction is run on a small scale, the consequences would be minimal if it were to get out of control.

The general procedure can be extended to the synthesis of

Si_2H_6 and Si_2D_6 from Si_2Cl_6. However, the diethyl ether must then be replaced by a less volatile solvent, such as dipropyl ether or dibutyl ether.

*General Procedure**

The apparatus shown in Fig. 13 is used for the preparation of silane and stannane. For the synthesis of silane-d_4, germane-d_4, and stannane-d_4, a similar apparatus without the addition funnel

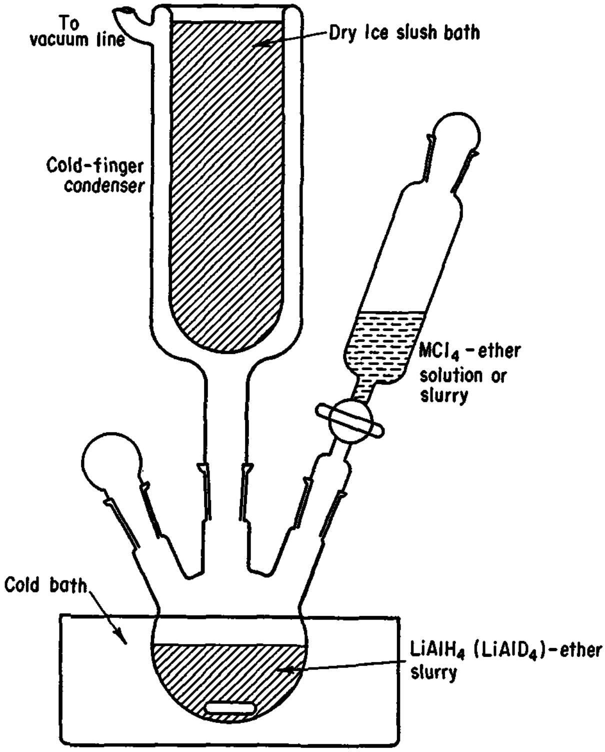

Fig. 13. Apparatus for the preparation of silane, stannane, silane-d_4, germane-d_4, and stannane-d_4.

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* These syntheses are based in part on reference 5. A detailed description of a vacuum line suitable for these syntheses is given in reference 3. For additional discussion of vacuum-line techniques, see reference 6.

is used. A suspension of $LiAlH_4$ (or $LiAlD_4$) is placed in the 300-ml. three-necked round-bottomed flask. The flask is equipped with an efficient magnetic stirrer, a cold-finger condenser, and a 150-ml. addition funnel which contains the silicon tetrachloride–ether solution or tin tetrachloride–ether slurry. For best results, all joints are greased with Dow-Corning silicone grease. The apparatus is attached to a vacuum line in such a way that volatile reaction materials (products and some ether solvent) can be removed through a series of five U-traps. The cold bath surrounding the reaction flask is maintained at the desired temperature by the controlled addition of powdered Dry Ice to the bath solvent, and the cold-finger condenser is cooled to −78.5° (Dry Ice slush).*

Lithium hydroaluminate is highly reactive and gives hydrogen on hydrolysis. Care must be exercised in the disposal of the unreacted hydroaluminate left after reaction in the preparations described below. Slow addition of a dilute solution of water in dioxane, tetrahydrofuran, or 1,2-dimethoxyethane to the reaction mixture will suffice to decompose the $LiAlH_4$ safely. As an added precaution, the decomposition should be done under a nitrogen atmosphere to guard against explosion of the hydrogen evolved.

A. SILANE AND SILANE-d_4

$$SiCl_4 + LiAlH_4 \rightarrow LiCl + AlCl_3 + SiH_4$$
$$SiCl_4 + LiAlD_4 \rightarrow LiCl + AlCl_3 + SiD_4$$

Procedure (SiH_4)

■ **Caution.** *Silane is a flammable gas, its mixtures with oxygen are explosive, and it often spontaneously violently inflames in air. It must be handled with great care in a vacuum line. Of course, the same precautions apply to silane-d_4.*

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* A variety of solvents, i.e., ethanol, isopropyl alcohol, acetone, and trichloroethylene, can be used in preparing Dry Ice cooling baths. The low flammability of trichloroethylene makes it safer than the others.

The apparatus is assembled and prepared for the reaction as described under General Procedure, the reaction flask and addition funnel having been charged with 1.14 g. (0.030 mole) of lithium hydroaluminate in 70 ml. of diethyl ether and 2.30 ml. (0.020 mole) of silicon tetrachloride in 50 ml. of ether, respectively. The cold bath and the cold-finger condenser are maintained at −15 to −20° and −78.5°, respectively, during this entire synthesis. After the apparatus is evacuated, care being taken to avoid excessive "bumping" of the solvent as ether refluxing begins, the U-trap nearest the reaction apparatus is cooled to −95° (toluene slush) and the remaining four traps are cooled to −196° (liquid nitrogen). The silicon tetrachloride–ether solution is added through the addition funnel, over a 15-minute period, to the cooled, stirred lithium hydroaluminate suspension.* The silane is removed continuously at a *moderate* rate, in order to prevent violent refluxing of the ether. The rate is readily controlled by adjusting the opening of the stopcock between the reaction vessel and the vacuum line. The reaction mixture is stirred for 15–20 minutes after the silicon tetrachloride addition is completed, in order to ensure complete reaction. During this time, the system can be closed off from the vacuum line to prevent excessive removal of ether. After the final quantity of silane is pumped into the vacuum line, the reaction vessel may be vented to the air and removed from the vacuum line.

The contents of the liquid-nitrogen traps (silane and traces of ether) are combined in one trap, and the material in the −95° trap (mainly diethyl ether) is discarded. The silane is freed of last traces of ether by passing it five times through a −130° trap (*n*-pentane slush) into a −196° trap. Typically, this procedure gives 0.016 mole of pure silane (80% based on $SiCl_4$).

Hydrogen chloride is a common impurity which can be almost entirely removed by using a −160° trap (isopentane slush)

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* ■ **Caution.** *In order to prevent air from accidentally entering the system, stop the addition of $SiCl_4$-Et_2O solution while a small amount of liquid is still present in the addition funnel. This is important since silane will inflame or explode upon exposure to oxygen.*

instead of a −130° trap. The last traces of hydrogen chloride can be removed from the silane by treatment with a little water or wet 1,2-dimethoxyethane, followed by passage through a −130° trap.

Procedure (SiD_4)

The apparatus used is a 100-ml. round-bottomed flask equipped with a cold-finger reflux condenser and a magnetic stirring bar. The apparatus is attached to the vacuum line along with two 100-ml. detachable bulbs from which dry ether solvent and silicon tetrachloride are distilled into the reactor. The entire system is preconditioned by allowing deuterium oxide to stand in the line at its room-temperature vapor pressure and exchange with water present. The preconditioning is necessary to ensure the highest possible isotopic purity of the SiD_4 prepared in the synthesis. After one hour the D_2O is pumped from the system, and the apparatus is thoroughly evacuated to remove last traces of D_2O.

After the preconditioning operation, the reactor is opened and charged with 0.63 g. of $LiAlD_4$ (0.015 mole, >98% D)* and reevacuated. Thirty milliliters of diethyl ether is dried *in vacuo* over $LiAlH_4$ in one of the detachable bulbs, and then distilled into the reactor, which is held at −196° (liquid nitrogen). A small plug of glass wool in the neck of the bulb will serve to keep small particles of $LiAlH_4$ from transferring into the reactor during distillation of the ether. Silicon tetrachloride (1.72 ml., 0.015 mole) is placed in the other detachable bulb, degassed by brief pumping, and then distilled into the reactor. The cold-finger condenser is cooled to −78.5° (Dry Ice slush), the U-trap nearest the reactor is cooled to −95°, and the remaining four traps are cooled to −196°. The reactor is allowed to warm slowly in air to 0° (over a 30-minute period), the volatile products being removed as they form at a rate slow enough to prevent

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* Alfa Inorganics, Inc., 8 Congress St., Beverly, Mass.

violent refluxing of the ether. For best results the reaction mixture should be stirred periodically during the reaction period. The reactor is allowed to stand at 0° for 30 minutes to ensure complete reaction before the last traces of SiD_4 are pumped into the vacuum line.

The contents of the liquid-nitrogen traps (SiD_4 and traces of ether) are combined into one trap, and the material in the $-95°$ trap (mainly diethyl ether) is discarded. The product is freed of last traces of ether by passing five times through a $-130°$ trap into a $-196°$ trap. About 0.013 mole of SiD_4 (87% yield based on $LiAlD_4$), having an isotopic purity of >96%, is obtained.

Properties

The infrared spectrum of silane[7] gas in the NaCl region shows absorptions at 2191(s) (Si—H stretching frequency) and 914(s) $cm.^{-1}$. The spectrum of silane-d_4[8] shows absorptions at 1597(s) (Si—D stretching frequency) and 681 $cm.^{-1}$. The mass spectrum of SiH_4 has peaks at m/e 14–16 and 28–34, attributable to SiH_x^{2+} and SiH_x^{+} ions, respectively.[9] Peaks corresponding to the analogous ion fragments in the mass spectrum of SiD_4 occur at m/e 14–18 and 28–38. The presence of carbon dioxide impurity in the silane is indicated by an absorption at 2300 $cm.^{-1}$ in the infrared spectrum or by a peak at $m/e = 44$ in the mass spectrum.

Silane may be stored in the gas phase at room temperature for several months without noticeable decomposition. Since silane does not dissolve appreciably in grease, storage vessels equipped with greased stopcocks may be used.

