Inorganic Syntheses

Volume IX

Advisory Board

McGraw-Hill Book Company
New York San Francisco Toronto London Sydney

Inorganic Syntheses

Volume IX

Inorganic Syntheses

Volume IX

Advisory Board

McGraw-Hill Book Company
New York San Francisco Toronto London Sydney

INORGANIC SYNTHESES, VOLUME IX

Library of Congress Catalog Card Number 39-23015

65722

1234567890MP72106987

PREFACE

With the appearance of Volume IX, INORGANIC SYNTHESES announces a new publication policy. In the past, volumes of INORGANIC SYNTHESES have appeared at irregular intervals. Beginning with Volume IX, one volume will be published each year. Since it has always been difficult for the general chemical public to know just who is receiving manuscripts at a given time, a new position has been created, that of secretary to the Editorial Board. Unlike the position of editor-in-chief, which rotates with each new volume, the secretaryship is a nonrotating position. The major responsibilities of the secretary are to receive all submitted manuscripts and to forward them to the appropriate editor-in-chief. Thus, in the future, persons wishing to contribute manuscripts to INORGANIC SYNTHESES should send them to:

Professor Stanley Kirschner, Secretary
Inorganic Syntheses
Department of Chemistry
Wayne State University
Detroit, Michigan 48202

The editor-in-chief for Volume X is Dr. Earl L. Muetterties; for Volume XI is Dr. William L. Jolly; for Volume XII is Dr. Robert W. Parry; for Volume XIII is Dr. F. A. Cotton.

The present volume contains fifty contributions, a somewhat smaller number than customary. It is anticipated that future volumes will be composed of a similar number in light of the new publication policy. When the decision was made to have Volume IX appear within one year of

Volume VIII, it was decided not to include review articles, such as have been included in previous volumes. Most certainly, however, it should be reemphasized that our policy continues firm in having each synthesis checked experimentally in a laboratory different from that in which it originated. Furthermore, each synthesis has been reviewed by members of the Editorial and Advisory Boards and, after editing, has been sent to both submitter and checker for final approval.

The following new members of the Editorial Board have been elected since the publication of Volume VIII:

M. F. Hawthorne, University of California (Riverside)
George W. Parshall, E. I. du Pont de Nemours & Company
Roland Ward, University of Connecticut
Aaron Wold, Brown University

One person intimately connected with the present volume deserves special mention. Dr. Burl E. Bryant, of North Texas State University, and his students acted as checkers on three syntheses, and the thoroughness and dispatch with which they discharged their responsibility is rare in the experience of INORGANIC SYNTHESES. Unfortunately during the last stages of editing, word was received of Dr. Bryant's untimely death.

The editor-in-chief takes pleasure in expressing his appreciation to colleagues on the Editorial and Advisory Boards for their assistance in the preparation of Volume IX. Special thanks are due also to Miss Janet D. Scott for her careful checking of nomenclature on each synthesis. Most certainly the tireless efforts of Mrs. Diann Small in typing manuscript are appreciated. During the assembling of the final manuscript when the editor-in-chief was in residence in London, the coordinating services of Dr. Sally M. Horner proved indispensable.

S. Young Tyree, Jr.

NOTICE TO CONTRIBUTORS

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

There can be no rigid definition of what constitutes a suitable synthesis. Certainly a synthesis which presents a new or revised experimental procedure applicable to a variety of related compounds, at least one of which is critically important in current research, is eminently suitable. However, syntheses of individual compounds that are of interest or importance are also acceptable. The Editorial Board evaluates each procedure on its own merit. To aid in that evaluation, the Board applies the following general criteria for acceptability:

1. The procedure should be the best one available. Due consideration in making this judgment will be given to yield and purity of product, availability of starting materials, simplicity of the procedure, generality of the procedure, safety of the operations, and the importance and utility of the product.

2. Except under unusual circumstances, syntheses of compounds which are commercially available will not be accepted. If the product can be purchased, the author should provide justification for his procedure.

Authors should be guided in the preparation and submission of manuscripts by the following directions.

1. Each manuscript should be concisely written in English and in conformity with the style used in previous volumes of INORGANIC SYNTHESES. This style requires, in order, the name of the product as a title, equations summarizing the significant reactions in the experimental procedure, the names and affiliations of the authors, an introduction, a section on procedure, a discussion of the properties of the product, and a list of references.

