Isomerization of 1-Bromopentaborane(9) by Base Catalysis[1]

Sir:

The reversible conversion of 1-BrB_5H_8[2] to the previously unknown and far more volatile isomer 2-BrB_5H_8 is catalyzed by hexamethylenetetramine. Also effective is dimethyl ether, but with side reactions qualitatively varying with temperature; one result is a new synthesis of 1-$\text{CH}_3\text{B}_5\text{H}_8$.

The relatively low volatility of 1-BrB_5H_8 would relate to the negative charge at the apex of the B_5H_9 skeleton[3]; and the enhanced B–Br bond polarity would gain effect from a probable molecular packing with the apex bromine atom near to the four basal boron atoms of another molecule. Such packing would be inconvenient for 2-BrB_5H_8. The $\text{CH}_3\text{B}_5\text{H}_8$ isomers show a smaller and opposite difference of volatility.

Syntheses. Direct Al_2Cl_6-catalyzed bromination of B_5H_9 gave exclusively 1-BrB_5H_8,[2] but one experiment without any catalyst (12 hr., warming to 25°) gave a 4% fraction later recognized as 2-BrB_5H_8, with an 82% yield of 1-BrB_5H_8.

Isomerization. Freshly vacuum-sublimed $(\text{CH}_2)_6\text{N}_4$ (*ca.* 100 mg.) and 0.936 mmole of 1-BrB_5H_8 (20 hr., sealed tube, 35°) gave 0.461 mmole of 1-BrB_5H_8 and 0.454 mmole of far more volatile material having the same molecular weight (143.0 *vs.* 142.05 calculated). Hydrolytic analysis of this gave 1.007Br^-, 5.024B(OH)_3, and 10.80H_2 per molecule. These results (and the absence of side reactions) prove the isomer.

Reversal of the isomerization was demonstrated by exposing 78 mg. of pure 2-BrB_5H_8 to $(\text{CH}_2)_6\text{N}_4$ (18 hr., 24°). The yield of 1-BrB_5H_8 was 12 mg. (15%) and the recovery of 2-BrB_5H_8 was 65 mg. (83%).

Physical Properties. As indicated by the data of Tables I and II, the isomers could be separated easily by high-vacuum fractional condensation; melting ranges: 36.5–36.7° for 1-BrB_5H_8; for 2-BrB_5H_8, −56.0 to −55.7°.

Table I. Volatility of Liquid 1-BrB_5H_8
($\text{Log}\,P = 5.0374 + 1.75\log T - 0.0033T - 2420/T$)
($t_{760} = 183.1°$; Trouton constant = 20.9 e.u.)

Temp., °C.	36.5	45.9	50.8	56.0	61.8	70.0
P_{obsd}, mm.	3.63	6.03	7.80	10.12	13.31	19.50
P_{calcd}, mm.	3.63	6.05	7.79	10.11	13.37	19.50

Table II. Volatility of Liquid 2-BrB_5H_8
($\text{Log}\,P = 5.8959 + 1.75\log T - 0.0045T - 2367/T$)
($t_{760} = 139.6°$; Trouton constant = 21.16 e.u.)

Temp., °C.	17.80	30.85	34.45	38.50	52.75	59.60
P_{obsd}, mm.	5.82	12.20	14.80	18.35	36.9	50.0
P_{calcd}, mm.	5.80	12.24	14.82	18.31	36.7	50.0

The Dimethyl Ether Reactions. A reaction occurring during 3 days at 0° can be summarized as follows, with stoichiometry in millimoles.

$$\begin{array}{lclclclclcl}
1\text{-BrB}_5\text{H}_8 & + & (\text{CH}_3)_2\text{O} & \longrightarrow & \text{B}_5\text{H}_9 & + & \text{H}_2 & + & \text{CH}_3\text{Br} & + & 2\text{-BrB}_5\text{H}_8 \; + \\
2.437 & & 2.435 & & 0.28 & & 0.02 & & 0.31 & & 0.606 \\
-1.237 & & -2.135 & & \multicolumn{7}{r}{\text{oily residue } (\text{CH}_3\text{OB}_5\text{H}_7\text{Br})_x} \\
\cline{1-1}\cline{3-3}
1.200 & & 0.300 & & & & & & & &
\end{array}$$

However, a 48-hr. run at 24° gave different results.