B. GERMANE-d_4

$$GeCl_4 + LiAlD_4 \rightarrow LiCl + AlCl_3 + GeD_4$$

Procedure

The reactor consists of a 100-ml. round-bottomed flask equipped with a cold-finger condenser and a magnetic stirring bar. The apparatus is attached to the vacuum line along with two detachable bulbs, from which dry diethyl ether and germanium tetrachloride are distilled into the reaction vessel. In order to obtain GeD_4 of the highest possible isotopic purity, the entire system is preconditioned with D_2O (see SiD_4 Procedure, above) prior to the synthesis.

After preconditioning the apparatus, the reactor is opened and charged with 0.42 g. (0.010 mole) of $LiAlD_4$ (>98% D) and then reevacuated. Twenty milliliters of lithium hydroaluminate–dried diethyl ether and 1.4 ml. (0.0123 mole) of germanium tetrachloride are distilled into the reactor, which is cooled to −196°.* The cold-finger condenser is cooled to −78.5° (Dry Ice slush), the U-trap nearest the reactor is cooled to −95° (toluene slush), and the four remaining U-traps are cooled to −196°. The reaction mixture is allowed to warm slowly to room temperature over a 15 to 20-minute period, during which time the reaction mixture is periodically stirred with a small magnet. While the reaction mixture is warming to room temperature, volatile reaction products are removed at a rate so as to maintain gentle reflux on the −78.5° cold finger. The reaction is complete when the reactor reaches room temperature.

The material in the −95° trap (mainly solvent) is discarded. The product in the −196° traps is freed of last traces of ether solvent by passing it five times through a −130° trap (*n*-pentane slush). The yield is 0.0019 mole of GeD_4 (19%, based on $LiAlD_4$), and the deuterium content of the product is greater than 96%.

Properties

The GeD_4 prepared has a vapor pressure of 186 mm. at −112°. The infrared spectrum of the gas shows absorptions at 1522 (Ge—D stretching frequency) and 596 cm.$^{-1}$.[10] The mass spectrum shows peaks at m/e = 35–41 and m/e = 70–82

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* Details concerning these steps in the synthesis are given above, under SiD_4 Procedure.

due to GeD_x^{2+} and GeD_x^+ ions, respectively.[8] Traces of carbon dioxide impurity may be detected by a peak at m/e = 44 in the mass spectrum or by an absorption at 2300 cm.$^{-1}$ in the infrared spectrum.

Germane-d_4 may be stored at room temperature in a glass vessel equipped with a greased stopcock for several months without appreciable decomposition.

C. STANNANE AND STANNANE-d_4

$$SnCl_4 + LiAlH_4 \rightarrow LiCl + AlCl_3 + SnH_4$$
$$SnCl_4 + LiAlD_4 \rightarrow LiCl + AlCl_3 + SnD_4$$

Procedure (*SnH_4*)

The apparatus is assembled as described under General Procedure. The reaction flask is charged with 2.7 g. (0.072 mole) of lithium hydroaluminate and 70 ml. of anhydrous diethyl ether. The cold-finger reflux condenser is filled with a −78.5° bath (Dry Ice slush). The cold bath for the reactor is maintained at −60 to −70°. The system is opened to the vacuum pump, and a −95° bath (toluene slush) is placed around the U-trap nearest the reaction vessel. The remaining four U-traps are cooled to −196° with liquid nitrogen. Eight milliliters of tin(IV) chloride (0.068 mole) and 130 ml. of diethyl ether are carefully mixed together to make a slurry of the solid white etherate which forms.* This slurry is slowly added from the dropping funnel in small portions over a period of about one hour. It is usually necessary to agitate the slurry in some manner since the solid etherate tends to settle to the bottom and hinder steady addition; stirring with a glass rod is sufficient. Addition of the slurry should be sufficiently slow so that most of the stannane traps out in the first three −196° traps. The appearance of much stannane in the last trap is an indication

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* The solid etherate can be dissolved by addition of ether, but experiments have shown that the yield of SnH_4 is higher if the slurry is used instead of a solution.

that the rate of addition is too fast and that the product is being swept through the condensation train. Considerable hydrogen is also evolved in this preparation, and it hinders the condensation of stannane. We have found that our best yields are obtained if a stopcock between the −196° traps and the vacuum pump is partially closed, thus maintaining the pressure in the reaction system around 50 to 100 mm.

After the addition of the tin(IV) chloride–etherate slurry is completed, the reaction mixture is allowed to warm slowly (over a period of at least 30 minutes) to −20°. The mixture is then quenched to −78°, and the reaction flask is removed from the vacuum line. The material in the −95° trap (mostly solvent) is discarded. The crude product in the −196° traps is combined and passed four times through a −112° trap (carbon disulfide slush) to remove traces of solvent. This procedure typically gives 0.020 mole (30% yield) of stannane with a vapor pressure of 17 mm. at −112°.

Procedure (SnD_4)

The apparatus used is a 100-ml. round-bottomed flask equipped with a cold-finger reflux condenser and a magnetic stirring bar. This system is connected to a vacuum line with five U-traps between the reactor and pump and two detachable bulbs from which reactants are distilled into the reactor. Prior to the synthesis the entire vacuum system is preconditioned with deuterium oxide, as has been described above (see SiD_4 Procedure).

After preconditioning and evacuating the system, the reactor is opened, charged with 0.270 g. (0.0065 mole) of $LiAlD_4$ (>98% D), and then evacuated again. Ten milliliters of dried diethyl ether and 0.9 ml. anhydrous tin(IV) chloride (0.0077 mole) are distilled into the reactor, which is cooled to −196°.*

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* Details concerning these steps in the synthesis are given above under SiD_4 Procedure.

The cold-finger reflux condenser and vessel around the reactor are filled with −78° baths (Dry Ice slushes). The U-trap nearest the reactor is cooled with a −95° bath (toluene slush), and the remaining four U-traps are cooled to −196°. The reactor and cold finger are allowed to warm slowly to room temperature (over a period of about 90 minutes), and volatile products are taken off at 5-minute intervals. A magnetic stirring bar is used to stir the reactants. The reaction is stopped when the reactor reaches room temperature.

The material in the −95° traps (mostly solvent) is discarded. The product in the four −196° traps is combined and passed four times through a −112° trap (CS_2 slush) to remove traces of solvent. The yield is 0.0017 mole of stannane-d_4, or 25% based on $LiAlD_4$. The vapor pressure at −112° is 17.4 mm., and the deuterium content is >98%.

Properties

Stannane has a reported vapor pressure at −111.6° of 17.5 mm.[11] The infrared spectrum of the gas in the NaCl region shows absorptions at 1860(s) (Sn—H stretch), 760(m), 703(s), and 677(s) cm.$^{-1}$.[12] The stannane-d_4 prepared absorbed at 1455(s) cm.$^{-1}$. The presence of carbon dioxide in the stannane may be detected by a peak at $m/e = 44$ in the mass spectrum.

Stannane decomposes thermally in a few hours at room temperature. The decomposition is catalyzed by the metallic tin mirror which forms;[13] however, traces of oxygen have been reported to inhibit the decomposition.[4] Thus stannane is best stored at room temperature with traces of oxygen present or pure at liquid-nitrogen temperature.

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37. TRIALKOXYARSINES

(*Trialkyl Arsenites*)

$$AsCl_3 + 3ROH + 3NR'_3 \rightarrow As(OR)_3 + 3R'_3NHCl$$

Submitted by KURT MOEDRITZER*
Checked by CLIFFORD O. DENNEY† and JOHN T. YOKE III†

Trimethoxyarsine was first reported by Crafts.[1] It was obtained by three methods: from silver arsenite and methyl iodide, from arsenic trioxide and tetramethoxysilane, and from arsenic trihalide and sodium methoxide. Better yields have been obtained by applying the method of this synthesis; the procedure seems to be generally applicable to the preparation of trialkoxyarsines.

■ **Caution.** *Although the toxicity of trialkoxyarsines has not been investigated in detail, precautions similar to those suggested for the handling of volatile arsenic compounds should be taken. Therefore these preparations should be performed in a well-venti-*

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lated hood, and contact of the arsenic-containing solutions with the skin should be avoided.

Procedures

A. TRIMETHOXYARSINE

(Trimethyl Arsenite)

A four-necked 3-l. flask fitted with a thermometer, reflux condenser, dropping funnel, and mechanical stirrer is charged with 750 ml. of *n*-hexane, 750 ml. of anhydrous ethyl ether, 104 g. (3.25 moles) of anhydrous methanol, and 370 g. (3.05 moles) of *N*,*N*-dimethylaniline.* A drying tube is attached to the outlet of the condenser to prevent moisture from entering the reaction vessel. The dropping funnel is charged with 182 g. (1 mole) of freshly distilled arsenic trichloride,† and this is added drop by drop to the well-stirred ice-cooled contents of the reaction flask. The temperature in the flask is maintained at *ca.* +5°. During the course of the addition, a white precipitate of *N*,*N*-dimethylaniline hydrochloride is formed.

When the addition of the arsenic trichloride is completed, the reaction mixture is stirred for another 1 to 2 hours at room temperature. The solution is filtered with careful exclusion of the moisture of the atmosphere,‡ and the *N*,*N*-dimethylaniline hydrochloride precipitate is washed with cold ethyl ether. The combined filtrates are distilled using a 60-cm. vacuum-jacketed column filled with glass helices.§ The trimethoxyarsine distills at 129–130°/760 mm.; yield 129 g. (77%). Yields of 118–126 g. are obtained using triethylamine.

