"T" stopcock and proceed into a previously evacuated cell. For some of the more dilute solutions an absorption cell with a side arm was used. For the most dilute solutions a third method involving the use of a two compartment flask and then pouring the mixed solution into the cell was employed.

The concentration ranges covered were: 0.01 to 0.1 M base, initial MnO_4^- from 0.01 to 0.5 mM and initial BH_4^- from 0.001 to 0.2 mM. The rate for each kinetic experiment was evaluated assuming first order each in BH_4^- and MnO_4^-. For about three quarters of the runs this rate constant remained constant to 25% over at least 75% of the reaction. About half of the runs gave rate constants in the range of 1500 to 2500 liter/mole-second. The rest of the runs ranged up to 70,000 liter/mole-sec. Sources of chemicals, cleaning procedures for glassware, time of standing of solutions before use, glass surface area, addition of manganese dioxide and variation in O_2 content of the solutions were without effect on the rate. The rates were measured at 20°.

Conclusion

Despite the complexity of this system (which is evident from the fact that the reducing agent contains eight equivalents per mole and manganese has many possible oxidation states) we can be confident of many features of the mechanism.

Permanganate oxidations in basic solution resulting in manganate are usually considered to proceed by one of two mechanisms. The first mechanism is by the generation of hydroxyl radicals (the active oxidizing agent) as shown by

$$MnO_4^- + OH^- = MnO_4^= + OH\cdot \qquad (4)$$
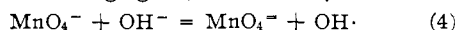
The second mechanism is a two-equivalent reduction of MnO_4^- by a reducing agent (R) to give hypomanganate which is followed by the rapid generation of $MnO_4^=$ as shown by equations 5 and 6

$$MnO_4^- + R = MnO_4^{-3} + R' \qquad (5)$$

$$MnO_4^- + MnO_4^{-3} = 2MnO_4^= \qquad (6)$$
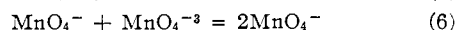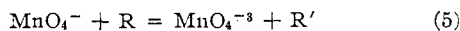
It should be noted that the hydroxyl radical mechanism implies a hydroxide ion dependence.

The evidence for the hypomanganate mechanism for the borohydride case includes: (a) the absence of a strong hydroxide ion dependence, (b) the observation that the rate of reduction of manganate by borohydride is slow, (c) the impossibility of stopping the reduction at the manganate stage

with barium and (d) the lack of influence of barium on the potentiometric manganese dioxide end-point. According to the hypomanganate mechanism, the manganate formed arises from the oxidation of hypomanganate by permanganate (reaction 2). Some of the hypomanganate follows another path—reduction to manganese dioxide with the liberation of hydrogen (reaction 3). The hydrogen producing path may consist of more than one step. The path involved in the H_2 production does not involve the catalysis of the hydrolysis of BH_4^- since all the H_2 was shown to originate from the BH_4^-. Since both manganese dioxide and manganate are found, hypomanganate must be very reactive toward both reduction and oxidation.

The transition state for a two equivalent reduction of MnO_4^- by BH_4^- may be analogous to the transition state suggested by Halpern and Taylor[13] for the $HCOO^-$ reduction of MnO_4^-. They suggest that the covalently bound H in $HCOO^-$ is transferred as a hydride to an oxygen of MnO_4^- giving Mn(V) with a formula $HOMnO_3^=$. Both BH_4^- and $HCOO^-$ are negative ions and have covalently bound H.

Speculation on the transition state for the reaction producing H_2 should wait until it is known whether both hydrogen atoms come from the same ion of BH_4^- or a poly-boron species is involved.

All reductions by borohydride have been reported to be kinetically first order in borohydride.[2,3,9] The order with respect to oxidants has been reported to be one for organic oxidants and zero for ferricyanide.[3] The order with respect to acid is one for water,[2,14,15] one for ferricyanide[3] and has not been reported for organic oxidants. The MnO_4^-–BH_4^- reaction is the first for which no acid dependence has been found.

