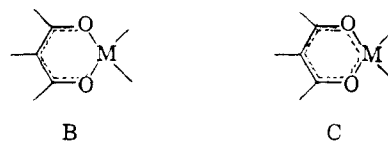


parent stability of the known halomethyl chelates A ($R_1, R_3 = \text{CH}_2\text{Br}, \text{CH}_2\text{I}$).

It is anticipated that should any ring cleavage occur in a reaction carried out in the presence of excess β -dicarbonyl compound, exchange should occur. Using C^{14} labelled 2,4-pentanedione and metal 2,4-pentanedionates in approximately equivalent amounts and adding enough N-bromosuccinimide to monobrominate both diketone and chelate, it was found that the exchange which occurred was less than or at most equal to the exchange which occurs in the absence of N-bromosuccinimide. It was shown thus that the reaction of N-bromosuccinimide in chloroform with the 2,4-pentanedionates of beryllium(II), aluminum(III) and chromium(III) proceeds essentially without additional exchange. However, in addition to route b (Table II) it is possible to obtain the same results by routes such as c (Table II) if it is assumed that halogenation of the chelate ring occurs very much faster than halogenation of the diketone and that the intermediate chromium complex formed by ring cleavage combines much more rapidly with the bromo diketone than the diketone. To eliminate this possibility, a competitive bromination was carried out in which essentially 1 equivalent each of 2,4-pentanedione and chromium(III) tris-(2,4-pentanedionate) were allowed to react with only one equivalent of N-bromosuccinimide. Approximately 55% of the available bromine appeared in the chelate indicating that the reaction rates are quite comparable. Thus, the bromination of chromium(III) tris-(2,4-pentanedionate) proceeds without any intermediate ring cleavage. Presumably, the other chelates react similarly.

The structure of β -dicarbonyl compounds has been assumed generally to be either the resonance stabilized form B or the aromatic system¹⁷ C. Evidence for the aromaticity of β -dicarbonyl chelates stems principally from the extraordinary stability, hydrolytic and/or thermal, of some of the

(17) R. H. Holm and F. A. Cotton, *THIS JOURNAL*, **80**, 5658 (1958).



members.^{18,19} Yet attempts to demonstrate this aromaticity conclusively have failed.^{17,20} Aromatization of these chelate rings would require the donation of non-bonding p -electrons on coordinated oxygen atoms to 3d, 4p, or 4d orbitals on the metal. Such an electron shift does not appear too probable in view of the formal negative charge already on the metal atom. The consequence of this electron shift toward the metal would be a decrease in electron charge on the remainder of the ring and a reduced tendency toward electrophilic substitution. This is not observed in the competition for bromine between equivalent quantities of 2,4-pentanedione and chromium(III) tris-(2,4-pentanedionate). In chloroform it has been estimated that 2,4-pentanedione exists as approximately 90% enol.²¹ If it assumed that the chromium chelate is 100% enolic, it would account for 53% of the enol in the system. The actual isolation of 55% of the bromine on the chelate is within experimental error and suggests that, assuming electrophilic substitution, little if any aromatic character exists. Likewise, the rate of exchange between 2,4-pentanedione and its metal chelates can be rationalized on the basis of charge/radius ratios²² and the availability of empty orbitals on the metal²³ and does not support any appreciable aromatic character.

(18) M. Calvin and K. W. Wilson, *ibid.*, **67**, 2003 (1945).

(19) W. Gerrard, M. F. Lappart and R. Shafferman, *Chem. and Ind. (London)*, 722 (1958).

(20) A. H. Maki and B. R. McCarvey, *J. Chem. Phys.*, **29**, 31 (1958).

(21) W. C. Fernelius, M. Shamma, L. A. Davis, D. E. Goldberg, B. B. Martin, D. F. Martin, F. D. Thomas, II, WADC Technical Report 56-203, part III.

(22) R. W. Taft, Jr., and E. H. Cook, *THIS JOURNAL*, **81**, 46 (1959).

(23) H. Taube, *Chem. Revs.*, **50**, 69 (1952).

