rate ion. The latter species may be attributable to impurity in the $NaBH(OMe)_3$ sample or to a disproportionation upon dissolution.[20]

Acknowledgment. We wish to thank Messrs. Malcolm Judkins and Robert Marianelli for obtaining the ^{11}B nmr spectra. This research was supported by the U. S. Atomic Energy Commission.

(20) H. C. Brown, E. J. Mead, and P. A. Tierney, *J. Am. Chem. Soc.*, **79**, 5400 (1957).

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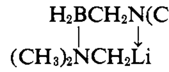
Received May 12, 1966

A Lithium-Substituted Borane Derivative and New Classes of Boranes

Sir:

We wish to report the isolation of a novel lithium-substituted borane derivative, lithiomethyldimethylamino(dimethylaminomethyl)dihydroborane (I). A

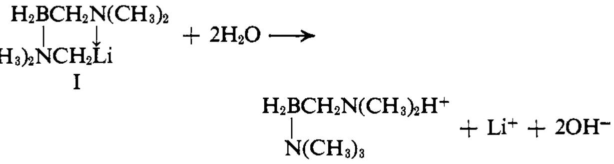


$$\begin{array}{c} H_2BCH_2N(CH_3)_2 \\ |\qquad\quad\downarrow \\ (CH_3)_2NCH_2Li \end{array}$$

I

cyclic structure is probable in view of its constitution and volatility. It is a white, highly crystalline solid, melting at 112–114°, subliming at 80° under high vacuum. It is soluble in benzene, hexane, and ether. On exposure to air it reacts vigorously, nearly inflaming after a short induction period.

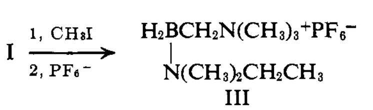
The composition of I was determined by a number of chemical methods.[1] A neutralization equivalent of 67 ± 1 agrees favorably with the value of 68.0 calculated from the equation



$$\begin{array}{c} H_2BCH_2N(CH_3)_2 \\ |\qquad\quad\downarrow \\ (CH_3)_2NCH_2Li \\ \text{I} \end{array} + 2H_2O \longrightarrow \begin{array}{c} H_2BCH_2N(CH_3)_2H^+ \\ | \\ N(CH_3)_3 \\ \text{II} \end{array} + Li^+ + 2OH^-$$

The titration curve that would be expected for the simultaneous titration of a strong base and a moderately strong base was obtained. The hydrolysis of the carbon–lithium bond and the $-CH_2N(CH_3)_2$ group account for the formation of 2 moles of hydroxide/mole of I. Concentration of the titrant solution and addition of ammonium hexafluorophosphate solution led to the isolation of the hexafluorophosphate salt of the new borane cation II. Its structure was identified by independent synthesis as discussed later.

Reaction of I with methyl iodide gave a white solid iodide salt which was converted to the hexafluorophosphate salt by metathesis. *Anal.* Calcd for $H_2B[N(CH_3)_2C_2H_5]CH_2N(CH_3)_3PF_6$: C, 31.6; H, 7.95; N, 9.2; P, 10.2. Found: C, 31.9; H, 7.98; N, 9.2; P, 10.3.



$$\text{I} \xrightarrow[2,\ PF_6^-]{1,\ CH_3I} \begin{array}{c} H_2BCH_2N(CH_3)_3{}^+PF_6^- \\ | \\ N(CH_3)_2CH_2CH_3 \end{array}$$

III

The presence of the $H_2B<$ moiety in III, and consequently in I, was confirmed by hydrolysis of III in the presence of platinum.[2] The hydrolytic hydrogen value of 6.7 ± 0.2 × 10^{-3} mmole/mg agreed well with that calculated for III, 6.6 × 10^{-3} mmole/mg. Recovery of 85% of the ethyldimethylamine (identified by infrared analysis) liberated in the hydrolysis substantiated the $-H_2BN(CH_3)_2C_2H_5$ group in III. Isolation of this amine clearly confirms the position of the lithium–carbon bond in I.

Synthesis of I was effected by stirring 2 moles of butyllithium with 1 mole of $H_2B[N(CH_3)_3]_2{}^+Cl^-$ for several hours. The product was then isolated by volatilization from the residue after evaporation of hexane solvent. The reaction temperature and stoichiometry are critical. If about 1.5 moles of butyllithium are used, different products result, one of which is the new borane-substituted amine, trimethylamine (dimethylaminomethyl)borane (IV). It was found that the best yields of IV

$$(CH_3)_3NBH_2CH_2\ddot{N}(CH_3)_2$$

IV

were obtained by rapid addition of the butyllithium while keeping the temperature near 20°.