Acknowledgment.—Mr. R. Fox assisted with some of the experiments.

(13) J. Halpern and S. M. Taylor, Disc. Faraday Soc., **29**, 177 (1960).

(14) J. B. Brown and M. Svenson, J. Am. Chem. Soc., **79**, 4241, 6581 (1957).

(15) R. E. Davis and C. G. Swain, ibid., **82**, 5949 (1960).

Decaborane, "6-Benzyl" B₁₀H₁₃ Chemistry

BY ROBERT J. F. PALCHAK,[1a] JOHN H. NORMAN[1b] AND ROBERT E. WILLIAMS[1c]

RECEIVED DECEMBER 9, 1960

Benzyldecaborane has been prepared by alkylation of decaboranylsodium with benzyl bromide in ether solution. Chemical, mass spectral and n.m.r. evidence lead to the conclusion that the benzyl group is substituted on either the 1 or 6-boron atom of decaborane. Arguments are presented for the preferred 6-position. Decaboranylsodium in ether reacts with iodine to produce iododecaborane, ethoxydecaborane and ethoxyiododecaborane.

Introduction

Decaborane (I), a strong monoprotic acid in water–alcohol and water–dioxane solutions, can be titrated potentiometrically with a strong base. Back titration with aqueous hydrochloric acid re-

produces the titration curve, and I may be recovered in good yield from the acidified solution.[2] I behaves as a weak monoprotic acid in acetonitrile and as a stronger diprotic acid in dimethylformamide.[3]

(1) (a) Hercules Powder Company, Allegany Ballistics, Laboratory, Cumberland, Md. (b) General Atomic Division, General Dynamics Corp., P. O. Box 608, San Diego 12, California. (c) National Engineering Science Company, Pasadena, California.

(2) G. A. Guter and G. W. Schaeffer, J. Am. Chem. Soc., **78**, 3546 (1956).

(3) R. Atterberry, J. Phys. Chem., **62**, 1458 (1958).

In ether solutions I appears to behave as a monoprotic acid toward metal alkoxides and metal hydrides, e.g., sodium hydride or sodium borohydride, to form decaboranylsodium, $B_{10}H_{13}Na$, (II) and as a monoprotic or a diprotic acid toward Grignard reagents to yield $B_{10}H_{13}MgX$ or $B_{10}H_{12}$-$(MgX)_2$.[4] These metal derivatives prepared in ether solutions are reactive intermediates and have been used to prepare a number of substituted decaboranes.

This paper is concerned primarily with the reactions of II in ether and with the structure of benzyldecaborane, $C_6H_5CH_2B_{10}H_{13}$ (III), a product from the reaction between II and benzyl bromide.

Experimental[5]

Decaboranylsodium.—In a typical experiment 1.56 g. (0.0128 mole) of freshly sublimed decaborane was added to 2.784 g. (0.0703 mole) of 60.62% sodium hydride in 45 ml. of n-propyl ether. The reaction proceeded to apparent completion in 10 min. with the formation of an orange-yellow solution and a white insoluble solid. Total gas evolution, as measured in a calibrated vacuum line, was 0.0155 mole or 1.21 hydrogen atoms per mole of decaborane.

Reaction between Tetra-bridgedeuteriodecaborane and Sodium Hydride.—$B_{10}H_{10}D_4$ (0.01 g., 10^{-4} mole) made by exchange of $B_{10}H_{14}$ in an ether solution with D_2O, was added to a frozen mixture of 10 ml. of dry propyl ether and 0.003 g. (10^{-4} mole) of sodium hydride. The mixture melted and the reaction began. The deuterium concentration in the evolved gas gradually increased from 2.4 mole % at the start to 18.5 mole % at the end of the reaction.