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY, PROVIDENCE, RHODE ISLAND]

Ethane 1,2-Diamineborane

BY HENRY C. KELLY AND JOHN O. EDWARDS

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Ethylenediamine absorbs diborane in a 1:1 mole ratio to form a compound of empirical formula $(\text{CH}_2\text{NH}_2\text{BH}_3)_2$, named ethane 1,2-diamineborane. Preparation has been carried out by heterogeneous absorption of diborane by ethylenediamine in the high vacuum apparatus and by reaction of ethylenediamine with the tetrahydrofuran-borane complex. Chemical composition has been verified by molar ratio of reactants and chemical analysis. The compound, a white crystalline solid, is stable in air and undergoes decomposition when heated to 89°. On prolonged heating *in vacuo* at 90–110°, two moles of hydrogen are liberated per mole starting material. Ethane, 1,2-diamineborane is a highly selective reducing agent exhibiting a reactivity comparable to sodium borohydride. Reactions with various organic and inorganic reagents, solubility characteristics and possible structural assignments are discussed.

Introduction

Nitrogen derivatives of the boron hydrides have been known for a considerable length of time. Early work in this field is described by Stock,¹

(1) A. Stock, "Hydrides of Boron and Silicon," Cornell Univ. Press, Ithaca, N. Y., 1933.

who with co-workers prepared and studied various properties of the diammoniate of diborane.^{2–5}

(2) A. Stock and E. Kuss, *Ber.*, **56**, 789 (1923).

(3) A. Stock and E. Pohland, *ibid.*, **58**, 657 (1925).

(4) A. Stock and E. Pohland, *ibid.*, **59**, 2210 (1926).

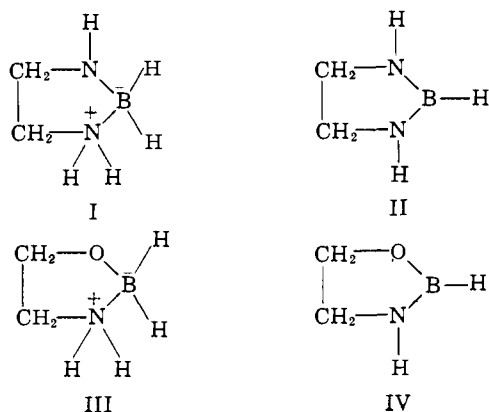
(5) A. Stock, E. Wiberg, H. Martini and A. Nicklas, *Z. Physik. Chem., Bodenstein-Festband*, **93** (1931).

During an investigation of the existence of borane (BH_3), Burg and Schlesinger⁶ prepared trimethylamineborane from trimethylamine and borane carbonyl. Investigations by Brown and Schlesinger^{7,8} on the relative basicities of pyridine, trimethylamine and other amines toward the BH_3 group aided in the development of steric strain theories in organic chemistry. An excellent review of the subject of borane chemistry is available through publications of Lappert⁹ and Stone.¹⁰

It seemed desirable at this time to undertake an investigation of the reactivity of diborane with certain organic difunctional reagents, notably ethylenediamine and ethanolamine. It was thought that these efforts would lead to synthesis of

compounds containing the $\text{R}-\text{N}:\text{BH}_3$ linkage with

possible cyclization to five membered ring compounds of the type



Although a ring system analogous to III has been observed in the preparation of aminoethylalkylarylborinates,^{11,12} compounds of this type having boron hydrogen bonds are unreported.

Diborane is a very reactive reducing agent, and the handling difficulties due to its toxicity, volatility and inflammability in air are obvious. Its compounds with amines, such as the adduct described here, retain some of the reducing properties while alleviating handling problems. This paper deals with the preparation and characterization of a new useful reagent from ethylenediamine and diborane. Ethane 1,2-diamineborane is a solid exhibiting good kinetic stability. It reduces acetone to isopropanol and acrolein and cinnamaldehyde to allyl and cinnamyl alcohol, respectively. Acetyl chloride is reduced to ethanol when the reaction is carried out in diglyme (diethylene glycol dimethyl ether); no reaction occurs in the absence of solvent. No reaction was observed

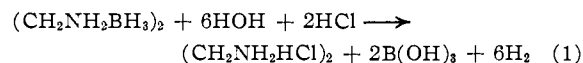
with ethyl anisate, ethyl acetate, acetonitrile, 1-nitropropane or benzalaniline. Inorganic reagents AgNO_3 and $\text{Cu}(\text{NO}_3)_2$ are reduced directly to the pure metal with no boride formation or contamination by oxides or other materials.

