

Isomerization of 1-Bromopentaborane(9) by Base Catalysis¹

Sir:

The reversible conversion of 1-BrB₅H₈² to the previously unknown and far more volatile isomer 2-BrB₅H₈ 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-CH₃B₅H₈.

The relatively low volatility of 1-BrB₅H₈ would relate to the negative charge at the apex of the B₅H₉ skeleton³; 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-BrB₅H₈. The CH₃B₅H₈ isomers show a smaller and opposite difference of volatility.

Syntheses. Direct Al₂Cl₆-catalyzed bromination of B₅H₉ gave exclusively 1-BrB₅H₈,² but one experiment without any catalyst (12 hr., warming to 25°) gave a 4% fraction later recognized as 2-BrB₅H₈, with an 82% yield of 1-BrB₅H₈.

Isomerization. Freshly vacuum-sublimed (CH₂)₆N₄ (ca. 100 mg.) and 0.936 mmole of 1-BrB₅H₈ (20 hr., sealed tube, 35°) gave 0.461 mmole of 1-BrB₅H₈ 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 10.80H₂ 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-BrB₅H₈ to (CH₂)₆N₄ (18 hr., 24°). The yield of 1-BrB₅H₈ was 12 mg. (15%) and the recovery of 2-BrB₅H₈ 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-BrB₅H₈; for 2-BrB₅H₈, –56.0 to –55.7°.

Table I. Volatility of Liquid 1-BrB₅H₈
(Log P = 5.0374 + 1.75 log T – 0.0033T – 2420/T)
(t₇₆₀ = 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-BrB₅H₈
(Log P = 5.8959 + 1.75 log T – 0.0045T – 2367/T)
(t₇₆₀ = 139.6°; Trouton constant = 21.16 e.u.)

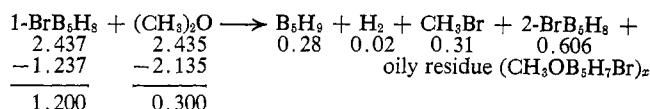
| Temp., °C. | 17.80 | 30.85 | 34.45 | 38.50 | 52.75 | 59.60 |
|--------------------------|-------|-------|-------|-------|-------|-------|
| P _{obsd} , mm. | 5.82 | 12.20 | 14.80 | 18.35 | 36.9 | 50.0 |
| P _{calcd} , mm. | 5.80 | 12.24 | 14.82 | 18.31 | 36.7 | 50.0 |

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

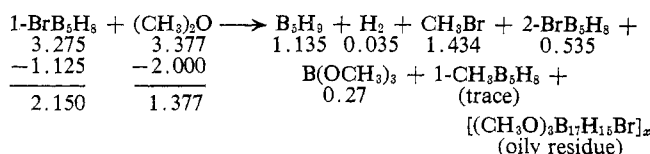
(1) Supported by the Office of Naval Research through Contract No. Nonr-228(13). Reproduction in whole or in part is permitted for any purpose of the U. S. Government.

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

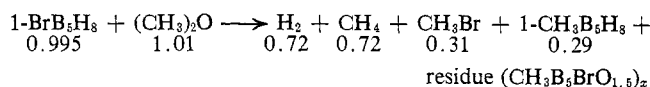
(3) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p. 110.



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



Then a 30-hr. process at 38° destroyed all BrB₅H₈ but gave a fair yield of 1-CH₃B₅H₈ (characteristic infrared peaks, 1225, 1229, and 1232 cm.^{–1}; no appearance of 2-CH₃B₅H₈ peaks at 1106, 1111, and 1154 cm.^{–1}); stoichiometry



Comparison of the latter two experiments suggests that B(OCH₃)₃ served as a methylating agent. One may speculate whether the unknown CH₃OB₅H₈ was an unstable intermediate.

Methylpentaboranes. The (CH₃)₂O reactions yielded 1-CH₃B₅H₈ but no 2-CH₃B₅H₈; apparently catalysts were lacking. The isomerization is irreversible, as shown by full recovery of 2-CH₃B₅H₈ which had remained with 2,6-(CH₃)₂C₅H₃N for 5 days at 27°—conditions causing complete conversion of 1-CH₃B₅H₈.

Table III. Infrared Spectra of Pentaborane Derivatives

| 1-BrB ₅ H ₈ | 2-BrB ₅ H ₈ | 1-CH ₃ B ₅ H ₈ | 2-CH ₃ B ₅ 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) |

B₅H₈.⁴ This isomerization, when catalyzed in the vapor phase by (CH₃)₂NB₂H₅, does not depend upon transfer of BH₃ groups, for only 4% of a sample of 1-CH₃B₅H₈ isomerized during a one-boron B¹⁰-B¹¹ exchange with (CH₃)₂NB₂H₅ at 100°. This and other boron isotopic exchanges will be described more fully elsewhere.

For the volatility of 2-CH₃B₅H₈ (m.p. -55°), log *P* = 6.889 + 1.75 log *T* - 0.0055*T* - 2212/*T* (accuracy as in Table II; example, 19.0 mm. at 0°); thus it is roughly half as volatile as 1-CH₃B₅H₈ (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).

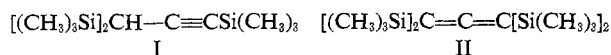
(5) G. E. Ryschkewitsch, *et al.*, *Inorg. Chem.*, **2**, 891 (1963).

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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 alkyl-lithium reagent to form a dilithium derivative.¹ We find that propyne reacts with *n*-butyllithium in hexane to form a tetralithium compound, C₃Li₄, perhaps admixed with some C₃Li₃H. Derivatization of the poly-lithiated propyne with trimethylchlorosilane leads to a mixture consisting mostly of the tri- and tetrasilyl derivatives I and II.



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 C₁₂H₂₈Si₃ (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.

(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°.

for C₁₅H₃₆Si₄ (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 C₁₂H₂₈Si₃, 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

Polyolithiation 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 polyolithium 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-

(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).