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* Triethylamine (308 g.) may be used, but then a smoke and a crusty deposit of Et_3NHCl form during the addition of the $AsCl_3$. The bulk of the Et_3NHCl precipitate is very voluminous and at times is difficult to filter. The use of *N*,*N*-dimethylaniline (suggested by the checkers) avoids these problems.

† The checkers successfully used freshly opened bottles of analytical reagent grade $AsCl_3$ without further purification.

‡ The checkers used a dry-nitrogen-filled plastic glove bag.

§ The checkers used a 1-m. vacuum-jacketed Oldershaw column, with a 2:1 reflux ratio.

B. TRIETHOXYARSINE

(Triethyl Arsenite)

The same method, but using 148 g. (3.25 moles) of anhydrous ethanol instead of methanol in the procedure given above, may be utilized to prepare triethoxyarsine; yield 148 g. (70.5%); b.p. 59°/14 mm. or 167°/760 mm. Yields of 135–145 g. are obtained using triethylamine.

C. TRI-*n*-BUTOXYARSINE

(Tri-*n*-butyl Arsenite)

Tri-*n*-butoxyarsine may be prepared according to the procedure given above by using 240 g. (3.25 moles) of dried 1-butanol instead of the methanol and 308 g. (3.05 moles) of triethylamine instead of the *N*,*N*-dimethylaniline. Yield: 244 g. (83%); b.p. 101°/3 mm. The checkers used *N*,*N*-dimethylaniline and obtained a yield of 192 g. (66%), b.p. 102°/4 mm.

Properties[2]

Trimethoxyarsine (d_0^{20} 1.4264; n_D^{20} 1.4402) is a colorless liquid which is readily hydrolyzed by atmospheric moisture, forming a white precipitate of arsenic trioxide. The compound is soluble in carbon tetrachloride, benzene, chloroform, hydrocarbons, and ethers. The product is shown to be at least 99.5% pure (with respect to hydrogen-containing impurities) by proton nuclear magnetic resonance (n.m.r.), since a single sharp peak at −3.52 p.p.m. (relative to internal tetramethylsilane) is seen in the n.m.r. spectrum of the neat liquid. Similar properties are shown by triethoxyarsine (d_0^{20} 1.2132; n_D^{20} 1.4360) and tri-*n*-butoxyarsine (d_0^{20} 1.0723; n_0^{20} 1.4476).

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Inorganic Syntheses, Volume XI
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38. SULFUR IMIDES

$$S_2Cl_2 \xrightarrow{NH_3} S_8 + S_7NH + S_6(NH)_2 + S_5(NH)_3 + NH_4Cl$$

Submitted by H. G. HEAL* and J. KANE*
Checked by L. R. MORSS,† J. MERBAUM,† and W. L. JOLLY†

The basic procedure of this synthesis was first published by Becke-Goehring and her collaborators[1] as a method for preparing heptasulfur imide. Her method of purifying the heptasulfur imide (recrystallization from methanol) requires considerable experience to give a product free from sulfur and other imides, and makes no provision for isolating the diimides and triimides. Weiss[2] made an important advance by working up the crude product chromatographically on an alumina column, thus enabling him to separate and characterize the 1,5-hexasulfur diimide. The further improvement of replacing alumina by silica gel, which is less destructive to the imides, permits the isolation of all three diimide isomers[3,4] and the two triimide isomers[5] from the same crude reaction product. Besides affording a route to the diimides and triimides, column chromatography facilitates the preparation of large amounts of heptasulfur imide of high purity.

The references just cited provide only outline descriptions of the chromatographic separations. In this synthesis, detailed procedures are presented. The preparation requires 1 day for the sulfur chloride–ammonia reaction plus 2 to 7 days of intermittent attention (depending upon which imides are required) for the subsequent chromatography and recrystallization.

Very little is known about the stoichiometry or mechanism of this preparation, and the products certainly include substances

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not listed in the above equation. Tetrasulfur tetraimide is the only imide derived from octasulfur which does not form in appreciable quantities in the preparation described here. It is best made by reduction of tetrasulfur tetranitride.[6]

There is an extensive chemistry of heptasulfur imide, from which many inorganic and organic derivatives have been made.[6] The chemistry of the diimides[6] and triimides is only just beginning to be studied, and promises to be even more interesting.

Procedure

A 5-l. three-necked round-bottomed flask is equipped with a large electrically driven paddle stirrer, an ammonia-gas inlet tube of 6 to 7-mm. internal diameter, reaching nearly to the bottom of the flask, and bent so as not to foul the stirrer, and either a thermocouple in a thin glass tube or a thermometer,* reaching low enough to be immersed in the liquid. At least one of the necks must be left open as an exit for gas. The flask stands in a large basin to hold solid carbon dioxide and methanol or acetone; this basin must be deep enough to enable most of the flask to be submerged in the cooling bath. To permit control of the cooling rate, it should be possible to raise and lower the basin. The whole apparatus is set up in a fume hood.

Into the flask is put 2250 ml. of dimethylformamide, of a good laboratory grade, but not dried or otherwise specially purified. A fast stream of ammonia gas is bubbled in through the gas inlet, with stirring and cooling, until the dimethylformamide is saturated with ammonia and the temperature has fallen to −5 to −10° (10–20 minutes). Laboratory-grade ammonia, taken directly from a cylinder without drying, is satisfactory. (The unimportance of using dry reagents can be appreciated from the fact that sulfur imides are also formed in good yield from disulfur dichloride and aqueous ammonia.[7]) Reagent-

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* A low-temperature thermometer with the graduations above −20° visible outside the neck of the flask is convenient for this purpose.

grade disulfur dichloride (250 ml., 3.1 moles) is then added gradually in 5-ml. portions during a period of approximately 3 hours. Each portion is squirted quickly and directly into the dimethylformamide from a small glass pipet (equipped with a rubber bulb or syringe), which is introduced into the reaction vessel through the gas exit. A fast flow of ammonia is maintained throughout the addition. The reaction mixture becomes inky blue, and clouds of fumes are evolved. If solid yellow or red substances collect above the blue liquid level, the disulfur dichloride is not being squirted directly enough into the liquid or too much splashing is occurring. Each injection of disulfur dichloride causes a rise of temperature, and the next injection is not made until the temperature has again fallen to between −5 and −10°. When the addition is completed, the ammonia flow is discontinued, and the mixture is stirred for 1 hour. The cooling bath is lowered to prevent the temperature from falling too low. The mixture is then poured into 8 l. of a slurry of crushed ice and 1% hydrochloric acid, in a plastic, glass, or earthenware container of at least 15 l. capacity. Without delay, 1:1 hydrochloric acid (conveniently prepared by mixing the concentrated acid with crushed ice) is now added, with stirring, until the mixture is acidic. As much as 3 kg. of concentrated acid may be required. The color changes from deep violet to brown to yellow or olive. A lump of doughy material separates out, which on standing becomes a gritty yellow solid. The precipitated matter is allowed to settle for 2–3 hours or overnight, but not longer, or the yield may be reduced. The cloudy yellow supernatant liquid is decanted and discarded. The gritty solid is transferred completely to a coarse-porosity sintered-glass funnel, where it is thoroughly washed with water. It is dried over calcium chloride in an evacuated desiccator, and should then weigh 130–150 g.

■ ***Caution.*** *The crude reaction product contains a substance (not yet identified, but definitely not any of the imides) which causes irritation and cracking of the skin and burning of the eyes, nose, and* *lips. Rubber gloves should be worn, and operations performed in a hood, while the reaction mixture is being worked up. These precautions are unnecessary when working with the purified imides.*

The crude dry product should not be stored longer than a few days before it is chromatographed, or there will be appreciable decomposition and reduction of yield. This product consists mainly of sulfur imides and sulfur. It is first finely ground in a nonmetallic mortar, and then shaken with five successive 400-ml. portions of dry, peroxide-free ethyl ether. If appreciable amounts of imides remain in the solid residue, it will be necessary to regrind the solid and to extract again. The ether-insoluble portion of the solid is nearly all sulfur, and can be discarded. The ether extracts are combined, and the ether is evaporated under reduced pressure, taking precautions to avoid bumping. About 50–70 g. of residue, consisting of sulfur imides mixed with some sulfur, remains.

The carbon disulfide required as solvent in the subsequent chromatographic separations should be distilled before use to remove dissolved sulfur, which is often present even in the reagent-grade solvent.* The chromatographic column is made up without a stopcock, as shown in Fig. 14, or a standard chromatographic column with a Teflon stopcock is used. The flow of solvent can be stopped when required in the non–stopcock apparatus by capping the siphon exit with the device shown. To prevent fire and poisoning of the operator by vapor, the column must be set up in a fume hood with a good draft. The operation should not be attempted under dry winter conditions when there is a risk of electrostatic ignition. One problem that must be countered is the rapid evaporation of carbon disulfide at the tip of the stopcock, which can cause the accumulation of solid imides and ice at the tip. If the fractions are collected

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* Carbon disulfide must be distilled in a tight all-glass apparatus in a hood. The boiling flask should be immersed in a water bath no hotter than 65°, and heated by completely submerged heating wire connected to a remote variable transformer.