Experimental

(a) **Materials.**—Ethylenediamine (Eastman 98%) was dried by refluxing several hours over metallic sodium and distilled, b. $115.7\text{--}116.0^\circ$; lit. 116.1° .¹³ Boron fluoride diethyl ether complex was used as obtained from Eastman or vacuum distilled prior to use. Lithium Aluminum Hydride (95%) was obtained from Metal Hydrides Inc. Tetrahydrofuran (Matheson, Coleman and Bell) and diglyme (Eastman) were refluxed several hours with LiAlH_4 and distilled from LiAlH_4 . THF b. $65.3\text{--}65.7^\circ$; lit. $65\text{--}66^\circ$. Diglyme b. 161° ; lit. 162° . Anhydrous diethyl ether (Mallinckrodt) was stored over CaH_2 or used without further treatment. Diborane was prepared by the method of Finholt, *et al.*¹⁴ It was subjected to fractional condensation on the high vacuum apparatus until tensiometrically pure, v.p. at $-112^\circ = 225\text{ mm.}$; lit.¹⁶ $= 225\text{ mm.}$

(b) **Apparatus.**—A high vacuum apparatus of the type invented by Stock¹ and described in detail by Sanderson¹⁸ was employed for the reactions studied here.

(c) **Analytical.**—Active or hydridic hydrogen was determined by adding concentrated HCl to an aqueous slurry of a 0.1–0.2 g. sample of ethane 1,2-diamineborane contained in a small reaction flask. Hydrogen evolved according to the reaction



was calculated from the volume of water displaced from a one-liter bulb utilizing the relation $PV = nRT$. Active hydrogen was also determined by the iodate procedure of Jensen, *et al.*^{17,18} This method was modified only by adding large amounts of water to dissolve the sample. Results were slightly lower than those obtained by hydrolysis, e.g., a sample of $\text{En}(\text{BH}_3)_2$ gave %H (active) = 6.37, 6.39 (iodate); 6.64 (hydrolysis).

The composition of ethane 1,2-diamineborane was established by the following experiment. After hydrolysis of a sample of the solid, the pH of the hydrolysate was adjusted near 2.0 with concentrated NaOH . Titration with standard 0.1 N NaOH resulted in a curve such as shown in Fig. 1. Vertical line A represents neutralization of excess H_3O^+ . Mannitol was added at (B) causing a decrease in pH due to the increase in acidity of the boric acid complex. The solution was then titrated to the boric acid end-point (C). Further titration gave an inflection at (D), midpoint of line CE, which is the pK value for the first ionization constant of the ethylenediammonium ion.¹⁹ Line E represents the equivalence point of the first amine hydrochloride group. Horizontal distance (CE) is one-half the distance (AC) as demanded by the hydrolysis equation. Thus on a single sample one may determine hydridic hydrogen, boron, the presence of ethylenediamine dihydrochloride and one-half the quantity of amino nitrogen. These results (Fig. 1) substantiate the empirical formula $(\text{CH}_2\text{NH}_2\text{BH}_3)_2$.

(d) **Preparation and Stability.**—The reaction of diborane with ethylenediamine in the absence of solvents is highly exothermic. The following constitutes a typical vacuum line preparation. 0.64 g. (10.6 mmoles) ethylenediamine

(13) Handbook of Chemistry and Physics, 34th Ed., Chem. Rubber Publ. Co., Cleveland, Ohio, 1952.

(14) A. E. Finholt, A. G. Bond, K. E. Wilzbach and H. I. Schlesinger, *THIS JOURNAL*, **69**, 2692 (1947).

(15) H. E. Wirth and E. D. Palmer, *J. Phys. Chem.*, **60**, 911 (1956).

(16) R. T. Sanderson, "Vacuum Manipulations of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(17) D. A. Lytle, E. H. Jensen and W. A. Struck, *Anal. Chem.*, **24**, 1843 (1952).

(18) E. H. Jensen, "A Study on Sodium Borohydride," Nyt Nordisk Forlag Arnold Busck, Copenhagen, 1954.

(19) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution, Theory of Reversible Step Reactions," P. Haase and Son, Copenhagen, 1941, p. 206.

(6) A. Burg and H. I. Schlesinger, *THIS JOURNAL*, **59**, 780 (1937).

(7) H. I. Schlesinger and H. C. Brown, *ibid.*, **62**, 3429 (1940).

(8) H. C. Brown, H. I. Schlesinger and S. Z. Cardon, *ibid.*, **64**, 325 (1942).

(9) M. F. Lappert, *Chem. Revs.*, **56**, 959 (1956).

(10) F. G. A. Stone, *ibid.*, **58**, 101 (1958).