Benzyldecaborane.—Benzyl bromide (51.6 g., 0.3 mole) was added to decaboranylsodium [prepared from 36 g. (0.3 mole) of decaborane and 7.5 g. (0.3 mole) of sodium hydride] in 250 ml. of anhydrous ether. The mixture was stirred and warmed at 45° for 6.5 hr. It then was cooled and maintained at 20° for 15 hr., after which it was heated to reflux for an additional 2 hr. The resultant orange product was filtered and the ether was removed at reduced pressure. The residual orange tar was exhaustively extracted with pentane and the pentane extract was concentrated by warming at reduced pressure to yield 56.3 g. of a red-orange viscous liquid. The viscous liquid was heated under high vacuum to yield 8 g. of sublimed decaborane and 42 g. of residue. The residue was heated to 150–180° at 8×10^{-2} mm. to yield 24 g. of a pale yellow distillate, b.p. 134° (10^{-3} mm.), and 15.6 g. of undistilled tar. Molecular distillation of this tar resulted in recovery of an additional 1.6 g. of product. There remained 11 g. of black carbonaceous appearing residue in the still pot. The 25.6 g. of combined distillate (49% of yield based on unrecovered decaborane) was crystallized from pentane to yield colorless, long flat crystals, m.p. 63.5–64.5°. Anal. Calcd. for $C_7H_{20}B_{10}$: C, 39.56; H, 9.49; B, 50.93. Found: C, 39.6 ± 0.4; H, 9.5 ± 0.3; B, 50.85 ± 0.07.

Benzyldecaborane as prepared by the method of Siegel[4] was identical to that prepared from decaboranylsodium.[6]

Dibenzyldecaborane.—A mixture of 10.4 g. (0.06 mole) of benzyl bromide and 0.06 mole of benzyldecaboranylsodium in 200 ml. of anhydrous ether was heated at reflux for 4 hr. The mixture was cooled and maintained at room temperature for 20 hr., after which it was filtered. The orange filtrate was concentrated at reduced pressure to an orange tar. The tar was dissolved in pentane and the re-
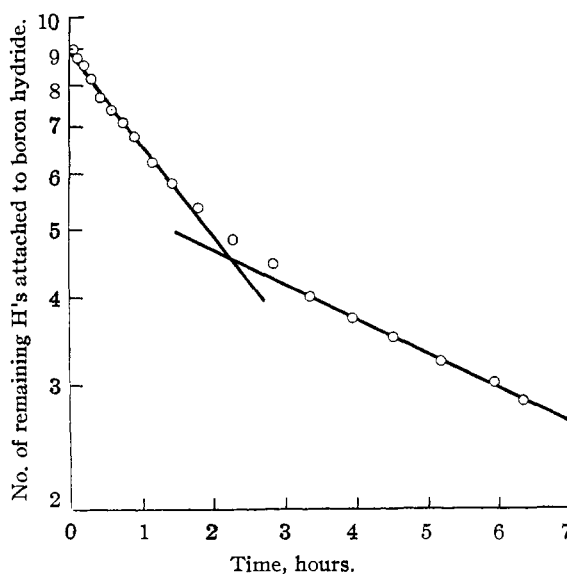
(4) B. Siegel, J. L. Mack, J. U. Lowe, Jr., and J. Gallaghan, J. Am. Chem. Soc., **80**, 4523 (1958).

(5) All experiments were conducted in an atmosphere of high purity nitrogen; melting points are uncorrected. Mass spectra were obtained on a Consolidated Electrodynamics Corp. Model 21-103C mass spectrometer. B^{11} n.m.r. spectra were obtained on a Varian Associates high resolution nuclear magnetic resonance spectrometer operating at 12.8 mc.

(6) Dr. S. G. Gibbons has suggested[7] that the unexpected bands at 7.79 μ, 9.18 μ in the infrared spectrum of benzyldecaborane prepared by Siegel, et al.,[4] probably arise from silicone stopcock grease (bands at 7.9, 9.15 and 12.28 μ).

(7) (a) Private communication. (b) S. G. Gibbons and D. Shapiro, J. Chem. Phys., **30**, 1483 (1959).