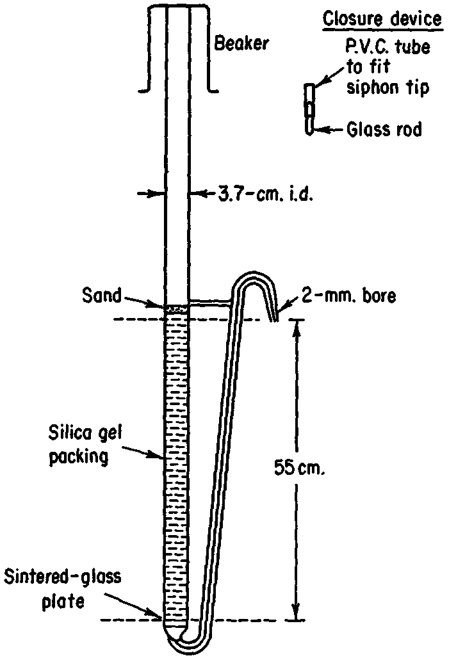

Fig. 14. Chromatographic column for separating sulfur imides.

manually, the fractions can be collected in a graduated cylinder, with the column tip dipping well down into it, each fraction being immediately poured into a beaker when the required volume is collected. If the fractions are collected automatically, using an electrically operated turntable, the tip of the column should be carefully shielded, as shown in Fig. 15.

To charge the column, it is first filled with carbon disulfide, and then the chromatographic silica gel ($\approx$700 g.), 200–300 mesh,* is added as a slurry in the same solvent and topped with several millimeters of sand. The column must be free of bubbles and layers. The dried sulfur imide mixture is dissolved in the minimum of warm carbon disulfide (about 400–600 ml.), and the solution is added to the column, which has been drained

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* If ungraded silica gel is used, its capacity per unit volume will be considerably less, and the amount of crude product chromatographed must be reduced.

until the liquid level is at the top of the sand layer. The solution is loaded onto the column by adjusting to a drop rate of about 200 drops/minute (300 ml./hour); when it has drained down to the top of the packing, the inside wall of the upper part of the column is rinsed down with a few milliliters of the solvent, and this is allowed to drain down once more to the top of the adsorbent. Elution is then begun by filling the column to near the top with carbon disulfide. The collection of eluate should commence soon after the sulfur (the color of which is visible on the column) begins to leave the column. The best point for beginning the collection of eluate is the first appearance of S_7NH. A very sensitive test for all the imides is the violet color produced by shaking a carbon disulfide solution with a potassium hydroxide in methanol. Fractions of 100-ml. volume are collected in previously weighed 150–250 ml. beakers. The fractions are left to evaporate in the fume hood, in a good draft (several hours), and are then covered to minimize accumu-

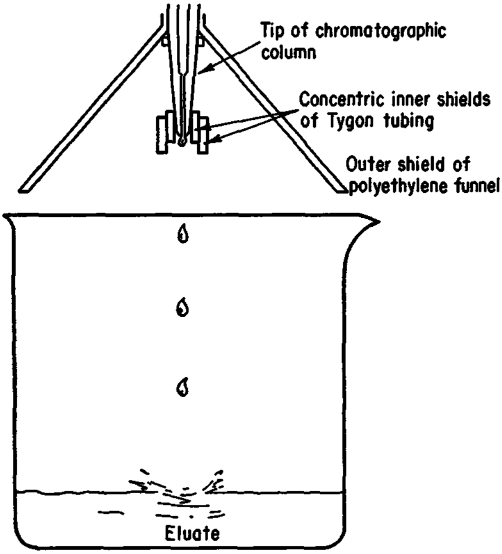

Fig. 15. Method of shielding tip of chromatographic column.

lation of dust. The contents of the fractions are determined by thin-layer chromatography (see below), while they are evaporating. For heptasulfur imide and the three diimides it may be necessary to collect as many as 90 fractions in all. With experience, the size of the later fractions can be increased to 200 ml., and the number correspondingly reduced. A flow rate of 300 ml./hour is satisfactory.

Heptasulfur imide follows soon after the sulfur, with which it overlaps slightly. It is best to reject the early sulfur-contaminated fractions, which entails little loss. The pure fractions are combined, and on evaporation deposit large, nearly colorless rhombs of the imide. Yield: 25–45 g. To remove any remaining traces of sulfur, the imide can be recrystallized by evaporation of a warm solution in carbon disulfide, or by allowing a saturated solution in boiling carbon tetrachloride or hot toluene to cool.

The *1,4-hexasulfur diimide* fraction comes off the column after the heptasulfur imide, and should be clearly separated both from it and from the other diimides which follow. Yield: 8 g.

The *1,3- and 1,5-hexasulfur diimides* are only partially separated by the column, a long run of fractions being obtained which contain comparable amounts of the two. The extreme head fractions are mainly 1,5-diimide and the extreme tail fractions 1,3-diimide (almost pure). About 3.7 g. of each imide is present in all. Their separation is tedious and requires continual infrared monitoring. It can be done entirely by chromatography, but it is more convenient to employ fractional crystallization from carbon disulfide. Chromatographic fractions are combined to give a mixture containing 70% or more of the desired isomer, and dissolved in the minimum of warm carbon disulfide. (See solubilities under Properties.) The solution is allowed to evaporate spontaneously to about a third of its original volume, and decanted away from the crystals which have separated. These are redissolved, and the process repeated. The progress of purification can easily be followed by infrared spectroscopy (see below), and the operation is straightforward, if slow. If desired, some of the latter crystallization steps can be effected by allowing the saturated solutions to cool slowly and quietly to below 0° in a dry location (as the freezing compartment of a refrigerator).*

In order to prevent "creeping" of deposited solid up the side of the beaker during crystallization, the beaker should be loosely covered with a clock glass and left to stand on a shallow water bath containing warm (50–60°) water, which is placed in the fume hood in a slight draft. This results in some condensation of solvent on the sides of the beaker and continuous washing down of any crystals formed there.

The *1,3,5- and 1,3,6-pentasulfur triimides* come off the column after the diimides, but they cannot easily be isolated by merely continuing elution in the procedure just described, because inordinately large volumes of solvent would be needed.†

For the triimides, it is expedient to increase the scale of the preparation, and then to effect a preliminary concentration of the triimides from the other imides so that the chromatography can be done on a much smaller column. The crude imide mixture is made as just described, but using 3 l. of dimethylformamide and 420 ml. (5.2 moles) of disulfur dichloride. After grinding finely once or twice as before, it is extracted with successive portions of dry, peroxide-free ethyl ether, totaling 3 l. The combined ether extracts are left to evaporate spontaneously until 150–300 ml. of cold liquid is left. Evaporation is continued until it is judged that more than half of the solute has crystallized. The solution is decanted away from the mass of crystals of heptasulfur imide and hexasulfur diimides, and allowed to evaporate to dryness, leaving 30–40 g. of solid, which consists

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* The recrystallizations can be carried out using other solvents having higher boiling points and less danger of ignition. All the imides are soluble in hot toluene, and the 1,3-diimide and 1,3,6-triimide are particularly soluble in carbon tetrachloride.

† However, if monitoring reveals that the diimides have been eluted in the first 20–40 fractions, the triimides can be conveniently recovered by continuing the elution more or less as described below.

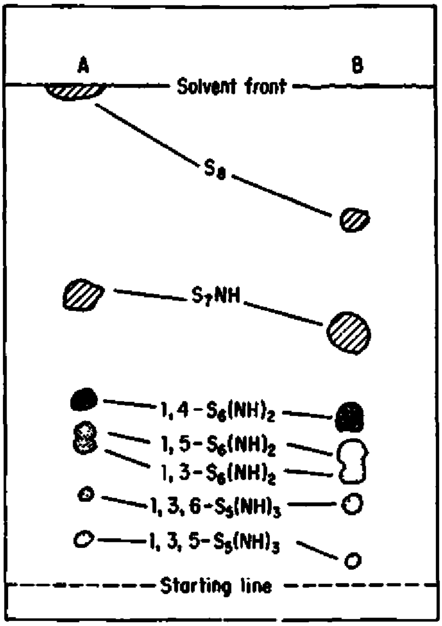

Fig. 16. Thin-layer chromatograms. (A) TLC spots if S_8 moves with solvent front; (B) TLC spots if S_8 moves more slowly (silica gel H; 10–40 μ, activated 20 minutes at 110°C).

mainly of the diimides and contains nearly all the triimides. This mixture is subjected to chromatography as above, but using a column about 4 cm. in diameter and with 27 cm. depth of adsorbent. Immediately following the 1,3-diimide, the 1,3,6-triimide comes off. Yield: 0.5–1.35 g. The 1,3,5-triimide is more strongly adsorbed, and is best stripped from the column by changing the solvent to two volumes of benzene plus five volumes of carbon disulfide. Yield: about 0.3 g.

The following monitoring methods are recommended: Thin-layer chromatography gives a qualitative, or roughly quantitative, indication of the components of a solution. Plates 20 cm. high are convenient. They should be coated with silica gel (with or without calcium sulfate binder). Three samples can be analyzed on a 5-cm.-wide plate. A small drop of eluate solution is applied to the plate from a melting-point capillary or a hypodermic syringe in small drops. The size of drop and concentration do not, within reason, matter. Multiple spotting

TABLE I

Imide	Infrared spectrum		Melting point	Solubility in CS_2 at 18° (molal)	R_f	
	N-H region, cm.$^{-1}$	S-N region, cm.$^{-1}$			S_8 at solvent front	S_8 at R_f = 0.73
S_7NH	3332	807	113.5°	0.57	0.58	0.50
1,4-$S_6(NH)_2$	3330	820 780	133°	0.15	0.34	0.30
1,5-$S_6(NH)_2$	3330	814	155° (decomp.)	0.023	0.24	0.21
1,3-$S_6(NH)_2$	3335	777 836	130° (decomp.)	0.038	0.22	0.17
1,3,6-$S_5(NH)_3$	3332	831 810.5	133° (decomp.)	0.049	0.16	0.12
1,3,5-$S_5(NH)_3$	3336	842 820.5	128° (decomp.)	0.008	0.09	0.04

will be necessary, beginning with the 1,3-diimides. The plate is developed with carbon disulfide, and sprayed with 0.1-*M* silver nitrate solution, which makes sulfur and all the imides visible as gray-to-black spots. Typical spot patterns are shown in Fig. 16. The exact R_f values depend upon conditions, but the order and relative spacings of the spots do not. A reference sample of sulfur may be desirable to prevent its being mistaken for S_7NH; the other components are easily recognized unless the spots are larger than 5 mm. when spotted, or unless the plates are overloaded.