(11) R. L. Letsinger and N. Remes, *THIS JOURNAL*, **77**, 2489 (1955).

(12) G. S. Rondstedt, R. M. Scribner and C. E. Wulfman, *J. Org. Chem.*, **20**, 9 (1955).

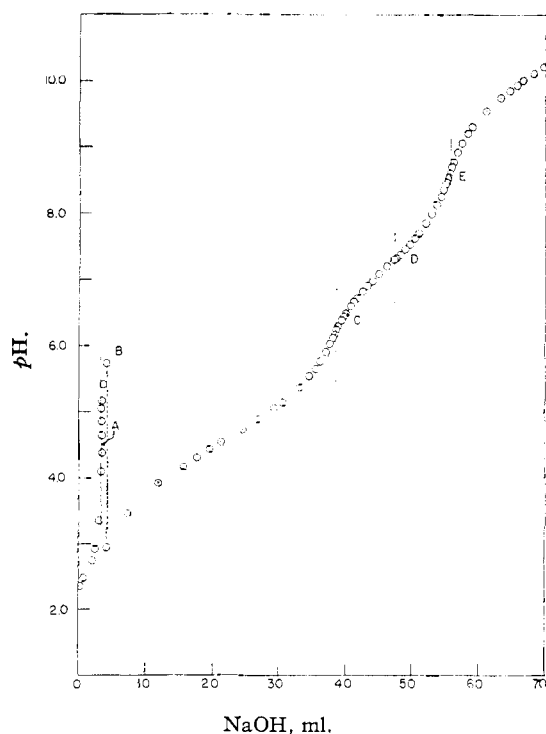
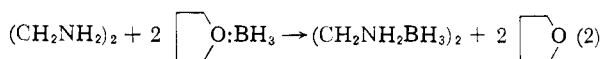


Fig. 1.—Titration of aqueous hydrolysate: sample wt. = 0.1489 g.; $N_{\text{NaOH}} = 0.09530$; A, 3.43; C, 38.45; D, 47.18; and E = 55.90 ml. *Anal.* Found % H (active) = 6.80; B = 24.3; N = 31.3; $pK_{\text{enH}_2} = 7.30$. *Calcd.* % H (active) = 6.83; B = 24.6; N = 31.9; $pK_{\text{enH}_2} = 7.31$.¹⁹

was cooled to -80° and treated *in vacuo* with 13.3 mmoles B_2H_6 . The reaction bulb was warmed to -10° and maintained at -10 to 0° for 22 hr., whereupon the reaction was 66% complete. The bulb was then warmed and maintained at room temperature for 3 days. A total of 1.55 mmoles H_2 were evolved and 2.8 mmoles B_2H_6 recovered. Thus 10.5 mmoles B_2H_6 were absorbed giving a white crystalline compound of empirical formula $(\text{CH}_2\text{NH}_2\text{BH}_3)_2$, wt. = 0.93 g.; theor. = 0.93 g.

A more practical method of preparation of larger quantities of $\text{En}(\text{BH}_3)_2$ involves reaction of ethylenediamine with the tetrahydrofuran-borane complex.



In the presence of excess ethylenediamine a viscous oil is obtained as a separate phase. This is presumably ethylenediamine unsaturated with respect to diborane. Although treatment of the supernatant THF solution with diethyl ether successfully precipitates the amineborane in high purity, over-all yields are low. Attempts to extract pure product from the oil by treatment with THF results in low yields of impure product. Pure material may be obtained by extraction with water, but the recovery is again poor.

Most favorable yields are obtained by maintaining an excess of THF- BH_3 during the course of the reaction as illustrated by the following preparation. To a stirred slurry of 52.9 g. LiAlH_4 (1.39 moles) in about 500 ml. Et_2O was added with stirring under a stream of dry nitrogen 276 g. $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (1.94 moles). The evolved diborane passed through a cold finger condenser (-80°) into a one-liter flask containing 150 ml. of tetrahydrofuran. After one-fourth the total quantity of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ had been added, 17.1 g. of ethylenediamine diluted with 95 ml. THF was added to the THF- BH_3 solution simultaneously with addition of the remainder of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ to the diborane generator. Exit gases were passed through a second cold finger condenser (-80°) and finally through a trap containing moist

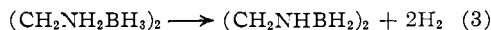
acetone to destroy unreacted B_2H_6 . On completion of addition of $\text{BF}_3 \cdot \text{Et}_2\text{O}$, dry N_2 was passed through the system for 80 minutes. The reaction product, consisting of a clear colorless solution and white precipitate, was allowed to warm to room temperature under N_2 overnight. Solvent was removed under vacuum and proved active indicating the presence of excess THF- BH_3 . 23.5 g. of white crystalline solid were obtained. Crude yield = 94%.