2. Each manuscript should be typewritten, double spaced on $8\frac{1}{2}$- by 11-in. paper. All nomenclature should be consistent and unambiguous and should conform as closely as possible to "The Definitive Rules for Nomenclature of Inorganic Chemistry," *J. Am. Chem. Soc.*, **82,** 5523, 1960. Specific questions of nomenclature should be raised with the editor. Abbreviations should conform to those used in publications of the American Chemical Society, particularly *Inorganic Chemistry.*

3. Each manuscript should be submitted to the Secretary of the Editorial Board, Professor Stanley Kirschner, Department of Chemistry, Wayne State University, Detroit, Michigan, 48202, U.S.A.

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

The Editorial Board determines whether submitted syntheses meet the general specifications outlined above. Every synthesis which qualifies is submitted to a checker. The checker attempts to carry out the procedure as written, and is encouraged by the editor to criticize the procedure and the write-up, and to suggest useful modifications. In the event that a checker fails to reproduce a synthesis, the synthesis will be either rejected or submitted to another checker, at the discretion of the Editorial Board.

CONTENTS

CHAPTER I

CHAPTER II

CHAPTER III

CHAPTER IV

CHAPTER V

CHAPTER VI

CHAPTER VII

CHAPTER VIII

CHAPTER I

See: Niobium(V) chloride and hexachloroniobates(V), synthesis 23
Potassium fluorosulfite, synthesis 28
Tetrahalo complexes of dipositive metals in the first transition series, synthesis 36
Potassium tetranitrodiamminecobaltate(III), synthesis 45
Salts of dinitrodiglycinatocobaltate(III), synthesis 46

CHAPTER II

See also: Uranium(IV) acetate, synthesis 11
Metal iron(III) oxides, synthesis 40
Salts of dinitrodiglycinatocobaltate(III), synthesis 46

1. DICHLOROBIS(HYDROXYLAMINE)ZINC(II)

(Crismer's Salt)

$$2NH_2OH \cdot HCl + ZnO \rightarrow [Zn(NH_2OH)_2Cl_2] + H_2O$$

Submitted by John E. Walker* and David M. Howell*
Checked by Richard J. Thompson† and Billy C. Archibald†

Unsubstituted aliphatic monoximes can be produced[1,2] by treatment of an aldehyde or ketone in aqueous or alcoholic media with Crismer's salt, $[Zn(NH_2OH)_2Cl_2]$. The thermal decomposition of Crismer's salt *in vacuo* has been used to prepare pure hydroxylamine.[3] The following procedure, a rapid preparation producing a high yield of this complex, is a modification of a method first used by Crismer.[2]

Procedure

Caution. Thermogravimetric studies show that $[Zn(NH_2OH)_2Cl_2]$ *detonates at about 170°.*

Fifty grams (0.72 mol) of hydroxylammonium chloride is dissolved in 400 ml. of boiling ethanol with constant stir-

---

* Northeastern University, Boston, Mass.
† Texas Technological College, Lubbock, Tex.

ring. Then 25 g. (0.31 mol) of zinc oxide is added to the solution with constant stirring and with the solution maintained at the boiling temperature. As the last traces of zinc oxide dissolve, a precipitate begins to form. The solution is removed from the source of heat and allowed to cool overnight at room temperature. The precipitate is then filtered and washed with cold water. The yield is 50 g. (80%). *Anal.* Calcd.: Zn, 32.30; Cl, 35.08; N, 13.83. Found (by checkers): Zn, 32.27; Cl, 34.48; N, 14.6.

Properties

Crismer's salt is soluble in hot water and is slightly soluble in methanol and ethanol. It is insoluble in acetone, benzene, carbon tetrachloride, and petroleum ether. The white crystalline substance melts at 155 to 158° and exhibits a slight decomposition at 120°.

The infrared absorption spectrum of the compound in the NaCl region from 2 to 15 μ, using either KBr disk or Nujol mull technique, exhibits the following bands: 3110 (m), 2700 (m), 2370 (w), 1600 (m), 1560 (m), 1540 (m), 1410 (w), 1230 (m-w), 1170 (w), 990 (m), cm.$^{-1}$; (m = medium; w = weak).

References

1. P. Billon: *Ann. Chim. (Paris),* **7,** 314–332 (1927).
2. A. Crismer: *Bull. Soc. Chim.,* [3], **3,** 119 (1890).
3. *Idem., ibid.,* [3], **6,** 793 (1891).