Fig. 1.—Kinetic study of deuterium–hydrogen exchange with benzyldecaborane in cineole.

sultant solution was filtered to remove a white, flocculent precipitate. The filtrate was concentrated to a small volume and refrigerated to yield white crystals. These crystals were dissolved in pentane and recrystallized to yield 2 g. of colorless crystals (10% yield), m.p. 111–116°. A mass spectrum of this material showed these crystals to be dibenzyldecaborane. Anal. Calcd. for $C_{14}H_{26}B_{10}$: C, 55.3; H, 8.67; B, 35.78. Found: C, 55.8, 55.7; H, 9.0, 9.10; B, 35.2, 35.2.

Iodination of Decaboranylsodium.—A solution of 12.7 g. (0.05 mole) of iodine in 110 ml. of anhydrous ether was added dropwise to a stirred solution of 0.05 mole of decaboranylsodium in anhydrous ether cooled to −80°. The iodine color disappeared immediately on contact with the cold decaboranylsodium solution, and the mixture became bright orange as the reaction proceeded. Mass spectrometric analysis of the mixture after half the iodine had been added indicated the presence of iododecaborane, decaborane and ethyl iodide. The remainder of the iodine solution was added, and the mixture was maintained at −10° for 20 hr. and then it was filtered. The dark filtrate was concentrated at reduced pressure to yield a blue-black oil. The oil was extracted with pentane to yield an amber liquid. The mass spectrum of this amber liquid exhibited peaks attributable to decaborane, iododecaborane, ethoxydecaborane and ethoxiododecaborane. Hawthorne, et al.,[8] observed alkoxydecaboranes from similar reactions.

Deuteration of Benzyldecaborone.—(a) An ether solution of benzyldecaborane was shaken with a tenfold excess of 99.8% D_2O to yield $C_6H_5CH_2B_{10}H_9D_4$. The appearance of a band at 7.3 μ in the infrared spectrum confirmed bridge deuteration.[9] (b) Benzyldecaborane (0.331 g.), dissolved in 2.73 g. of cineole, was mixed with 15 ml. of 99.8% D_2O. The mixture, maintained at 60 ± 0.3°, was stirred vigorously. Samples were periodically withdrawn and analyzed mass spectrometrically. The data are shown in Fig. 1.

Results and Discussion

Reactions of Decaboranylsodium.—Decaborane undergoes a rapid exothermic reaction in ether with sodium hydride, sodium amide, sodium and lithium methoxides with the formation of a yellow-orange solution of the corresponding decaboranylsodium or lithium. A fine, white, solid, insoluble in ether and soluble in tetrahydrofuran is also formed. This solid has spontaneously ignited when dried in

(8) M. F. Hawthorne and J. J. Miller, J. Am. Chem. Soc., **82**, 500 (1960).

(9) (a) M. F. Hawthorne and J. J. Miller, ibid., **80**, 754 (1958); (b) J. J. Miller and M. F. Hawthorne, ibid., **81**, 4501 (1959).

air. The reaction between decaborane and lithium hydride, sodium or lithium borohydrides proceeds slowly at ether reflux temperatures to yield the same products. To determine the extent of this reaction a propyl ether solution of decaborane was added to a tenfold excess of sodium hydride, and the liberated hydrogen was measured. The ratio of 1.2 moles of hydrogen per mole of reacted decaborane indicated the presence of at least two acidic hydrogens. Decaborane and an excess of Grignard reagents have reacted in a similar manner to give $B_{10}H_{12}(MgX)_2$.[4]

The reactivity of decaboranylsodium has been demonstrated by its reaction with benzyl bromide to prepare benzyldecaborane, $C_6H_5CH_2B_{10}H_{13}$, the same as previously prepared from decaboranylmagnesium chloride and benzyl chloride.[4] Benzyldecaborane reacted with sodium hydride and then with benzyl bromide to give dibenzyldecaborane, $(C_6H_5CH_2)_2B_{10}H_{12}$, in low yield. Because of the limited quantity of dibenzyldecaborane, further reaction with sodium hydride and benzyl bromide to prepare the tribenzyl derivative was not attempted.