Anal. 89.3% purity. The crude material was unstable on standing in the desiccator at room temperature. After two days, the purity dropped to 83.4% and a distinct amine-like odor could be detected.

Purification was accomplished by treatment with water. 2.09 g. of crude material was treated with 10 ml. of cold H_2O and the slurry agitated at $0-5^\circ$. After filtration, the solid was washed with cold water and dried. Yield = 1.00 g. An additional 0.16 g. was recovered by recrystallization from the concentrated filtrate to give a total recovery of 66.5% based on $\text{En}(\text{BH}_3)_2$ contained. *Anal.* % H (active) = 6.81; purity = 99.7%. Use of excess H_2O caused losses due to solubility of the product; thus, 1.65 g. $\text{En}(\text{BH}_3)_2$ of 99.5% purity was recovered from 3.82 g. crude product when treated with 40 ml. H_2O and worked up in a similar manner. Extraction with 0.02-1.13 M NaOH resulted in purities of 95.7 to 98.5% while precipitation of product from THF with Et_2O led to purities below 85%. % purity in this paper refers to % active hydrogen based on active hydrogen content of $\text{En}(\text{BH}_3)_2$ as 100%.

Pure ethane 1,2-diamineborane is remarkably stable on standing in air or in diglyme solution. A solid sample originally analyzing 6.82% H (active) dropped only to 6.75% after standing 4 months in a vial at room temperature. Diglyme solutions of $\text{En}(\text{BH}_3)_2$ retained 97.0 and 98.5% original active hydrogen after standing one week at room temperature under 1 atm. N_2 , and *in vacuo*, respectively.

When heated in a capillary at 1 atm., ethane 1,2-diamineborane began to decompose at 89° . No liquification was observed; the particles were reoriented and a gas was slowly evolved over the range $89-115^\circ$. At 123.5° all remaining solids decomposed rapidly. Dehydrogenation of monoamineboranes is common.²⁰⁻²⁴ The following results suggest the reaction



2.93 mmoles of ethylenediamine absorbed 2.92 mmoles of B_2H_6 in the high vacuum apparatus with evolution of 0.61 mmoles of H_2 . The sample was then heated *in vacuo* to 55° with no evolution of gas. On heating to 100° , however, H_2 was evolved. The temperature was maintained at $90-110^\circ$ for 9 hr. resulting in evolution of 4.78 mmoles of H_2 , the major portion coming off during the first 3 hr. Diborane was admitted and the sample maintained at $100-110^\circ$ for 13 hr., then cooled to room temperature under B_2H_6 . Absorption of B_2H_6 was negligible indicating no formation of aminodiborane, but an additional 0.35 mmoles of H_2 had been evolved; total = 5.73 mmoles, theor. = 5.83 mmoles (equation 3). The product was a glassy white solid, insoluble in ether but highly soluble in water. On heating it began to decompose at 119° ; at 124° decomposition was rapid.

(e) *Reactivity.*—Ethane 1,2-diamineborane is very soluble in tetrahydrofuran, diglyme, methanol and ethanol; slightly soluble in water; only slightly soluble in CCl_4 , CHCl_3 and CS_2 and essentially insoluble in diethyl ether and benzene. In neutral or alkaline water, hydrolysis is very slow.

Acetone.—3.23 mmoles of $\text{En}(\text{BH}_3)_2$ contained in a reaction bulb on the high vacuum apparatus were treated with 20.35 mmoles of acetone (v.p. at $0^\circ = 68$ mm.; lit.²⁵ = 66 mm.). The exothermic reaction accompanied by hydro-

(20) R. E. McCoy and S. H. Bauer, *THIS JOURNAL*, **78**, 2061 (1956).

(21) E. Wiberg, A. Bolz and P. Buchheit, *Z. anorg. allgem. Chem.*, **256**, 285 (1948).

(22) A. Burg and C. Randolph, Jr., *THIS JOURNAL*, **71**, 3451 (1949).

(23) A. Burg and C. D. Good, *J. Inorg. & Nuclear Chem.*, **2**, 237 (1956).