Because of the fact that a boron–nitrogen bond between tertiary boron and nitrogen is analogous to a carbon–carbon bond, IV is structurally similar to N,N-3,3-tetramethylbutylamine. It is a colorless liquid of low volatility (vapor pressure less than 1 mm at room temperature) which freezes to a crystalline solid melting at −25.5 to −23°. It decomposes slowly, about 75% per day, at room temperature according to

$$\underset{\text{IV}}{2(CH_3)_3NBH_2CH_2\ddot{N}(CH_3)_2} \longrightarrow 2(CH_3)_3N\colon + \underset{\text{V}}{[BH_2CH_2N(CH_3)_2]_2}$$

This decomposition reaction was useful in characterizing IV. A 55.0-mg sample of IV was heated several hours at 120° in a closed vessel. The volatile product at −40° was distilled and found to be 0.404 mmole (96% of theory) of trimethylamine. The residue remaining was 0.208 mmole (98.5% of theory) of (dimethylaminomethyl)borane cyclic dimer (V),[3] identified by its infrared spectrum.

Trimethylamine (dimethylaminomethyl)borane (IV) dissolves readily in water to give a basic solution from which the moderately soluble hexafluorophosphate salt of cation II can be precipitated. The infrared spectrum of this salt shows a sharp single NH absorption at 3260 cm^{-1} and a multiplet BH absorption at 2350 cm^{-1}.[4] The somewhat low value of the BH stretching frequencies has also been observed for amine alkyboranes.[5,6] Hydrolysis gave a hydrolytic hydrogen value of 0.0072 ± 0.0001 mmole/mg, identical with that calculated for the formation of 2 moles of hydrogen/formula weight of $(CH_3)_3NBH_2CH_2N(CH_3)_2H^+PF_6^-$.

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[1] Because of its reactivity I has not given satisfactory elemental analyses.

(2) A modification of the general technique suggested by H. C. Miller (personal communication) was used. See N. E. Miller, J. A. Forstner, and E. L. Muetterties, *Inorg. Chem.*, **3**, 1690 (1964).

(3) N. E. Miller and E. L. Muetterties, *ibid.*, **3**, 1196 (1964).

(4) The splitting of the BH stretching absorptions was similar to that observed in solid-state spectra of $H_2B(NR_3)_2{}^+$ salts.[6]

(5) N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 1033 (1964).

(6) M. F. Hawthorne, *ibid.*, **83**, 831 (1961).

Reaction of IV with anhydrous hydrogen chloride gave the chloride salt of II as a white solid. Upon metathesis, the hexafluorophosphate salt was recovered in 40% yield.

Diborane reacts rapidly with IV at low temperature, to give the adduct VI. The adduct is a white, hard

$$\underset{\text{IV}}{2(CH_3)_3NBH_2CH_2\ddot{N}(CH_3)_2} + B_2H_6 \longrightarrow \underset{\text{VI}}{2(CH_3)_3NBH_2CH_2N(CH_3)_2BH_3}$$

crystalline solid which sublimes unchanged at 100° under high vacuum. Hydrolysis of VI confirmed its composition, giving a hydrolytic hydrogen value of 0.0343 mmole/mg, in good agreement with that calculated for hydrolysis of five BH bonds/formula weight of VI, 0.0347 mmole/mg.

The borane cation II and the cation of III are members of two related new classes of cationic boranes. They are stable in aqueous acid or base and do not reduce aqueous silver ion. A contributing factor in the aqueous stability of II is the strong basicity of its conjugate base IV. The enhancement of base strength by boron hydride substitution is well established. Both $H_2B(NH_3)_2^+$ and $B_{10}H_8(NH_3)_2$, for example, are known to be weak acids of very strong conjugate bases.[7,8]

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This work was also supported in part by a grant from the research fund of the University of South Dakota.

(7) D. R. Schultz and R. W. Parry, *J. Am. Chem. Soc.*, **80**, 4 (1958).

(8) W. H. Knoth, *ibid.*, **88**, 935 (1966).

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May 27, 1966

Insertion by Triplet Methylene Radicals in Alkane Systems[1]

Sir:

It is commonly believed,[2] based on earlier reports,[3,4] that triplet methylene radicals do not insert into C–H bonds. This letter reports contrary evidence and some quantitative measurements.

Since the finding that photolysis of ketene[5] and of diazomethane[6] both yield triplet methylene besides the singlet radical, we have been interested in the ramifications of this complication for the interpretation of the chemistry of these systems. It is now established[7] that $^3CH_2$ abstracts hydrogen from C–H bonds, and Whitten and Rabinovitch[7a] proposed that at least part of the pentene products[2c] from reaction of $^3CH_2$ with butene-2 have their origin in initial H abstraction. In an effort to clarify these matters, we have investigated the reaction of $^3CH_2$ with propane, *n*-butane, and isobutane, and with alkane–ethylene mixtures.