Decaboranylsodium and iodine react rapidly to give decaborane, iododecaborane and ethyl iodide after the addition of 0.5 mole of iodine per mole of sodium salt; the addition of a second 0.5 mole per mole of sodium salt gives iododecaborane, ethoxydecaborane and ethoxyiododecaborane. Hawthorne and Miller recently have described a preparation of alkoxydecaboranes using this procedure.[8]

To determine further its similarity to organometallics, decaboranylsodium was treated with acetaldehyde. The crude product obtained was only stable at Dry Ice–acetone temperature. Rapid, exothermic decomposition at warmer temperatures prevented identification. Thus, if any decaboranylmethylcarbinol was formed, its presence could not be confirmed. No success was achieved in attempts to combine the decaboranyl salt with anhydrous acetone to prepare decaboranyldimethylcarbinol, with solid carbon dioxide to prepare decaborane carboxylic acid or with ethyl chloride to prepare ethyldecaborane.

Mass Spectra of Benzyldecaboranes.—The mass spectra of benzyldecaborane and dibenzyldecaborane are presented in Table I. The empirical formulas of the two compounds are quite well demonstrated by these spectra. Parent peaks of 214 and 304, suggesting $B_{10}C_7H_{20}$ and $B_{10}C_{14}H_{26}$, are confirmed by peak intensities of the spectra. The 215 and 305 isotopic peaks (C^{13}) are compatible with seven and fourteen carbons, respectively. Both spectra are also in agreement with ten boron atoms in the ions in the "parent" (those fragments having lost only an electron) area. The most prevalent fragment (m/e 91) is the benzyl ion.

Mass Spectra of Deuteriobenzyldecaboranes.—The monoisotopic fragmentation pattern of the parent group of benzyldecaborane fortunately consists principally of the parent peak, $C_6H_5CH_2$-$B_{10}H_{13}^+$ and essentially no peaks for $C_6H_5CH_2$-$B_{10}H_{13}^+{}_{-n}$ ($n < 6$); thus the effects of deuteration could be easily observed and interpreted. Peaks

TABLE I

PARTIAL MASS SPECTRA OF MONO- AND DIBENZYLDECABORANES AT AN ELECTRON ACCELERATING POTENTIAL OF 70 VOLTS

$C_6H_5CH_2B_{10}H_{13}$		$(C_6H_5CH_2)_2B_{10}H_{12}$	
		306	0.7
215	2.8	305	6.0
214	34.1	304	43.4
213	75.0	303	91.9
212	81.8	302	100.0
211	54.1	301	67.7
210	26.5	300	31.4
209	13.9	299	11.1
208	18.6	298	4.3
207	31.3	297	3.7
206	38.0	296	5.8
205	89.2	295	9.9
204	100.0	294	20.3
203	89.2	293	36.0
202	66.1	292	47.4
201	51.6	291	47.8
200	32.1	290	38.6
199	23.0	289	27.3
198	15.3	288	18.3
197	9.2	287	12.7
196	5.0	286	9.1
195	2.6	285	6.4
194	2.4	284	4.2
91	216.0	283	2.7

for loss of hydrogen do start increasing in intensity with $C_6H_5CH_2B_{10}H_7^+$, but this effect on deuteration calculations is negligible.

The initial step in interpreting the mass spectrum of a partially deuterated benzyldecaborane was to reduce the polyisotopic spectrum to a monoisotopic spectrum with respect to boron, using the naturally occurring ratio of 80% B^{11} to 20% B^{10}. However, it was impractical to reduce the data in this manner in the presence of so many polydeuteriobenzyldecaborane species. Instead, a calculation of per cent. deuteration readily was made. For this calculation the peaks of a deuterated benzyldecaborane were determined for the peaks within the parent group. In the case of deuterated benzyldecaboranes, peak intensities were determined from the maximum m/e peak to the point where the intensities pass through a minimum in intensity, e.g., the peaks 215 to 209 in the C_6H_5-$CH_2B_{10}H_{13}$ spectrum of Table I. This series of intensities then was related to all pertinent isotopic species of $C_6H_5CH_2B_{10}H_{13}^+$. Each of these peak intensities (P_n) was weighted by the number of peaks (n) between the 214 peak intensity (P_0) and the given peak intensity (P_n); e.g., the 212 and 218 peaks would be (P_2) and (P_4), respectively. Then the sum of the weighted peak intensities ($\Sigma n P_n$) divided by the sum of the peak intensities (ΣP_n), plus a boron and carbon isotope correction factor (2.000–0.078), was taken to be the number of deuterium atoms (D) substituted for hydrogens.