(24) Callery Chemical Co., *Tech. Bull. C-200* (1958).

(25) T. E. Jordan, "Vapor Pressure of Organic Compounds," Interscience Publishers, Inc., New York, N. Y., 1954.

gen evolution was moderated by cooling the sample. After standing overnight at room temperature, the volatile components of the clear solution were vacuum distilled and subjected to fractional condensation using a carbon tetrachloride slush bath (-22°). 2.80 mmoles acetone (v.p. at $0^{\circ} = 66.2$ mm.) were recovered along with a small amount of less volatile material identified as ethylenediamine from its vapor tension (2.5 mm. at 0° , 15.0 mm. at 28.5° ; lit. 2.1 mm. at 0° , 15.0 mm. at 28.5°). The white solid residue was treated with 1.0 ml. of H_2O , followed by 2.0 ml. of 4 *N* HCl. A small amount of non-condensable gas was removed and the volatile material vacuum distilled from the reaction bulb and recondensed on anhydrous $MgSO_4$. Vacuum distillation from $MgSO_4$ gave 12.21 mmoles of isopropanol (70%). Vapor pressure at $0^{\circ} = 9.1$ mm., at $28.2^{\circ} = 52.4$ mm.; lit. at $0^{\circ} = 8.9$ mm., at $28.2^{\circ} = 51.8$ mm.

Acrolein.—A slurry of 4.79 mmoles of $En(BH_3)_2$ in 2.0 ml. of H_2O was treated at -80° with 9.05 mmoles tensiometrically pure acrolein (v.p. at $0^{\circ} = 82$ mm.). The reaction bulb was warmed to 0° and maintained at this temperature until the reaction had greatly subsided. After standing at room temperature for 24 hr., volatile material was distilled away and dried over anhydrous $MgSO_4$. This mixture of product alcohol and ethylenediamine could not be separated by fractional condensation. After treatment with 10 drops of 2.4 *N* HCl followed by several grams of anhydrous $MgSO_4$, distillation gave 0.3046 g. (58%) of pure allyl alcohol (v.p. at $0^{\circ} = 5.3$ mm., at $28^{\circ} = 32.5$ mm.; lit. at $0^{\circ} = 4.9$ mm., at $28^{\circ} = 31$ mm.).

Cinnamaldehyde.—To a slurry of 31.3 mmoles of $En(BH_3)_2$ in 8 ml. of tetrahydrofuran at -80° was added 20 ml. of an ether solution of 84.1 mmoles cinnamaldehyde (purified by the method described in Organic Syntheses²⁶ and freshly distilled, b. $68-70^{\circ}$ at 1 mm., $n_D^{25} = 1.6211$; lit. $n_D^{20} = 1.6195$). The reaction bulb was warmed to near 0° producing a vigorous reaction which was moderated by cooling. After standing 24 hr. at room temperature, volatile materials were removed by vacuum distillation. The viscous residue was treated with 15 ml. of Et_2O and 27 ml. of H_2O and allowed to stand with frequent stirring for 2.5 hr. The layers were separated, the aqueous layer washed with Et_2O and the combined Et_2O extract dried over $MgSO_4$. After $MgSO_4$ had been removed by filtration, ether was removed by vacuum distillation giving 10.59 g. (93.6%) of a cloudy pale yellow viscous oil which gave a negative test with Schiff's Reagent but strongly decolorized a 5% solution of Br_2 in CCl_4 . This material was identified as cinnamyl alcohol by its refractive index ($n_D^{25} = 1.5780$, 1.5795) and infrared spectrum. Further purification was complicated by polymerization. The formation of hydrocinnamyl alcohol was not evident under these reaction conditions.

Acetyl Chloride.—To a solution of 3.02 mmoles of $En(BH_3)_2$ in 5 ml. of diglyme was added at -80° 5.09 mmoles of acetyl chloride. The reaction bulb was warmed to room temperature producing a moderate reaction and precipitating a white solid. After standing at room temperature for 2.5 days (H_2 evolved = 1.5 mmoles), volatile material was distilled off giving a syrupy white residue. Treatment of this residue with 4 ml. of H_2O produced 6.4 mmoles of H_2 . The volatile distillate was treated with 3 ml. of H_2O and fractionated from a -10° bath (salt water and ice). A volatile fraction was collected at -80° and condensed on anhydrous $MgSO_4$. Subsequent distillation gave 3.09 mmoles of ethanol (61%) v.p. at $0^{\circ} = 10.5$ mm., at $-5^{\circ} = 9.4$ mm.; lit. at $0^{\circ} = 12.2$ mm., at $-5^{\circ} = 8.3$ mm. The product gave a positive iodoform test.