CHAPTER III

See also: Diphenylbis(1-phenyl-1,3-butanedionato)tin(IV), synthesis 15

2. DIAMMINEDIHYDROBORON(1+) TETRAHYDROBORATE

(Diammoniate of Diborane)

$$4BF_3 + 3LiAlH_4 \xrightarrow{Et_2O} 2B_2H_6 + 3LiF + 3AlF_3$$
$$B_2H_6 + 2NH_3 \xrightarrow{\text{liq. } NH_3} [BH_2(NH_3)_2][BH_4]$$

SUBMITTED BY SHELDON G. SHORE,* KARL W. BODDEKER,* AND JO ANN PATTON*
CHECKED BY PAUL KUZNESOF† AND D. F. SHRIVER†

The diammoniate of diborane, which was first prepared by Stock and Kuss in 1923,[1] is formed as the sole reaction product on introduction of gaseous diborane, diluted with nitrogen, into liquid ammonia at −78°. While previous methods[2] allowed the preparation of only small amounts of the compound, scaling of the present procedure to yield practically any desired quantity appears to be possible. Of the several laboratory methods available for generating diborane,[3–5] a procedure adapted from the method of Shapiro and co-workers[3] is described below.

---

* The Ohio State University, Columbus, Ohio.
† Northwestern University, Evanston, Ill.

Procedure

Caution. Although the amount of free diborane present in the system at any given time is minimized in this synthesis, it should still be recognized that diborane is a flammable and toxic gas. This synthesis should be carried out in a hood, and due precaution should be taken to prevent leaks in the joints of the apparatus. A standard vacuum system and the apparatus shown in Fig. 1, consisting of diborane generator *A* and reaction vessel *B*, are employed. About 20 ml. of liquid ammonia, dried over sodium metal at −78°, is distilled into the evacuated reaction vessel, which is maintained at −78° (Dry Ice–isopropyl alcohol slush) through the reaction. After the diborane generator has been flushed thoroughly with dry nitrogen and the cooling jacket and trap have been filled with Dry Ice–isopropyl alcohol slush, 2 g. of powdered lithium tetrahydroaluminate* and 100 ml. of anhydrous

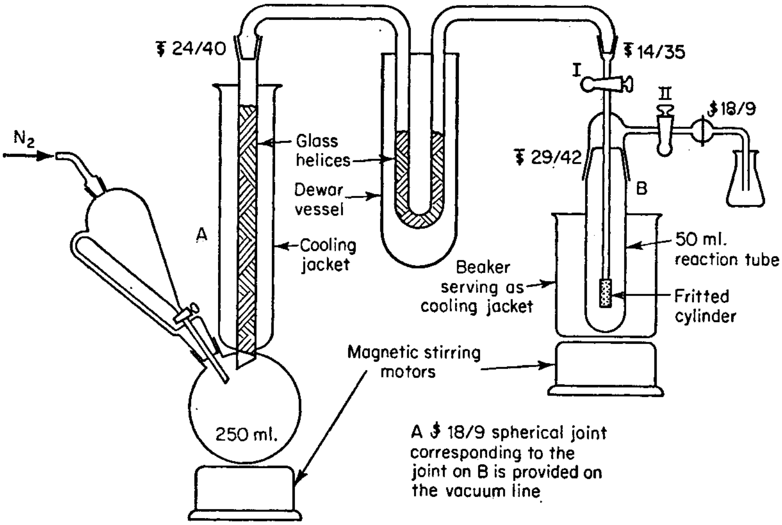

FIG. 1.

---

* By observing due caution, the hydride can be powdered quickly in an open hood. It should not be powdered by a grinding process. This compound is an incendiary substance.