$$D = \frac{\Sigma n P_n}{\Sigma P_n} + (2.000 - 0.078)$$

That the benzyl group does not become appreciably deuterated has been demonstrated by the lack

of a strong shift in the fragmentation peaks representing the benzyl group alone and by the ability to replace no more than 13 hydrogens with deuteriums. Under the conditions of this study, deuterium exchanged essentially with hydrogens attached to boron.

The deuteration experiments were undertaken to determine whether or not the acidic hydrogens of decaborane were lost on benzylation. Four hydrogens exchanged rapidly, certainly more than had been anticipated, for if one of the acidic positions had been occupied by a benzyl group, there should remain an odd number of acidic (replaceable) hydrogens. Infrared analysis of tetradeuterated benzyldecaborane then betrayed the exchange of bridge hydrogens for deuteriums. The exchange of decaborane bridge hydrogens with deuterium, using deuterium oxide in basic solvents, subsequently was described by Hawthorne and Miller.[9] An n.m.r. study[10] of the deuteration of decaborane also has been made.

To determine the position of the benzyl group in benzyldecaborane, more complete deuteration was necessary. Benzyldecaborane in ether underwent further exchange with deuterium oxide at an extremely slow rate at room temperature. To hasten the rate of exchange of other than the bridge hydrogens the use of cineole was suggested. N.m.r. evidence indicated that decaborane dissolved in cineole underwent rapid and extensive proton tautomerism.[11] In deuterium oxide and cineole the 13 boron bound hydrogens of benzyldecaborane underwent complete exchange with deuterium at a measurable rate. Decaborane, under similar conditions, underwent extensive hydrolysis.

It is now accepted that the "monoprotic or diprotic" acid behavior of decaborane does not have to be localized at two distinct acid protons upon the decaborane molecule but that the addition of a Lewis base creates reversibly an intermediate wherein bridge protons are released as H^+ ions. The most probable mechanism for this process has been discussed previously.[10] With this background the results of the benzyldecaborane deuteration in cineole can be better understood. In Fig. 1, the logarithms of the number of remaining boron hydrogens is plotted against time in hours. The logarithmic exchange curve is not linear because positionally different hydrogen atoms exchange at different rates. However, this complex curve can be resolved into at least three specifically distinguishable exchange reactions. The first reaction, reducing the number of remaining protons to nine, is compatible with the initial exchange of four bridge hydrogens as reported for decaborane.[9] The rapid bridge hydrogen exchange is followed by an exchange of three other hydrogens and of the final six hydrogens at two different slow rates. The total exchange reaction can be described by the following derived least squares equation

$$H = 4e^{-4t} + 2.9_4e^{-0.9t} + 5.9_8e^{-0.11t}$$

where H is the average number of exchangeable

(10) I. Shapiro, M. Lustig and R. E. Williams, J. Am. Chem. Soc., 81, 838 (1959).