In a separate experiment 2.31 mmoles of acetyl chloride and 2.87 mmoles of solid $En(BH_3)_2$ gave no reaction product after standing two weeks in the absence of a solvent.

Ethyl anisate, ethyl acetate, acetonitrile, 1-nitropropane and benzalaniline were not reduced when individually treated with solutions of excess ethane 1,2-diamineborane and allowed to stand several days at room temperature. Acetonitrile was studied in tetrahydrofuran solution, while the other experiments were carried out in diglyme. Ethyl acetate did not react even after heating 5 hr. at $70-80^{\circ}$. Vacuum distillation of volatile materials only resulted in recovery of solvent and starting materials. In each case, acid hydrolysis of the reaction mixture resulted in evolution

of a quantity of hydrogen corresponding to greater than 90% original activity.

Silver Nitrate.—An aqueous solution of $AgNO_3$ was added with stirring to an aqueous solution of $En(BH_3)_2$ instantly producing a finely divided black precipitate and evolving H_2 . The precipitate was filtered, washed with H_2O and dried overnight at 50° . This material proved to be 99.5% Ag when analyzed by the Volhard method.

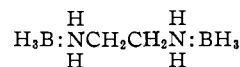
Cupric Nitrate.—An aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ was added with stirring to an aqueous solution of $En(BH_3)_2$. The solution turned brown followed by precipitation of a finely divided black solid. H_2 was evolved vigorously and the original basic solution turned purple and became strongly acidic. The precipitate was filtered, washed with water and acetone and dried at room temperature. An X-ray powder pattern revealed the sample to be pure copper.

Nickel Nitrate.—No reduction of Ni^{++} was observed after treatment of an aqueous solution of $En(BH_3)_2$ with $Ni(NO_3)_2$ solution followed by heating.

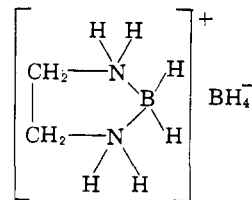
Boron Fluoride Etherate.—In an attempt to displace B_2H_6 from ethane 1,2-diamineborane, 7.17 mmoles freshly distilled $BF_3 \cdot Et_2O$ (b. 24° at 1 mm. Hg) was added to a solution of 3.56 mmoles $En(BH_3)_2$ in 2.2 ml. of diglyme and the reaction mixture allowed to stand 4 hr. at room temperature. After removal of 1.0 mmoles noncondensable gas and 0.5 mmole B_2H_6 , the reaction mixture was treated with an additional 7.17 mmoles $BF_3 \cdot Et_2O$ and allowed to stand overnight at room temperature. A total of 9.10 mmoles H_2 were evolved. The low yield of B_2H_6 (1.4 mmoles, 39% theory) may be due to increased acidity of amino hydrogens after displacement of $-BH_3$ groups by BF_3 .

Discussion

The reaction product of ethylenediamine and diborane has been named ethane 1,2-diamineborane implying the structure



It should be noted that an alternate structure may be written consistent with analytical data obtained and which is analogous to the structure of the diammoniate of diborane recently established by Parry, *et al.*²⁷



At this time, we prefer the diamineborane adduct representation on the basis of dehydrogenation experiments and solubility data. The question is open, however, since the true structure has not been rigorously established.

It is encouraging that the maximum quantity of hydridic hydrogen obtainable from a 1:1 molar adduct is incorporated into the product on synthesis and retained for long periods of time when the material is pure. This is in contrast to the behavior of most primary and secondary amineboranes which readily dehydrogenate to the corresponding aminoboranes. For example, methylamineborane and dimethylamineborane undergo decomposition with evolution of hydrogen even at 0° .²⁰

(26) O. Grummitt and E. I. Becker, *Org. Syn.*, **30**, 77 (1950).

(27) R. W. Parry and collaborators, *THIS JOURNAL*, **80**, 14 (1958).

It is interesting to compare the hydridic hydrogen content (a measure of reducing capacity per unit weight) of ethane 1,2-diamineborane with that of other amineboranes which are commercially available²⁴ (Table I).