The infrared spectra of carbon disulfide solutions of the imides can be used for the qualitative and quantitative analysis of solutions and mixtures. See Table I.

Properties

The cyclic sulfur imides are odorless, nearly colorless solids. All are well crystallized; the 1,3,5-triimide appears as fine needles, whereas all the others are orthorhombic crystals (although some of the diimides may crystallize as blunt needles). The 1,4-diimide darkens to an orange color in a few hours when exposed to both air and light, but keeps well in darkness. The others can be stored in diffuse light in moist air for weeks to months without noticeable decomposition. They are all insoluble in, and unaffected by, water. Their toxicity has not been investigated, but nothing has happened to suggest any risk of poisoning when they are handled with ordinary care.

Table I, showing the imides in order of elution from the chromatographic column, is a summary of useful physical data. The infrared spectral data refer to carbon disulfide solutions.

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39. NITROSYL HALIDES

$$2NO_2 + KX = XNO + KNO_3 (X = F, Cl, Br)$$

Submitted by CHARLES T. RATCLIFFE* and JEAN'NE M. SHREEVE*
Checked by KENNETH J. WYNNE†

The synthesis of nitrosyl fluoride has been previously carried out by burning nitric oxide and fluorine at low temperatures in a

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fluorothene vessel.[1] Other methods include the decomposition of various nitrosyl adducts.[2] In the present method, nitrogen dioxide is allowed to react at room temperature with an excess of potassium fluoride to produce nitrosyl fluoride, in nearly quantitative yields, as the only volatile product.[3] The rate of formation of nitrosyl fluoride may be dramatically increased by first forming a potassium fluoride–hexafluoroacetone adduct which is subsequently thermally decomposed to yield potassium fluoride having a high surface area.

Nitrosyl chloride can be obtained by direct combination of chlorine with nitric oxide, by the reaction of $NOHSO_4$[4] or $NaNO_2$[5] with HCl, or as a by-product in the preparation of KNO_3 from KCl and NO_2,[6] in which KCl is moistened with 2.4% water. Nitrosyl bromide is usually prepared by direct combination of bromine with nitric oxide. Nitrosyl chloride and nitrosyl bromide can be prepared by reacting the appropriate potassium halide with nitrogen dioxide at room temperature. The reaction rate increases with increased size of the halide, and NOCl and NOBr can be obtained in a reasonable length of time by powdering the halide salt before adding NO_2.

Storage of nitrosyl fluoride in the glass reaction vessel containing KF is possible for a few days; however, the use of an inert-metal vessel containing anhydrous KF is preferred for an extended period of time. Nitrosyl chloride is stable at room temperature but will always contain a small amount of NO and Cl_2 because of its reversible decomposition of 0.5%. The reversible decomposition of nitrosyl bromide is appreciable enough at room temperature (7%) to require storage at a lower temperature, or the gas can be prepared immediately prior to use.[7]

Nitrosyl fluoride is useful in the preparation of trifluoroamine oxide, F_3NO,[8,9] and for storing many volatile Lewis acids as stable solid adducts.[10] Nitrosyl chloride tends to form addition compounds with metal chlorides. The nitrosyl halides are powerful oxidizing agents and are good nitrosylating agents.

Procedure

■ **Caution.** *Potassium fluoride, hexafluoroacetone,* and the nitrosyl halides are all reactive toward water. Therefore the preparation and storage of the nitrosyl halides require anhydrous conditions.*

In the following procedures a standard glass vacuum line with high-vacuum stopcocks (greased with Kel-F grease) and mercury manometer† is used. A −195° cold trap is placed between the vacuum line and the forepump, which has an operating vacuum of about 10^{-4} mm.

A. NITROSYL FLUORIDE

1. Via Potassium Fluorode Treated with Hexafluoroacetone

Anhydrous potassium fluoride can be purchased‡ or prepared from $KF{\cdot}2H_2O$ crystals of the dihydrate by slowly heating the salt to 450° for 6 hours, then powdering with a mortar and pestle, and reheating at 450° for 2 hours. The salt is then stored under vacuum until needed. Five grams of powdered anhydrous KF is added to a 50-ml. glass vessel equipped with a 19/38 joint and a vacuum stopcock. Two milliliters of acetonitrile (dried over calcium hydride) and 0.002 mole of hexafluoroacetone are added to the vessel under vacuum conditions, with occasional shaking to allow the gas to react with the salt-solvent mixture. Reaction of the hexafluoroacetone with the metal fluoride is usually complete in about 2 hours with shaking, as noted by a decrease in the vapor pressure within the vessel,

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* Obtainable from Columbia Organic Chemicals, Columbia, S.C.

† Because of the reactivity of the reagents and products, the use of the mercury manometer is limited to the measuring of hexafluoroacetone.

‡ Baker and Adamson, Morristown, N.J. The commercial material should be dried for 6–15 hrs. at 240°, powdered with a warm mortar and pestle, and reheated to 240° for several hours.

but the mixture can be allowed to sit overnight for complete reaction:

$$KF + CF_3COCF_3 \xrightarrow{CH_3CN} KOCF(CF_3)_2 \xrightarrow{100^\circ} KF + CF_3COCF_3 + CH_3CN$$

Most of the solvent is removed by pumping at ambient temperature. Then cleavage of the salt-acetone adduct and removal of the remaining solvent are carried out at 100° while pumping for 2 hours. A −195° cold trap is placed on the vacuum line to allow collection of the volatile materials for reuse in preparing more salt. This procedure allows the salt to be coated on the walls of the vessel in a finely divided state as the volatile acetonitrile and hexafluoroacetone are removed.[11]

Nitrogen dioxide* (0.002 mole) is condensed into the reaction vessel at −78°. After the vessel has warmed to room temperature, it will contain the colorless gas FNO in 95–100% yield based on the NO_2 added. The product may then be removed without purification, and more NO_2 condensed into the vessel. The procedure may be repeated. However, as less unreacted metal fluoride is exposed to the reacting NO_2, the reaction time usually increases. In order to remove the brown NO_2 color completely, it may be necessary to cool (−78 or −196°) and warm (25°) the reaction vessel several times. The reaction may be scaled to the amount of FNO needed by allowing more hexafluoroacetone to react with the metal salt. There does not seem to be a sharp correlation between the amount of FNO that can be prepared and the amount of hexafluoroacetone used in preparing the salt. As more NO_2 is added to the salt, the mixture will usually contain brown gas upon warming and react to give the colorless gas in about 5 minutes. As repeated aliquots of NO_2 are added, the mixture finally requires heating to allow complete reaction in a reasonable amount of time. Heating

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* Obtainable from the Matheson Co., East Rutherford, N.J.

the mixture above 90° enhances the attack of the glass by the FNO and gives an impure product.

When an incomplete reaction occurs, it is preferable to remove the volatile FNO while the vessel is held at −78°, leaving the unreacted N_2O_4 condensed in the vessel. Nitric oxide may be found in the FNO stored in glass over KF at room temperature if traces of water are present. Nitric oxide may be removed from the FNO by pumping on the vessel cooled to −140 to −196°. Any silicon tetrafluoride which may be formed is absorbed by the potassium fluoride.

2. Via Powdered Potassium Fluoride

The activation process described in the preceding discussion allows the reaction to go immediately at room temperature. With proper powdering and drying, the reaction will go to completion at room temperature without hexafluoroacetone treatment of the salt. However, the reaction time varies from 1 to 5 days, depending upon the condition of the salt, and a metal reaction vessel is required. Five grams of KF is dried at 450° for 6 hours, powdered thoroughly while the salt is still hot, and reheated to 450° for 5 hours. The hot salt is then added to a prefluorinated 75-ml. stainless or Monel vessel equipped with a removable stainless valve and containing steel roller bearings. The vessel is immediately evacuated and again heated under vacuum for a few hours. The salt is further powdered by either shaking or rolling the vessel for 3 or 4 hours.

The metal reaction vessel containing the powdered salt is cooled to −78°, and 0.004 mole of NO_2 is added under vacuum conditions. The metal vessel is then allowed to stand at room temperature for 12 hours. A sample of the gas can then be checked for completeness of reaction by infrared analysis or by observing the color of the product gas. If the reaction is not complete, the prepared FNO can be removed at −78° from the NO_2 condensed in the vessel; however, total reaction is necessary to ensure a pure product. Heating the metal vessel increases the reaction rate. Above 300° reaction with the metal vessel ensues, and the yield is diminished.

B. NITROSYL CHLORIDE AND NITROSYL BROMIDE

The increased reaction rate for NO_2 with KCl and KBr allows less rigorous treatment of the salt prior to reaction. It is preferable to carry out the reaction a short time before the product is needed. Five grams of KCl is dried at 300° for 3 hours, powdered with a mortar and pestle, and added to a 50-ml. glass vessel as described previously. The vessel is evacuated, and 0.002 mole of NO_2 is added under vacuum conditions. The reaction goes to completion within 12–36 hours. The reaction may be followed by the disappearance of the characteristic red-brown color of NO_2 and the appearance of the light yellow color associated with NOCl. The product can be used directly from the reaction vessel. The yield is essentially quantitative.