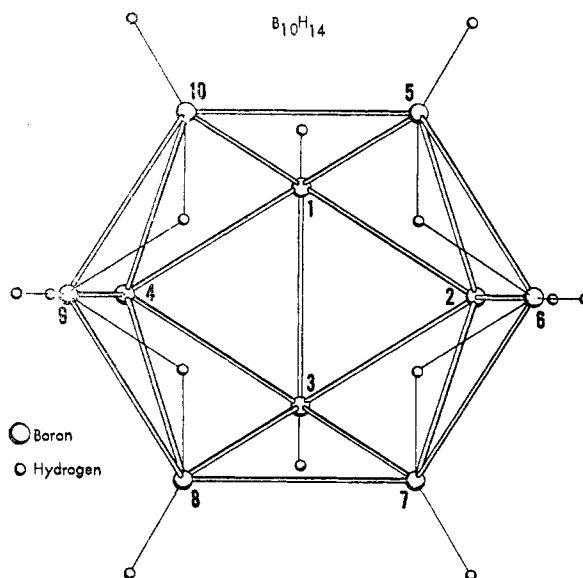(11) R. E. Williams, J. Inorg. and Nucl. Chem., to be published.

Fig. 2.—Decaborane.

hydrogens remaining on boron, t is the time in hours and the rate constant A is greater than 10 moles per hour. The curve does not follow the reaction to completion, for the experiment was halted when the observed amount of $C_7H_7B_{10}D_{13}$ was large enough to show that all the hydrogens were strongly involved in the exchange reaction.

It seems probable that the hydrogen symmetrically opposite to the benzyl group is one of the group of three hydrogens exchanged. Then two other hydrogens must exchange at a rate approximately equivalent to this one. One possible mechanism involves the rearrangement of the 8, 9 and 10 hydrogen atoms with the bridge deuteriums. It has been shown that in decaborane under similar conditions, a rearrangement of bridge hydrogens to adjacent terminal positions occurs.[10] In benzyldecaborane the same thing should happen except that the benzyl group has replaced one of the exchangeable hydrogens.

It might reasonably be asked why the 8, 9 and 10 attached protons are rearranged and not the 5 and 7. The previous n.m.r. work upon decaborane indicates that the positions exchanging most rapidly in descending order are the bridge protons, the 6 and 9; the 5, 7, 8 and 10 and finally the 1, 3 and 2, 4 protons[10] (Fig. 2). It should be noted that the benzyl group seemingly lends some stability to the decaborane molecule; decaborane is less resistant to hydrolysis and yields a more highly fragmented mass spectrum than benzyldecaborane.

As the following n.m.r. discussion will suggest, the benzyl group probably is attached to the 6 boron atom and might reasonably be expected to stabilize the substituted end of the molecule or "ring system" preferentially. Thus the opposed terminal protons, 8, 9, 10 could reasonably be expected to exchange more rapidly than 5 and 7 protons adjacent to the benzyl group or the "inert" 1,3 and 2,4 protons (Fig. 2).

The amount of completely deuterated benzyldecaborane obtained in this experiment is somewhat

higher than would be expected from a homogeneous reaction governed by the presented kinetics or any other investigated homogeneous kinetics system. While the rate constants given here may be somewhat affected by this process, early inflection points should not be altered.

B¹¹ Nuclear Magnetic Resonance Spectrum of Benzyldecaborane.—The B^{11} n.m.r. spectrum of benzyldecaborane prepared from $NaB_{10}H_{13}$ and benzyl chloride has been obtained at 12.8 mc. and is comparable to that of the benzyldecaborane prepared from a Grignard synthesis.[4] This spectrum can be interpreted since the B^{11} n.m.r. spectrum of decaborane has been assigned.[12]

Related work reveals that the substitution of an alkyl group for a hydrogen atom upon a boron atom not only collapses that doublet (C^{12} has no nuclear spin) but in all cases thus far observed, the B^{11} chemical shifts are to lower field. The degree of chemical shift appears to be more a function of the specific boron atom substituted than the size or spatial arrangement of the alkyl group. Examples of this shift to lower field have been observed in the alkyldiboranes,[13] 2,4-dimethylenetetraborane, 1- and 2-alkylpentaborane, 2-alkyldecaborane and others. The B^{11} resonances in triethylboron and tripropylboron are also found at the lowest field of some fifty boron containing compounds thus far observed.[14]

(12) Robert E. Williams and I. Shapiro, *J. Chem. Phys.*, **29**, 677 (1958).

(13) R. E. Williams, H. D. Fisher and C. O. Wilson, *J. Phys. Chem.*, **65**, in press (1961).