$$\begin{array}{lclclclclcl}
1\text{-BrB}_5\text{H}_8 & + & (\text{CH}_3)_2\text{O} & \longrightarrow & \text{B}_5\text{H}_9 & + & \text{H}_2 & + & \text{CH}_3\text{Br} & + & 2\text{-BrB}_5\text{H}_8 \; + \\
3.275 & & 3.377 & & 1.135 & & 0.035 & & 1.434 & & 0.535 \\
-1.125 & & -2.000 & & \multicolumn{7}{c}{\underset{0.27}{\text{B(OCH}_3)_3} + \underset{\text{(trace)}}{1\text{-CH}_3\text{B}_5\text{H}_8} \; +} \\
\cline{1-1}\cline{3-3}
2.150 & & 1.377 & & & & & & & & \\
 & & & & \multicolumn{7}{r}{\underset{\text{(oily residue)}}{[(\text{CH}_3\text{O})_3\text{B}_{17}\text{H}_{15}\text{Br}]_x}}
\end{array}$$

Then a 30-hr. process at 38° destroyed all BrB_5H_8 but gave a fair yield of 1-$\text{CH}_3\text{B}_5\text{H}_8$ (characteristic infrared peaks, 1225, 1229, and 1232 cm.$^{-1}$; no appearance of 2-$\text{CH}_3\text{B}_5\text{H}_8$ peaks at 1106, 1111, and 1154 cm.$^{-1}$); stoichiometry

$$\begin{array}{lclclclclcl}
1\text{-BrB}_5\text{H}_8 & + & (\text{CH}_3)_2\text{O} & \longrightarrow & \text{H}_2 & + & \text{CH}_4 & + & \text{CH}_3\text{Br} & + & 1\text{-CH}_3\text{B}_5\text{H}_8 \; + \\
0.995 & & 1.01 & & 0.72 & & 0.72 & & 0.31 & & 0.29 \\
 & & & & \multicolumn{7}{r}{\text{residue } (\text{CH}_3\text{B}_5\text{BrO}_{1.5})_x}
\end{array}$$

Comparison of the latter two experiments suggests that $\text{B(OCH}_3)_3$ served as a methylating agent. One may speculate whether the unknown $\text{CH}_3\text{OB}_5\text{H}_8$ was an unstable intermediate.

Methylpentaboranes. The $(\text{CH}_3)_2\text{O}$ reactions yielded 1-$\text{CH}_3\text{B}_5\text{H}_8$ but no 2-$\text{CH}_3\text{B}_5\text{H}_8$; apparently catalysts were lacking. The isomerization is irreversible, as shown by full recovery of 2-$\text{CH}_3\text{B}_5\text{H}_8$ which had remained with 2,6-$(\text{CH}_3)_2\text{C}_5\text{H}_3\text{N}$ for 5 days at 27°—conditions causing complete conversion of 1-CH_3-

Table III. Infrared Spectra of Pentaborane Derivatives

1-BrB_5H_8	2-BrB_5H_8	1-$\text{CH}_3\text{B}_5\text{H}_8$	2-$\text{CH}_3\text{B}_5\text{H}_8$
. . .	. . .	2975(0.54)	2975 (1.5)
. . .	. . .	2940 (0.65)	. . .
. . .	. . .	2931 (2.5)	2930 (0.86)
. . .	. . .	2862 (1.3)	2861 (0.32)
2622 (7.6)	2622 (7.2)	2600 (19)	2600 (19)
2480 (0.36)	2500 (0.41)	. . .	2440 (0.12)
. . .	. . .	1996 (0.13)	1940 (0.27)
1850 (1.8)	1800 (0.58)	1840 (2.0)	1855 (0.93)
1804 (0.89)	1718 (0.24)	1790 (1.3)	1811 (0.97)
1625R (0.91)	1625R (0.46)	. . .	. . .
1602Q (1.10)	1603Q (0.87)	1629 (0.34)	1600 (0.17)
1585P (0.56)	1584P (0.43)	. . .	. . .
1442 (2.3)	1393 (5.5)	1418 (2.9)	1435 (4.4)
1386 (1.6)	1342 (0.81)	1386 (2.9)	1386 (4.9)
. . .	. . .	1330R (0.82)	1330R (1.5)
		1321Q (1.30)	1315Q (1.6)
. . .	. . .	1314P (0.46)	1310P (1.3)
		1262 (0.32)	. . .
. . .	. . .	1232Q (2.1)	1154 (1.4)
		1229 (1.9)	
1198 (1.17)	. . .	1225 (1.8)	1111 (0.65)
1152 (2.5)	1120 (0.93)	1168 (0.20)	1106 (0.68)
1065 (0.82)	1029	1044R (0.28)	1036
1060 (0.90)	1025 } (3.8)	1036Q (0.52)	1031 } (0.74)
1055 (0.96)	1020	1026P (0.28)	1026
908 (2.2)	887	907 (5.1)	985 (0.17)
861 (1.1)	883 } (3.5)		890 (4.3)
	879		
		802 (0.70)	
. . .	856 (1.55)	797 (0.76)	. . .
		791 (0.70)	
764	764		
762 } (1.64)	762 } (0.63)	. . .	. . .
755	760		
648 (2.8)	639 (2.9)	643 (5.1)	643 (2.8)