Potassium bromide is prepared in the same manner as described for KCl. The addition of 0.002 mole of NO_2 to the reaction vessel allows essentially complete reaction to occur within 30 minutes. The yield is generally greater than 90%. The product obtained is a red-colored gas similar in appearance to NO_2. Nitrosyl bromide undergoes reversible decomposition at room temperature to the extent of about 7%. The presence of the excess KBr does not appear to affect this equilibrium.

When NO_2 and KI are allowed to react at room temperature, the only volatile products observed are NO and I_2. It has not been possible to isolate successfully a product identifiable as NOI.

Properties

Nitrosyl fluoride is colorless; it melts at $-132.5°$ and boils at $-59.9°$. Its vapor pressures at -88.8 and $-79.2°$ are 100 and

200 mm., respectively. It is readily converted to HF and HNO_2 on contact with water. However, at room temperature, the dry gas attacks glass only slowly. Its purity can be checked by its infrared spectrum.[12] Bands are observed at the following frequencies ($cm.^{-1}$): 2365(m), 1844(vs, doublet), 1290(m), 765.9(vs, triplet).

Nitrosyl chloride is an orange-yellow gas at room temperature and a deep red liquid when condensed. Its boiling point is −6.4° with vapor pressures at −46.3 and −34.0° of 100 and 200 mm., respectively. Nitrosyl chloride reacts readily with water to form HNO_2, HNO_3, NO, and HCl. Infrared absorption bands occur at the following frequencies[13] ($cm.^{-1}$): 3568(m), 2395(m), 2131(m), 1799(vs), 923(m).

Nitrosyl bromide is red in color and has a boiling point of about 0°. It also reacts readily with water, analogously to NOCl.[3] Infrared absorption occurs at the following frequencies[13] ($cm.^{-1}$): 3567(m), 2066(m), 1801(vs), 807(m).

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40. TRIMERIC PHENYLPHOSPHONITRILE BROMIDES

(1,3,5-Tribromo-1,3,5-triphenylcyclotriphosphazatrienes; 2,4,6-Tribromo-2,4,6-triphenyl-2,2,4,4,6,6-hexahydro-1,3,5,2,4,6-triazatriphosphorines)

$$3P(C_6H_5)Br_2 + 3Br_2 + 3NH_4Br \rightarrow [NP(C_6H_5)Br]_3 + 12HBr$$

Submitted by **PIERO NANNELLI,* SHU-KUNG CHU,† BALDEV MANHAS,‡ and THERALD MOELLER§**
Checked by **ROBERT L. McKENNEY, JR.¶**

Partial ammonolysis of phosphorus(V) chloride or bromide and of monoalkyl- or -aryl-substituted dichloro- or dibromophosphines in the presence of chlorine or bromine is a general method for the synthesis, respectively, of the corresponding simple or substituted phosphonitrile halides.[1–6] This type of reaction may yield either cyclic or linear polymers, depending upon the temperature, solvent, reaction time, and/or reagent ratio.

Specifically, the reaction involving phenyldibromophosphine, bromine, and ammonium bromide in *sym*-tetrabromoethane gives a mixture of the cis and trans isomers of cyclic trimeric phenylphosphonitrile bromide, various isomers of the corresponding cyclic tetramer, and some of the oily higher homologs.[5] However, the procedure is both experimentally difficult and very time-consuming. Substitution of bromobenzene for *sym*-tetrabromoethane reduces the reaction time and gives products that are more readily handled. Under these conditions, the trans isomer of trimeric phenylphosphonitrile

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bromide is the only product obtainable in substantial quantity. The cis isomer can be obtained by recrystallizing the crude trans compound from acetonitrile.

Procedure

Three hundred grams (3.06 moles) of ammonium bromide, which has been ground to 100–150 mesh and dried for 2 days at 110°, and 400 ml. of dry bromobenzene* are mixed in a 1-l. three-necked flask fitted with a mechanical stirrer, a dropping funnel with a sidearm connected to the flask, and an efficient reflux condenser provided with a drying tube containing calcium chloride. One hundred fifty grams (0.56 mole) of phenyldibromophosphine,[7] dissolved in *ca.* 50 ml. of bromobenzene, is added to the well-stirred mixture. Then a solution of 90 g. (0.56 mole) of dry bromine† in 50 ml. of the same solvent is added drop by drop with stirring. The bromine addition is carried out intermittently over a period of *ca.* 10 hours to allow the solid, which separates in the vigorous reaction that occurs as the bromine is added, to dissolve periodically. Hydrogen bromide is evolved; therefore the reaction should be carried out in a well-ventilated hood.

The reaction flask is then placed in an oil bath, the temperature of which is raised to 170–180° over a 3- to 4-hour period. The reaction mixture is stirred at this temperature until the evolution of hydrogen bromide ceases (24–48 hours). The unreacted ammonium bromide is removed by filtration through sintered glass while the mixture is still hot, and washed with a few milliliters of fresh dry bromobenzene. The combined filtrate and washings are transferred to a 1-l. single-necked flask arranged for vacuum distillation and placed in an oil bath. An

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* Drying over Linde 4-A molecular sieves is satisfactory.

† Bromine may be dried by cautiously shaking with concentrated sulfuric acid in a separatory funnel.

oil pump is attached, and the solvent is removed at 3.5 mm. of mercury while the bath temperature is gradually raised to 90°.*

The dark viscous residue is extracted in the flask with five successive 300-ml. volumes of boiling dry *n*-heptane.† Each extract is stored separately in a refrigerator at *ca.* 3°. On standing, these solutions deposit crude crystalline product and, possibly, an oily material that slowly solidifies under *n*-heptane. Complete crystallization may require scratching the inner walls of the containers and storage for a week.

Purification of the combined crude product is effected by two to three recrystallizations from *n*-heptane, with activated charcoal added initially to remove color. Dissolution in *n*-heptane is slow and requires both boiling with two to three times the volume of solvent required to dissolve the material from the original mother liquor and manual stirring to break up lumps. Recrystallization is also slow and requires storage of the solutions for 2–3 days in a refrigerator. The product obtained melts at *ca.* 145° and is, substantially, a mixture of the two crystalline modifications of the trans isomer. Yield, based upon phenyldibromophosphine, 39 g. (34.5%). *Anal.* Calcd. for $[NP(C_6H_5)Br]_3$: C, 35.67; H, 2.49; N, 6.93; P, 15.33; Br, 39.57; mol. wt., 606. Found: C, 35.97; H, 2.47; N, 6.94; P, 15.25; Br, 39.31; mol. wt., 621.

Careful recrystallization from *n*-heptane may permit separation of crystals of the two modifications by hand picking—m.p. 152–153°, triclinic, block-type crystals; m.p. 162–163°, unidentified crystal system, needlelike crystals, usually in clusters. The pure cis isomer is obtained by dissolving the trans mixture

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* The receiver should be cooled with a Dry Ice–acetone mixture, and the traps in the vacuum line cooled with liquid nitrogen.

† Each extraction requires 3–4 minutes of refluxing with frequent shaking. Excessively long refluxing causes dissolution of oily materials that separate in subsequent purification steps.

The final residue in the flask can be extracted with *ca.* 100 ml. of boiling toluene to give a solution which, when allowed to stand in a refrigerator, may deposit up to 1 g. of a mixture of isomers of the crude tetramer, m.p. 205°.

in a minimum quantity of hot acetonitrile, allowing the solution to crystallize for several days in a refrigerator, and recrystallizing from boiling *n*-heptane. The beautifully crystalline product melts at 194–195°. (A second recrystallization from *n*-heptane may be necessary in order to achieve product of this purity.) *Anal.* Found: C, 35.74; H, 2.53; N, 6.87; P, 15.30; Br, 39.59; mol. wt., 622.

Properties

The cis isomer of trimeric phenylphosphonitrile bromide is a colorless crystalline compound, melting at 194–195° (uncorrected). The trans isomer exists in two distinct crystalline forms which melt, respectively, at 152–153 and 162–163° (both uncorrected) and have different x-ray diffraction powder patterns.[5] The ^{31}P nuclear magnetic resonance spectrum of the cis isomer has a single peak (-16.4 p.p.m. vs. 85% aqueous orthophosphoric acid), indicating only one phosphorus atom environment, whereas that of the trans isomer (m.p. 152–153°) has two peaks (-20.1 and -18.0 p.p.m.) in the area ratio 1:2, indicating two phosphorus atom environments.[5] The infrared spectra of the two isomers are similar. The dipole moments are 5.27 and 2.36 D. for the cis and trans compounds, respectively.[5] Recrystallization from acetonitrile converts the trans to the cis isomer if the trans material is slightly impure (slight yellow color in solution). Otherwise, the lower-melting trans compound is formed. Recrystallization from bromobenzene effects partial conversion of the cis isomer to the trans. Both cis and trans isomers are moderately soluble in cold benzene, ethyl ether, and carbon tetrachloride, but only slightly soluble in cold petroleum ether or *n*-heptane.

Both isomers undergo ready nucleophilic displacement of bromine atoms.[5]

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41. XENON TRIOXIDE SOLUTION

$$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$$

Submitted by **EVAN H. APPELMAN***
Checked by **STANLEY M. WILLIAMSON†**

The xenon hexafluoride for this synthesis is best prepared by reaction of xenon with an excess of fluorine at 300° in a nickel or Monel apparatus.[1] Extremely pure XeF_6 is not required. Xenon hexafluoride attacks glass, and should be stored in a nickel or Monel container until ready for use. The hydrolysis reaction is violent, and if more than a hundred milligrams of XeF_6 is to be hydrolyzed, special safety precautions must be taken. Face shields, heavy gloves, and a sturdy plastic explosion barrier between the hydrolysis apparatus and the experimenter are strongly recommended. No more than about 3 g. of XeF_6 should be hydrolyzed in one batch.