Triplet methylene was produced[3] by photolysis (4358 A and 25°) of ~1:10 diazomethane–substrate gaseous mixtures that contained at least 800-fold excess of N_2 (~1.6 atm). In some experiments, admixture of from 5 to 20% ethylene was made. Increase in the proportion of N_2 (up to 2500:1) had little effect on product composition, so that $[^3CH_2/(^3CH_2 + {}^1CH_2)] \sim 1$.[8]

Analysis was made by gas chromatography, with calibration of virtually every product of interest with authentic samples. The side products in triplet systems are much more complex than those formed in largely singlet systems and makes the requisite analyses more exacting. Each substrate has only two distinguishable H sites which simplified the possible products. Background calibrations were made from blank experiments with no substrate and with substrate–oxygen mixtures.

The principal reactions of interest are

$$RH + {}^3CH_2 \longrightarrow CH_3 + R \text{ (primary H)} \tag{1a}$$

$$\longrightarrow CH_3 + R' \text{ (secondary or tertiary H)} \tag{1b}$$

$$2R \longrightarrow R_2 \tag{2}$$

$$2R' \longrightarrow R_2' \tag{3}$$

$$R + R' \longrightarrow RR' \tag{4}$$

$$2CH_3 \longrightarrow C_2H_6 \tag{5}$$

$$CH_3 + R \longrightarrow RCH_3 \tag{6}$$

$$CH_3 + R' \longrightarrow R'CH_3 \tag{7}$$

plus disproportionation reactions and cyclopropane formation with ethylene. Ethyl radicals also arise in these systems.[7a] They offer both complication and assistance from the occurrence of the reactions

$$2C_2H_5 \longrightarrow n\text{-}C_4H_{10} \tag{8a}$$

$$\longrightarrow C_2H_6 + C_2H_4 \tag{8b}$$

$$CH_3 + C_2H_5 \longrightarrow C_3H_8 \tag{9}$$

$$C_2H_5 + R \longrightarrow RC_2H_5 \tag{10}$$

$$C_2H_5 + R' \longrightarrow R'C_2H_5 \tag{11}$$

plus further disproportionation reactions.

The relative proportions of R and R′ deduced either from the products of reactions 10 and 11, or from reactions 2, 3, and 4, were in general agreement. For propane, the relative rate of secondary/primary H abstraction by $^3CH_2$ is 11 per bond. A value of 9 was given previously[7a] for propane systems in which $^3CH_2$ was only a minor fraction of the methylene. Since the ratio of secondary/primary H abstraction by CH_3 is

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(1) This work was supported by the Office of Naval Research.

(2) For example, see (a) W. Lwowski and F. P. Woerner, *J. Am. Chem. Soc.*, **87**, 5491 (1965); (b) H. M. Frey, *Chem. Commun.*, 260 (1965); (c) J. A. Bell, *Progr. Phys. Org. Chem.*, **2**, 1 (1964); (d) F. J. Duncan and R. J. Cvetanović, *J. Am. Chem. Soc.*, **84**, 3593 (1962).

(3) H. M. Frey, *ibid.*, **82**, 5947 (1960).

(4) K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *ibid.*, **83**, 2397 (1961); **84**, 1015 (1962).

(5) J. W. Simons and B. S. Rabinovitch, *J. Phys. Chem.*, **68**, 1322 (1964). See also S. Ho, I. Unger, and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **87**, 2297 (1965); K. W. Watkins, B. S. Rabinovitch, and D. F. Ring, *ibid.*, **87**, 4960 (1965); and ref 7b.

(6) F. H. Dorer and B. S. Rabinovitch, *J. Phys. Chem.*, **69**, 1952, 1964 (1965). Our results were communicated orally to Dr. H. M. Frey in Sept 1964, and were confirmed by him in later work.[2b]

(7) (a) G. Z. Whitten and B. S. Rabinovitch, *J. Phys. Chem.*, **69**, 4348 (1965); (b) R. W. Carr and G. B. Kistiakowsky, *ibid.*, **70**, 119 (1966); (c) H. M. Frey, private communication. It may be noted that D. B. Richardson, M. C. Simmons, and I. Dvoretzky [*J. Am. Chem. Soc.*, **82**, 5001 (1960); **83**, 1934 (1961)] earlier speculated that $^3CH_2$ abstracts H atoms, but on the basis of mechanistic surmises and alleged evidence that have been shown [D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962)] to be incorrect.

(8) Comparison of results of Watkins, *et al.*,[5] by the present technique for *cis*-butene-2 substrate, with data from earlier work[2d] on triplet radicals in $Hg(^3P_1)$-photosensitized ketene–butene mixtures, shows that the proportion of $^3CH_2$ in N_2 systems is at least as high as in $Hg(^3P_1)$ systems.