---

[1] Supported by the Office of Naval Research through Contract No. Nonr-228(13). Reproduction in whole or in part is permitted for any purpose of the U. S. Government.

[2] T. Onak and G. B. Dunks, *Inorg. Chem.*, 3, 1060 (1964), and earlier references there cited.

[3] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p. 110.

B_5H_8.[4] This isomerization, when catalyzed in the vapor phase by $(CH_3)_2NB_2H_5$, does not depend upon transfer of BH_3 groups, for only 4% of a sample of 1-$CH_3B_5H_8$ isomerized during a one-boron B^{10}–B^{11} exchange with $(CH_3)_2NB_2H_5$ at 100°. This and other boron isotopic exchanges will be described more fully elsewhere.

For the volatility of 2-$CH_3B_5H_8$ (m.p. −55°), $\log P = 6.889 + 1.75 \log T - 0.0065T - 2212/T$ (accuracy as in Table II; example, 19.0 mm. at 0°); thus it is roughly half as volatile as 1-$CH_3B_5H_8$ (34 mm. at 0°).[5]

Infrared Spectra. The infrared peaks shown in Table III were recorded accurately by the Beckman IR7 instrument. After each frequency (cm.$^{-1}$) the relative intensity $k = (100/P) \log I_0/I$ (path 10 cm.; pressure P in mm. at 25°) is given in parentheses. Assignments are omitted because they would be either obvious or controversial.

---

[4] T. P. Onak, *J. Am. Chem. Soc.*, **83**, 2584 (1961).

[5] G. E. Ryschkewitsch, *et al.*, *Inorg. Chem.*, **2**, 891 (1963).

Anton B. Burg, Jagtar S. Sandhu
Department of Chemistry
University of Southern California
Los Angeles, California 90007

Received May 27, 1965

The Tetralithium Derivative of Propyne and Its Use in Synthesis of Polysilicon Compounds

Sir:

Polymetalation of 1-alkynes has been observed recently in several laboratories. Eberly and Adams have reported the reaction of 1-butyne with excess alkyllithium reagent to form a dilithium derivative.[1] We find that propyne reacts with *n*-butyllithium in hexane to form a tetralithium compound, C_3Li_4, perhaps admixed with some C_3Li_3H. Derivatization of the polylithiated propyne with trimethylchlorosilane leads to a mixture consisting mostly of the tri- and tetrasilyl derivatives I and II.

$$\underset{\text{I}}{[(CH_3)_3Si]_2CH{-}C{\equiv}CSi(CH_3)_3} \qquad \underset{\text{II}}{[(CH_3)_3Si]_2C{=}C{=}C[Si(CH_3)_3]_2}$$