ether, reagent grade, are introduced into the generator bulb; for this purpose the dropping funnel is temporarily removed. A quantity of 10 ml. of boron trifluoride–ether* (excess with respect to lithium tetrahydroaluminate) is poured into the dropping funnel, and the system is again flushed with nitrogen. It is necessary to interrupt the nitrogen flow in order to connect the reaction vessel to the diborane generator. After the connection has been made, the stopcocks on *B* are opened carefully. Stopcock I is opened first, while the nitrogen-cylinder valve is still closed. The resulting decrease in pressure in the system *must* be compensated with nitrogen by carefully reopening the valve before stopcock II is opened. Thereafter, the nitrogen gas flow is adjusted in such a way as to result in a moderate rate of bubbling through the mineral oil in the attached flask. Boron trifluoride–ether is then allowed to drop slowly into the stirred suspension of lithium tetrahydroaluminate in ether. For details of the reaction, reference 3 should be consulted. The rate of introduction of the etherate can be increased by cooling the diborane generator bulb to the ice point; this cooling is required when working on increased scales.† At the same time the liquid in the reaction vessel is stirred with a magnetic stirrer assembly. Half an hour after the last drop of etherate has been added to the diborane generator, the reaction vessel, with stopcocks closed, is placed in a Dewar flask containing liquid nitrogen in order to freeze the reaction solution. The vessel is then connected to the vacuum system, again surrounded by a Dry Ice bath, and the solvent ammonia is removed by vacuum sublimation, through the side arm of *B*, into a trap which is cooled by liquid nitrogen. The last

---

* Boron trifluoride–ether can be purified by distillation at normal pressure (b.p. around 125°). It deteriorates even under anhydrous conditions; however, as long as it does not appear excessively crude it may be used for this reaction.

† It is advisable to surround the generator bulb by a strong plastic bag, in order to avoid contact of the hydride with water in case of accidental breakage.

traces of ammonia are expelled by allowing the vessel to warm to room temperature while pumping through the cooled trap. The remaining solid, nonvolatile product is transferred into appropriate vials inside a dry-box.

The yield of diammoniate depends primarily on the amount and "active content" of the lithium tetrahydroaluminate, since both ammonia and boron trifluoride are used in excess. Using fresh samples of hydride from Metal Hydrides, Inc., Beverly, Mass., which are rated at 95+% $LiAlH_4$, a maximum yield of 97% was obtained.

Analysis

The diammoniate can be identified by means of its x-ray powder diffraction pattern[7] and by chemical analysis. For analysis a sample of the substance is hydrolyzed with 6 *N* hydrochloric acid for several hours at 90° in a previously evacuated and sealed tube, which is equipped with a breakable side arm allowing gas transfer into the vacuum system. Hydridic hydrogen is measured volumetrically; nitrogen and boron are determined by standard acid-base titrations. *Anal.* Calcd. for $[BH_2(NH_3)_2][BH_4]$: hydridic H, 9.80; B, 35.05; N, 45.35. Found: hydridic H, 9.74; B, 34.5; N, 45.7.

Properties

The diammoniate of diborane obtained by this process is a white, free-flowing, microcrystalline powder which is soluble in liquid ammonia. It is readily attacked by moisture. Even under rigorously anhydrous conditions, at room temperature, it undergoes slow self-decomposition accompanied by evolution of hydrogen, resulting in a pressure increase in storage vessels. Stored at −78°, however, it appears to be stable over long periods of time. Although it can be handled for short intervals in the open air, dry-box operations are to be preferred. Above 75° it decomposes rapidly *in vacuo.*

Reactions, structural arguments, and references to pertinent literature can be found in a series of consecutive papers, the last one of which is cited.[6]

References

1. A. Stock and E. Kuss: *Ber.*, **56B**, 807 (1923).
2. R. W. Parry and S. G. Shore: *J. Am. Chem. Soc.*, **80**, 15 (1958).
3. I. Shapiro et al.: *ibid.*, **74**, 901 (1952).
4. H. C. Brown and P. A. Tierney: *ibid.*, **80**, 1552 (1958).
5. R. O. Buttlar: doctoral dissertation, Indiana University, 1962; D. G. Gaines: *Inorg. Chem.*, **2**, 523 (1963).
6. R. C. Taylor, D. R. Schultz and A. R. Emery: *J. Am. Chem. Soc.*, **80**, 27 (1958).
7. S. G. Shore and K. W. Böddeker: *Inorg. Chem.*, **3**, 914 (1964).