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In this procedure, magnesium oxide is used to remove the hydrofluoric acid formed in the hydrolysis. Hydrous zirconium phosphate is then used to remove the resulting magnesium ion, and hydrous zirconium oxide is used to remove the last trace of fluoride, as well as any phosphoric acid resulting from hydrolysis of the zirconium phosphate.

Xenon trioxide may also be prepared by hydrolysis of xenon tetrafluoride, but in that case the yield cannot exceed 33%.[2] ■ **Caution.** *Great care must be taken to avoid the formation of anhydrous xenon trioxide, which is highly explosive. Anybody intending to carry out this synthesis should first familiarize himself with the pertinent literature*[1,2] *and the admonition given under* Properties. *He should then follow the directions exactly.*

Procedure

The hydrolysis vessel is the 100-ml. Pyrex bulb shown in Fig. 17. The bulb is attached to a metal vacuum line and evacuated. The very bottom of the bulb is then cooled in liquid nitrogen, and about 3 g. of XeF_6 is distilled into the bulb. Then the entire body of the bulb is cooled in liquid nitrogen, and the bulb is detached from the metal vacuum line by sealing off at the constriction. While still immersed in the liquid-nitrogen bath, the bulb is removed to a protected location.

A glass-covered iron breaker is placed above the breakseal, and the semi-ball joint is connected to a separatory funnel fitted with a Teflon stopcock and containing 30 ml. of water. The joint should not be greased, but only wetted to make a good seal. After the breakseal is broken, the water is carefully drawn into the bulb. When all the water has been added, the bulb is removed from the liquid nitrogen and allowed to thaw. ■ **Caution.** *Appropriate precautions must be observed, for a serious explosion may take place at any time after the addition of the water has begun and before thawing is complete.* If the xenon hexafluoride contains appreciable amounts of the lower xenon

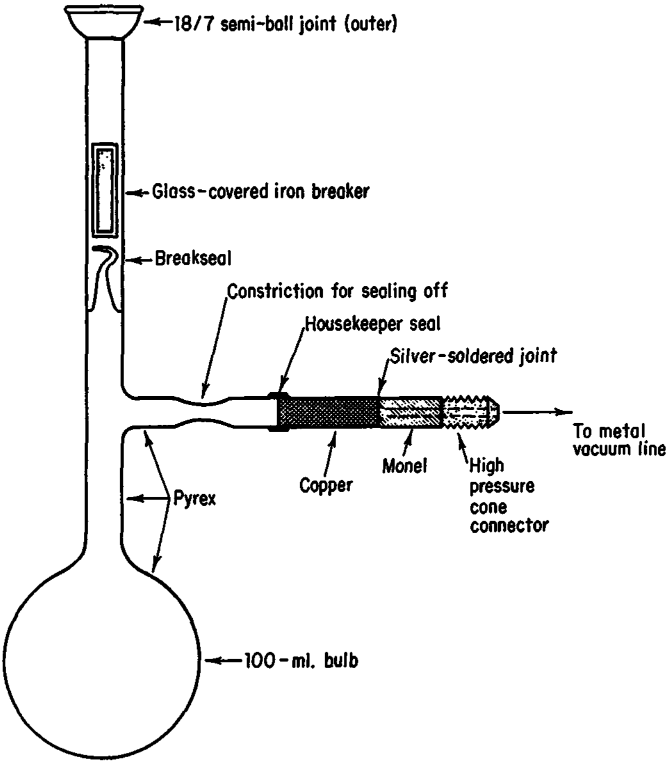

Fig. 17. Hydrolysis bulb. The ⅜ × ⅛-in. high-pressure cone fittings were obtained from Autoclave Engineers, Inc., Erie, Pa. However, many other common methods of connection to the metal vacuum line should be equally satisfactory.

fluorides, a yellow color will appear in the solid during the thawing, but this will not interfere with the hydrolysis. The thawed solution may be removed from the bulb by breaking off the neck below the breakseal.

The procedure is repeated with four more 3-g. portions of xenon hexafluoride, and the solutions are combined. Twenty grams of MgO is added, and the mixture is swirled until a drop of the solution phase tests slightly alkaline to indicator paper. The slurry is centrifuged, and the supernatant liquid is filtered through a sintered-glass filter of medium porosity. The solid residue is washed with successive portions of water until the filtered washings are less than 0.005 *M* in XeO_3, as determined by adding iodide and acid and titrating with thiosulfate.[2] About 350 ml. of wash water will be needed. The first 50 ml. of washings should be combined with the original filtrate; the remainder should be kept separate as a dilute XeO_3 fraction.

A chromatographic column of about 2 cm. i.d. is packed to a height of about 8 cm. with 50- to 100-mesh hydrous zirconium phosphate,* from which all fine powder has been removed by fractional settling in water. Another such column is packed in the same way with hydrous zirconium oxide,* from which fine powder has similarly been removed. The bottom of each column should contain a plug of glass wool supported on a coarse sintered-glass frit. Beneath the frit should be a stopcock with a Teflon plug. The zirconium phosphate is washed with about 400 ml. 4 *M* nitric acid.† The oxide is washed with 0.1 *M* nitric acid until washings give no turbidity with silver nitrate (10 l. or more of wash may be required).† Both columns are washed with water until the washings have a pH of 3 or greater. About 2 l. of water will be needed to wash the oxide column, while around 200 ml. will suffice for the phosphate. The filtered hydrolysis product is passed first through the phosphate, then through the oxide column. To avoid diluting the product with the wash solution that precedes the XeO_3 from the columns, the effluent is collected in a flask containing an acidified iodide solution until a drop of effluent darkens the iodide. Two 20-ml. portions of the dilute XeO_3 fraction obtained by washing the magnesium oxide are passed through the two columns in suc-

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* Hydrous zirconium oxide and phosphate may be obtained from Bio-Rad Laboratories, Richmond, Calif. As ordinarily supplied, the oxide is severely contaminated with chloride, but at a modest extra cost, Bio-Rad will provide oxide in the "nitrate form" from which most of the chloride has been leached with 0.1 *M* nitric acid. This is the material that has been used, but even it requires exhaustive washing to remove the last traces of chloride.

† Perchloric acid may be substituted for nitric.

cession and are combined with the original effluent to obtain a solution *ca.* 0.2 *M* in XeO_3, containing about 70% of the original xenon.

The rest of the XeO_3 may be obtained as a dilute solution (*ca.* 0.05 *M*) by passing the remainder of the washings of the MgO through the two columns in succession and then passing about 75 ml. of water successively through the columns. The only significant impurity in these solutions is nitric acid, present at concentrations around 0.005 *M*.

The XeO_3 solutions may be concentrated by distilling away the water under vacuum at room temperature. This may be done either on a vacuum line or over a desiccant in a vacuum desiccator. Solutions 2 *M* in XeO_3 may easily be prepared in this way, but extreme care must be taken not to reach dryness (*vide infra*).

The zirconium oxide cannot be regenerated, and should be discarded after use. The zirconium phosphate may be regenerated by passing through it about 400 ml. of 4 *M* nitric acid or perchloric acid and washing away the excess acid with water, as in the preparation of fresh material. After several cycles or prolonged standing, however, the phosphate will become pasty, and it must then be replaced.

Properties[2]

Slightly acidic aqueous solutions of XeO_3 are quite stable. However, in the presence of light a small amount of ozone is slowly generated, and for utmost stability the solutions should be stored in the dark. The solutions are strongly oxidizing and should be kept away from reducing materials. ■ ***Caution.*** *Anhydrous xenon trioxide is highly explosive, and solutions of the oxide must not be allowed to dry out except under carefully controlled conditions.* For example, care should be taken not to allow a solution to dry out in the neck or on the ground stopper of a volumetric flask. Twisting the stopper can cause the explosion of material dried there. Teflon stoppers are preferable; they may be obtained from Scientific Glass Apparatus Co., Bloomfield, N.J.

In acid or neutral solution the xenon is present as discrete XeO_3 molecules. In basic solutions a negative ion, $HXeO_4^-$, is formed. In neutral or alkaline solutions the XeO_3 slowly decomposes to xenon and oxygen. In strong base disproportionation takes place to produce perxenates, salts of xenon(VIII).

A xenon trioxide solution may be conveniently analyzed by adding iodide and dilute perchloric or sulfuric acid, and then titrating the liberated triiodide with thiosulfate. The net reaction is:

$$XeO_3 + 9I^- + 6H^+ \rightarrow Xe + 3I_3^- + 3H_2O$$

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42. SODIUM PERXENATE

[*Sodium Xenate(VIII)*]

$$HXeO_4^- + O_3 + 4Na^+ + 3OH^- + (x - 2)H_2O \rightarrow Na_4XeO_6 \cdot xH_2O(s) + O_2$$

Submitted by EVAN H. APPELMAN*
Checked by STANLEY M. WILLIAMSON†

In this procedure, sodium perxenate is precipitated from 1–2 *M* sodium hydroxide, presumably in accordance with the above equation. The actual stoichiometry with respect to ozone has

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not been determined, because ozone is very unstable in the alkaline solutions used. The ozone may be conveniently produced by using a conventional silent-discharge-type ozone generator.[1] The $HXeO_4^-$ ion is obtained by adding base to a xenon trioxide solution, the preparation of which is described in the preceding synthesis.

Freshly precipitated sodium perxenate has 2–8 waters of hydration per xenon.[2] Exhaustive drying at room temperature leaves *ca.* 0.6 water per xenon. In an earlier publication,[3] drying in vacuum at 110° was recommended to obtain the anhydrous product. This recommendation was based on thermogravimetric studies that indicated the complete loss of water at this temperature. More careful investigation has shown, however, that the loss of water is accompanied by loss of several percent of the xenon, leaving a contaminating residue of sodium hydroxide. It therefore seems advisable to be content with the slightly hydrated product obtainable at room temperature.