In a typical experiment propyne (10.4 g., 0.20 mole) was added slowly to 500 ml. of 1.6 *M* *n*-butyllithium in hexane, and the red-brown solution was heated to reflux for 16 hr. During this time butane was fractionated from the mixture through a short column, a total of 3.5 equiv. being recovered. Trimethylchlorosilane (135 ml., 1.0 mole) was then added and the mixture was refluxed again for 16 hr., after which time 150 ml. of 1,2-dimethoxyethane was added and refluxing was continued for an additional 2 hr. The precipitated lithium chloride was filtered off and the solvents were removed by distillation. The residue was separated by fractional distillation under vacuum, yielding 27 g. of I (b.p. 80–85°, 19 torr) and 17 g. of II (b.p. 119–121°, 19 torr) (50 and 25%, respectively, based on propyne). *Anal.* Calcd. for $C_{12}H_{28}Si_3$ (compound I): C, 56.21; H, 11.01; Si, 32.80; mol. wt., 256. Found: C, 56.36; H, 10.88; Si, 32.89; mol. wt., 256.[2] Calcd. for $C_{15}H_{36}Si_4$ (compound II): C, 54.77; H, 11.04; Si, 34.19; mol. wt., 328. Found: C, 54.22; H, 11.37; Si, 34.71; mol. wt., 328.[2]

In an experiment in which 6 equiv. of *n*-butyllithium was used for each equivalent of propyne, 3.85 equiv. of butane was recovered after 2-hr. reflux, indicating that the propyne was almost completely converted to the tetralithium derivative. Further refluxing for an additional 16 hr. led to the evolution of no more butane. Unchanged *n*-butyllithium was still present after this time, as shown by the isolation of 1.2 equiv. of *n*-butyltrimethylsilane (along with compounds I and II) upon derivatization with trimethylchlorosilane.

Compound I was identified as 1,3,3-tris(trimethylsilyl)propyne by its infrared and n.m.r. spectra. It shows a strong infrared band at 2180 cm.$^{-1}$ (C≡C stretch)[3] and no absorption in the region diagnostic for acetylenic C–H stretching (near 3300 cm.$^{-1}$).[3] The proton n.m.r. spectrum shows sharp resonances at τ 8.98, 9.90, and 9.92, with relative intensities 1:18:9, respectively, in agreement with the proposed structure. Thermolysis or photolysis effected substantially complete conversion of I to its allenic isomer 1,1,3-tris(trimethylsilyl)allene, which was separated by preparative gas chromatography. This isomer, which also had an analysis in agreement with the formula $C_{12}H_{28}Si_3$, had no infrared absorption in the acetylenic region, but showed a weak band at 3160 cm.$^{-1}$ (allenic C–H) and a strong band at 1910 cm.$^{-1}$ (C=C=C antisymmetric stretching).[4] The n.m.r. spectrum showed resonances at τ 5.90 (allenic H), 9.90, and 9.93 in the ratio 1:18:9.

The properties of the tetrasilyl derivative II show that it must also have an allenic structure. It shows no acetylenic C–C stretching absorption in the infrared but exhibits a strong band at 1890 cm.$^{-1}$ in the allenic region. The proton n.m.r. spectrum contains only a single sharp peak at τ 9.90.

Compound I is also somewhat acidic, reacting with *n*-butyllithium to form a monolithium derivative, which is converted to II in high yield upon treatment with trimethylchlorosilane. Isomerization from the acetylenic to the allenic structure could take place during formation of the lithium compound, but it seems more likely that it occurs during the reaction with trimethylchlorosilane. The formation of the unknown tetrakis(trimethylsilyl)propyne would be strongly hindered sterically, and so condensation with the fourth trimethylsilyl group may take place only after isomerization to the allenic form. Using similar arguments based on steric effects, Gilman and Aoki have explained the formation of poly(triphenylsilyl)acetylenes and -allenes, by different but related reactions.[5]

Polylithiation appears to be a general reaction for 1-alkynes bearing α-hydrogen atoms. 1-Butyne, 1-hexyne, and 1-octyne have all been observed to form polylithium derivatives. When 1-butyne is treated with excess *n*-butyllithium followed by trimethylchlorosilane under conditions similar to those described above, a mixture of the two isomers 1,1,3-tris(trimethylsilyl)-1,2-butadiene and 1,3,3-tris(trimethyl-

---

[1] K. C. Eberly and H. E. Adams, *J. Organometal. Chem.*, **3**, 165 (1965).

[2] Molecular weights by mass spectroscopy using a C.E.C. Model 21-101C spectrometer with an inlet temperature of 200°.

[3] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen and Co., London, 1958, pp. 58, 59.

[4] J. H. Wotiz and D. E. Marcuso, *J. Org. Chem.*, **22**, 207 (1957); L. J. Bellamy, ref. 3, pp. 61, 62.

[5] H. Gilman and D. Aoki, *J. Organometal. Chem.*, **2**, 44 (1964).