(14) T. P. Onak, H. Landesman, R. E. Williams and I. Shapiro, *ibid.*, **63**, 1533 (1959).

In consideration of the above information it is apparent that the spectrum recently published for benzyldecaborane prepared *via* the Grignard method is identical to that prepared from decaboranylsodium and decaborane is substituted at either the one or six positions. Such a spectrum would be expected if one quarter of the 1,3 and 6,9 doublet of the decaborane spectrum were collapsed and shifted to lower field by substitution of an alkyl group (Ref. 4, Fig. 2). Conversely, the one quarter collapse of the 5, 7, 8, 10 doublet would have created a different spectrum and the shift to low field would be more than twice as great as any "alkyl shift" to lower field thus far observed.

The 6-position is preferred to the 1-position for several reasons. Attack of an electron donor upon the 6,9-positions most easily explains the deuteration of decaborane in D_2O–dioxane. Substitution at the 6-position could, as mentioned above, deactivate the decaborane molecule at one end allowing three protons (in addition to the bridge protons) to be readily exchanged. In the products of Lewis base attack upon decaborane, *i.e.*, in $B_{10}H_{12}$-$(NCCH_3)_2$ the Lewis base (acetonitrile) is attached to the 6- and 9-positions.[15] It should be noted that small amounts of other space isomers, if they are present, could not be detected by n.m.r. analysis.

Acknowledgments.—We wish to acknowledge the many constructive suggestions received during the course of this work from Dr. George W. Schaeffer and Dr. Manny Hillman.

(15) J. van der Maass Reddy and W. N. Lipscomb, *J. Am. Chem. Soc.*, **81**, 754 (1959).

The Preparation and Properties of Silyl Methyl Ether[1]

BY BURT STERNBACH AND ALAN G. MACDIARMID[2]

Gaseous SiH_4 and gaseous CH_3OH have been found to react at room temperature in the presence of copper metal catalyst to give methoxysilanes. Reaction occurred in the absence of catalyst if liquid CH_3OH was present. The new compound, SiH_3OCH_3, has been prepared from $SiH_3I·N(CH_3)_3$ and CH_3OH, and its physical properties and a number of its chemical properties have been studied. Using B_2H_6 as a reference Lewis acid, SiH_3OCH_3 has been found to be a weaker Lewis base than $(CH_3)_2O$. Diborane was not a sufficiently strong Lewis acid to differentiate between the relative base strengths of SiH_3OCH_3 and $(SiH_3)_2O$.

In a previous paper[3] it was shown that gaseous CH_3OH would combine with gaseous SiH_4 at room temperature in the presence of copper metal catalyst to yield a mixture of methoxysilanes. No methoxysilane (silyl methyl ether), SiH_3OCH_3, was obtained. In one experiment CH_3OH and SiH_4 were found to combine in the absence of catalyst. The present investigation was carried out for the purpose of determining the exact conditions of reaction of CH_3OH with SiH_4 and for the purpose

(1) This report is based on portions of a thesis to be submitted by Burt Sternbach to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Alfred P. Sloan Research Fellow.

(3) B. Sternbach and A. G. MacDiarmid, *J. Am. Chem. Soc.*, **81**, 5109 (1959).

of preparing and studying SiH_3OCH_3—particularly its base strength with respect to the Lewis acid, B_2H_6.

Experimental

Apparatus.—All work was carried out in a Pyrex glass vacuum system. Melting points were determined by a magnetic plunger apparatus.[4] All temperatures below 0° were measured by an iron–constantan thermocouple, standardized by the National Bureau of Standards. Temperatures above 0° were measured by a mercury-in-glass thermometer standardized by the National Bureau of Standards.

Methanol.—Analytical grade methanol was used. Its purity was checked by means of a vapor pressure determination at 0° (found, 30.0 mm., literature value[5] 29.7 mm.).

(4) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p. 184.

(5) B. Pesce and V. Evdokimoff, *Gazz. chim. ital.*, **70**, 712 (1940).