Throughout the procedure, efforts should be made to minimize the uptake of carbon dioxide by the alkaline solution and the precipitated salt, in order to avoid contamination of the product by sodium carbonate.

Sodium perxenate may also be prepared without the use of ozone by allowing $HXeO_4^-$ to disproportionate in strong NaOH, but in that case the yield cannot exceed 50%.[2]

Procedure

A stream of ozonized oxygen is passed into 50 ml. of purified 0.2 *M* XeO_3 solution.[4] (■ ***Caution.*** *Ozone is extremely toxic. This operation must be performed in a good fume hood.*) While the ozone is bubbling through the solution, 5 ml. of CO_2-free 50% NaOH is added, and the introduction of ozone is continued until the yellow color of the supernatant solution is entirely discharged. The time required is dependent upon the ozone concentration, but a few hours generally suffices. The mixture is centrifuged, and the supernatant solution is discarded. The precipitate is washed with successive 5-ml. portions of water until the washes are distinctly yellow. The precipitate is then dried in a stream of pure dry nitrogen or argon. During the drying, the solid mass should be broken up from time to time with a glass stirring rod. When the solid appears dry, it is crushed gently in an agate mortar and then dried to constant weight in a vacuum desiccator containing solid sodium hydroxide and anhydrous magnesium perchlorate. The yield, based on the XeO_3 taken, is about 90%. *Anal.* Calcd. for $Na_4XeO_6 \cdot 0.6H_2O$: Na_2O, 37.5; XeO_4, 59.2; H_2O, 3.3. Found: Na_2O, 37.5 (from acid titer); XeO_4, 58.4 (from oxidizing power); H_2O, 3.1. The chief impurity consists of a few mole percent excess base, present principally as sodium carbonate.

Properties[2]

Sodium perxenate is stable at room temperature, but if left exposed to the air, it may absorb water and carbon dioxide. The salt is soluble in water to the extent of about 0.025 *M*, and the solutions are basic because of hydrolysis:

$$Na_4XeO_6(s) + H_2O \rightarrow HXeO_6^{3-} + OH^- + 4Na^+$$

In solution, the perxenate ion decomposes slowly to xenon(VI) and oxygen at a rate of about 0.5–1% per hour. The rate increases rapidly as the pH decreases, and the reaction becomes almost instantaneous below pH 7.

Solutions of sodium perxenate are very powerful oxidants, and accidental contact with reducing substances should be avoided. A frequent reaction product is xenon trioxide, the hazards of which are detailed in the preceding synthesis.[4]

Although a total analysis of sodium perxenate can be devised, two relatively simple analyses are generally sufficient to characterize the product:

1. Determination of the total oxidizing power gives the amount of Xe(VIII) and may best be effected by dissolving the perxenate in a sodium iodide solution, acidifying with dilute perchloric or sulfuric acid, and titrating the liberated triiodide with thiosulfate. The reaction proceeds according to the overall stoichiometry:

$$Na_4XeO_6(s) + 12I^- + 12H^+ \rightarrow Xe + 4I_3^- + 4Na^+ + 6H_2O$$

2. The amount of base present in the salt (the "Na_2O" content) may be determined by dissolving the perxenate in a measured excess of dilute perchloric or sulfuric acid and back-titrating with standard base. The net reaction is:

$$Na_4XeO_6(s) + 4H^+ \rightarrow XeO_3 + \tfrac{1}{2}O_2 + 4Na^+ + 2H_2O$$

The end point must be determined potentiometrically, because XeO_3 attacks most indicators.

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SUBJECT INDEX

The Subject Index for Volume XI begins a second cumulative index, which is planned to cover Volumes XI through XV. The names used in the index, as well as in the text, are based for the most part upon 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, Butterworths Scientific Publications, London, 1959; American version, *J. Am. Chem. Soc.*, **82**, 5523–5544 (1960); and also upon the following as yet unpublished rules: "Coordination Compounds" (Tentative Rules, IUPAC, 1965, when definitive to replace Section 7 of the 1957 Rules); "Tentative Rules for Nomenclature of Organometallic Compounds," IUPAC, 1967; "D-4 Nomenclature of Organosilicon Compounds," IUPAC, 1968; and "The Nomenclature of Boron Compounds" (Proposed Rules of the Committee on Inorganic Nomenclature, Division of Inorganic Chemistry, American Chemical Society, 1968). All of these rules have been approved by the ACS Committee on Nomenclature. Conformity with approved organic usage is also one of the aims of the nomenclature used here.

In line, to some extent, with *Chemical Abstracts* practice, more or less inverted forms are used for many entries, with the substituents or ligands given in alphabetical order (even though they may not be in the text); for example, derivatives of arsine, phosphine, silane, germane, and the like; organic compounds; metal alkyls, aryls, 1,3-diketone and other derivatives and specific neutral (nonelectrolyte) coordination complexes: *Iron, cyclopentadienyl-* (also at *Ferrocene*); *Cobalt(II), bis(2,4-pentanedionato)-* [instead of *Cobalt(II) acetylacetonate*]; *Rhodium(I),* trans-*carbonylchlorobis(triphenylphosphine)-*. In this way, or by the use of formulas, many entries beginning with numerical prefixes are avoided (as for halo, cyano, and a few other complexes); thus, *Chlorovanadate(III), tetra-*. Numerical and some other prefixes are also avoided by restricting entries to group headings where possible: *Sulfur imides*, with the formulas; *Molybdenum carbonyl*, $Mo(CO)_6$; both *Perxenate*, $HXeO_4^-$, and *Xenate(VIII)*, $HXeO_4^-$. In cases like the last, the cation has been omitted as of no significance in comparison with the emphasis given to the anion, e.g., also with less well-known complex anions: $CsB_{10}H_{12}CH$ is entered only as *Carbaundecaborate(1-), tridecahydro-* (and as $B_{10}CH_{13}^-$ in the Formula Index).

Under other general headings, such as *Cobalt(III) complexes* and *Ammines*, used for grouping coordination complexes of similar types having 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.

Two entries are made for compounds having two cations, and extra entries or cross references for synonyms. Unsatisfactory or special trivial names that have been retained for want of better ones or as synonyms are placed in quotation marks.

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 *Xenon fluorides,* are in lightface type unless all the formulas under them are boldfaced.

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. Stock Roman numerals and Ewen-Bassett Arabic numbers with charges are ignored in alphabetizing unless two or more names are otherwise the same. Footnotes are indicated by *n.* following the page number.

Inorganic Syntheses, Volume XI
Edited by William L. Jolly

FORMULA INDEX

The Formula Index for Volume XI, as well as the Subject Index, begins a second cumulative index. The chief aim of this index, like that of other formula indexes, is to help in locating specific compounds or ions, or even groups of compounds, that might not be easily found in the Subject Index, or in the case of many coordination complexes are to be found only as general entries 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 for a given formula.

Wherever it seemed best, formulas have been entered in their usual form (*i.e.*, as used in the text) for easy recognition: Si_2H_6, XeO_3, NOBr. However, for the less simple compounds, including coordination 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, as in the case of alkali and alkaline earth metals), or dropping it altogether: MnO_4Ba; $Mo(CN)_8K_2\cdot 2H_2O$; $Co(C_5H_7O_2)_3Na$; $B_{12}H_{12}^{2-}$. Where there is likely to be almost equal interest in two or more parts of a formula, two or more entries have been made: Fe_2O_4Ni and $NiFe_2O_4$; $NH(SO_2F)_2$, $(SO_2F)_2NH$, and $(FSO_2)_2NH$ (halogens other than fluorine are entered only under the other elements or groups in most cases); $[Co(NH_3)_6][FeCl_6]$ and $[FeCl_6][Co(NH_3)_6]$; $(B_{10}CH_{11})_2Ni^{2-}$ and $Ni(B_{10}CH_{11})_2^{2-}$.

Formulas for organic compounds are structural or semistructural so far as feasible: $CH_3COCH(NHCH_3)CH_3$. 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: only $Co(C_5H_7O_2)_2$, but $F_2(OF)_2C$ and $CF_2(OF)_2$. 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_5 (cyclopentadienyl), $C_5H_7O_2$ (2,4-pentanedionato). A few abbreviations for ligands used in the text are retained here for simplicity and are alphabetized as such: "en" (under "e") stands for ethylenediamine, "py" for pyridine, "pn" for 1,2-propanediamine (propylenediamine), "thd" for 2,2,6,6-tetramethylheptane-3,5-dionato, "DH" for dimethylglyoximato and "D" for the dianion, $(CH_3)_2C_2N_2O_2^{2-}$.

The formulas are listed alphabetically by atoms or by groups (considered as units) and then according to the number of each in turn in the formula rather than by total number of atoms of each element; this system results in arrangements such as the following:

NHS_7
$(NH)_2S_6$ (instead of $N_2H_2S_6$)
$NH_3B_{10}CH_{12}$

$[Mo(CO)_3C_5H_5]K$
$[Mo(CO)_3C_5H_5CH_3]$

FNO
$(FSO_2)_2NH$ (instead of $F_2S_2O_4NH$)
FSO_3H
F_2SO_3

$[Cr(en)_3][Ni(CN)_5]$ [instead of $(NH_2)_2C_2H_4$ or $N_2H_4C_2H_4$]
$[Cr(NH_3)_6][Ni(CN)_5]$

Footnotes are indicated by *n.* following the page number.