3. TRIMETHYLAMINE-BORANE, (DIMETHYLAMINO)BORANE, AND *N,N′,N″*-TRIMETHYLBORAZINE

$$(CH_3)_3NHCl + NaBH_4 \rightarrow (CH_3)_3N{\cdot}BH_3 + NaCl + H_2$$
$$(CH_3)_2NH_2Cl + NaBH_4 \rightarrow (CH_3)_2NBH_2 + NaCl + 2H_2$$
$$3CH_3NH_3Cl + 3NaBH_4 \rightarrow N_3(CH_3)_3B_3H_3 + 3NaCl + 9H_2$$

Submitted by J. Bonham* and R. S. Drago*
Checked by B. F. Spielvogel,† J. A. Phillips,† and C. R. Payet†

Many variations[1–3] have been used in the preparation of borazines and boranes. The first convenient syntheses[4,5] utilized lithium tetrahydroborate and an amine hydrochloride in ether. An attempt was made to modify these procedures so that the above boron-nitrogen compounds

---

* University of Illinois, Urbana, Ill.
† University of North Carolina, Chapel Hill, N.C.

could be prepared from the reaction of sodium tetrahydroborate with the correspondingly substituted ammonium chloride using only routine laboratory equipment and techniques. Unlike the lithium salt, the more economical and convenient sodium tetrahydroborate is insoluble in ether. In tetrahydrofuran, however, it seems to be slightly soluble (*ca.* 0.3 to 0.5 *g*/100 ml.). For this reason tetrahydrofuran was to be used as the solvent for the entire series of reactions, but with it no trimethylborazine could be obtained. Di-*n*-hexyl ether was added[3] after the completion of the initial reaction, and the mixture was heated to the reflux temperature of the ether (*ca.* 220°) in an attempt to trimerize the monomer, but with no success. Two similar procedures,[6,7] essentially those of Haworth and Hohnstedt using triethylene glycol dimethyl ether (triglyme), were employed to prepare trimethylborazine from sodium tetrahydroborate. The tri- and dimethylamine derivatives were prepared in tetrahydrofuran.

Procedure

All reactions are carried out using dry reactants, solvents, and a nitrogen atmosphere. The reactants are dried in an oven at 110° and stored in a desiccator. Tetrahydrofuran is dried by allowing it to stand over potassium hydroxide, decanting, and distilling from lithium tetrahydroaluminate. Care should be exercised during the addition of the lithium tetrahydroaluminate because water may still be present in appreciable quantities. (The checkers suggest a less hazardous procedure for obtaining dry tetrahydrofuran by refluxing over calcium hydride for one hour and distilling the solvent from the calcium hydride under a nitrogen atmosphere.) The boiling point of tetrahydrofuran is 63°, and because of its tendency to form peroxides, it should be stored in a dark, tightly sealed bottle away from light. The triethylene glycol dimethyl ether is simply distilled (b.p.

222°) using the normal precautions observed when peroxides may be present and is stored in the same manner as tetrahydrofuran. The nitrogen is dried by passage through a sulfuric acid trap and a drying tower.

The apparatus used in each of the three syntheses consists of a three-necked 500-ml. flask fitted with a nitrogen inlet, condenser with drying tube attached, pressure-equalized dropping funnel (when needed), heating mantle, and magnetic stirrer. Any special additions and techniques are described under the separate preparations.

A. TRIMETHYLAMINE-BORANE

To a suspension of sodium tetrahydroborate (7.6 g.; 0.2 mol) in 125 ml. of anhydrous tetrahydrofuran, trimethylammonium chloride (9.5 g.; 0.1 mol) is added and the mixture is allowed to stir for 2 hours. A moderate evolution of hydrogen occurs. The reaction is then refluxed overnight. After filtering the mixture through a sintered-glass funnel *in vacuo* directly into a 200-ml. flask to remove the sodium chloride and excess sodium tetrahydroborate, the filtrate is concentrated in a rotatory evaporator (or simple Kjeldahl bulb and take-off) under aspirator vacuum. Ether and low-boiling petroleum ether may be added to assist in the removal of the tetrahydrofuran. A white solid is collected, which yields the trimethylamine-borane upon sublimation at 40 to 60 mm. pressure and 60 to 70°. The yield is 4.9 g. (67%), m.p. 93 to 95°; reported m.p. 93°, b.p. 171°. *Anal.* Calcd. for $(CH_3)_3N\cdot BH_3$: C, 49.45; H, 16.48; N, 19.22. Found: C, 49.55; H, 16.44; N, 19.04.

B. (DIMETHYLAMINO)BORANE

Dimethylammonium chloride (8.1 g.; 0.1 mol) is added to a stirred suspension of sodium tetrahydroborate (7.6 g.; 0.2 mol) in 125 ml. of tetrahydrofuran. A moderate evolution of hydrogen occurs. The reaction is stirred overnight