TABLE I

ACTIVE HYDROGEN CONTENT OF AMINEBORANES		
No.	Compound	%H (hydridic)
1	Ethane 1,2-diamineborane	6.83
2	Trimethylamineborane	4.14
3	Dimethylamineborane	5.13
4	Pyridineborane	3.25

Thus, ethane 1,2-diamineborane contains 33% more active hydrogen per unit weight than its closest competitor, dimethylamineborane. Comparison with other available products is even more striking. Dimethylamineborane melts at 36° and frequently must be purified from an unstable form (m. 11°) by recrystallization from hot petroleum

ether or by vacuum distillation, b. 59–65° at 1–2 mm.^{24,25} The advantageous position of ethane 1,2-diamineborane is evident from a consideration of stability, handling difficulties and hydridic hydrogen content.

Ethane 1,2-diamineborane appears to exhibit selectivity and reactivity toward organic functional groups comparable to sodium borohydride. Its solubility in a variety of liquids plus its successful use as an aqueous slurry make it amenable for a variety of reducing reactions under a number of solvolytic conditions. It should prove an interesting addition to the list of complex hydride reducing agents.

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Preparation and Thermal Stability of Tetrakis-(pentafluorophenyl)-silane and Tris-(pentafluorophenyl)-phosphine¹

BY LEO A. WALL, ROBERT E. DONADIO AND WALTER J. PUMMER

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The completely fluorinated organo-metalloid compounds, tetrakis-(pentafluorophenyl)-silane, tris-(pentafluorophenyl)-phosphine and tris-(pentafluorophenyl)-phosphine oxide have been prepared from pentafluorophenylmagnesium bromide and the appropriate metalloid chloride. The thermal stability of each of these compounds has been compared with that of other aromatic substances. It was found in the case of the phosphine, where coordinating electrons exist on the metalloid atoms, that complete fluorine substitution increases its thermal stability and resistance to oxidation. On the other hand, complete fluorination decreases the thermal stability of the silane.

Pentafluorobromobenzene² and pentafluoroidobenzene³ have recently been synthesized in this laboratory and also in England.⁴ These substances react with magnesium to form nearly typical Grignard reagents.^{3,4} Several new compounds have already been prepared^{3,4} *via* these reagents, and the synthesis of many more is evidently possible.

Aromatic fluorocarbons are of interest as the basis for new thermally stable liquids and polymers. Before attempting the preparation of the larger molecules that make up such materials, it would be desirable, however, to have thermal decomposition data on the smaller molecules. In this paper we shall describe the synthesis and physical properties of two new compounds—tetrakis(pentafluorophenyl)-silane and tris(pentafluorophenyl)phosphine—and report the results of a qualitative study of the thermal decomposition

of these compounds, other aromatic fluorocarbons and related hydrocarbons.

Experimental^{5,6}

Tetrakis-(pentafluorophenyl)-silane (I).—This compound is readily formed when silicon tetrachloride is added to an ether solution of the pentafluorophenyl magnesium bromide.^{3,4} To the Grignard reagent, prepared from 24.7 g. (0.1 M) of pentafluorobromobenzene and 2.43 g. (0.1 g. atom) of magnesium turnings in 50 ml. of anhydrous ether, was added 4.25 g. (0.0025 M) of silicon tetrachloride dropwise while cooling by means of an ice-bath. When the addition was completed, the mixture was stirred for 1 hr. more at 0°, refluxed for 3 hr. and finally allowed to come to room temperature overnight. Ice water (25 ml.) was added to the cooled reaction mixture, followed by the addition of 25 ml. of 6 N hydrochloric acid. After 0.5 hr. of stirring, the mixture was poured into 100 ml. of N hydrochloric acid and filtered. From the 9 g. of brown filter cake, 5.5 g. of I (32% yield) was obtained as white needles by sublimation at 208° (1 mm.). After several recrystallizations from an acetone-benzene mixture, it melted at 248–250°. The infrared absorption spectrum showed peaks at wave lengths 6.57, 7.72, 9.1 and 10.26 μ . The remaining 3.5 g. of solid appeared to be inorganic in composition and acid insoluble.

(1) Based on work sponsored by the Bureau of Aeronautics and the Office of Naval Research, Department of the Navy, Washington, D. C.

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(5) Chemical analyses were performed by Robert Deardorff of the Analytical Chemistry Section of the National Bureau of Standards.

(6) Melting points were determined with a Fisher Johns apparatus calibrated with pure samples of naphthalene, benzoic acid and dimethylterephthalate.