CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE
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The Hydroboration of Some Unsaturated Organosilicon Compounds

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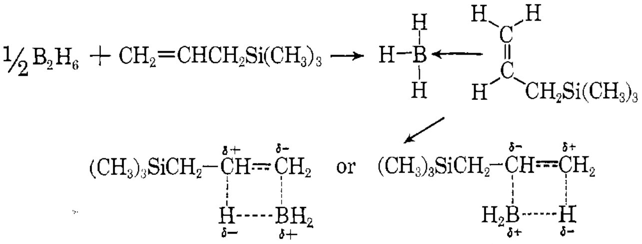
The hydroboration of allyltrimethylsilane resulted in the exclusive formation of tris-(γ-trimethylsilylpropyl)-borane. The direction of addition of the B–H linkages to the allylsilane was proven by oxidation of the borane obtained to give 3-trimethylsilylpropanol-1 as the only product alcohol. A possible explanation for this observed direction of addition is discussed. Trimethylvinylsilane was hydroborated and the product treated with methanol to produce a 59:41 mixture of $(CH_3)_3SiCH(CH_3)B(OCH_3)_2$ and $(CH_3)_3SiCH_2CH_2B(OCH_3)_2$. This mixture was converted to a mixture of the corresponding dichloroboranes. Treatment of the latter with aniline and pyrolysis of the product resulted in B-tris-(trimethylsilylethyl)-N-triphenylborazine.

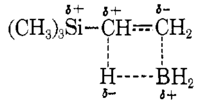
Several years ago we investigated the hydroboration of trimethylvinylsilane.[2] We have now hydroborated allyltrimethylsilane and oxidized the resulting triorganoborane, $[(CH_3)_3SiC_3H_6]_3B$, in order to determine the direction of addition of the B–H linkage to an olefinic silane in which the silicon atom is not directly attached to an olefinic carbon atom. Oxidation of the tris-(trimethylsilylpropyl)-borane obtained resulted in only one of the two possible silyl-substituted alcohols, 3-trimethylsilylpropanol-1, $(CH_3)_3SiCH_2CH_2CH_2OH$. Thus the borane formed in the hydroboration reaction was $[(CH_3)_3SiCH_2CH_2CH_2]_3B$.

This observed direction of addition can be understood if one considers Brown's four-center hydroboration mechanism[3] and the distribution of charge in the transition state. The two possible modes of addition in the present case are

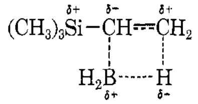


I II

The relative stability of I and II, and hence the direction of addition, can be assessed in terms of the carbonium ion character of I and II. I, as an incipient secondary carbonium ion, would be expected to be favored over the incipient primary carbonium ion, II, when the silyl group is not directly adjacent to the olefinic linkage.[4] However, when, as in the case of trimethylvinylsilane, the silicon atom is directly adjacent to the double bond, then other factors become important. In the case of trimethylvinylsilane, hydroboration resulted in a triorganoborane in which the β-trimethylsilylethyl and α-trimethylsilylethyl groups were present in *ca.* 2:1 ratio. Hydroboration to a lesser degree of substitution suggested that the directive effects in the hydroboration of trimethylvinylsilane favored the α-trimethylsilylethyl structure.[2] Here one may compare four-membered transition states III and IV. Again,



III



IV

one might expect the incipient secondary carbonium ion, III, to be more stable than the primary one, IV. However, another factor, the adjacent electropositive silicon atom ($Si^{\delta+}$ because of the intrinsic $Si^{\delta+}-C^{\delta-}$ bond polarity resulting from the electronegativity difference $\chi_C - \chi_{Si} \cong 2.5 - 1.9 \cong 0.6$) is of importance. In III one then has two adjacent partial positive charges, an unstable situation in terms of resonance theory; in IV the Si and C are separated from one another as shown, and hence IV is favored. Thus the direction of addition which gives the α-trimethylsilyl structure is favorable until steric factors become important and produce a greater extent of B–H addition in the opposite direction.

This principle, the reluctance of the electropositive silicon atom to tolerate an adjacent partial or full positive charge in its organic derivatives, appears to be a general one in organosilicon chemistry. For example, the addition of hydrogen iodide and hydrogen chloride to trimethylvinylsilane to give $(CH_3)_3SiCH_2CH_2X$ and also the direction of the mercuration of trimethylvinylsilane can be understood in these terms.[5] A number of rearrangements of organosilicon compounds which occur under conditions favorable for the formation of carbonium ions can be explained using this rule, as in eq. 1[6] and 2.[7]

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(2) D. Seyferth, *J. Am. Chem. Soc.*, **81**, 1844 (1959).

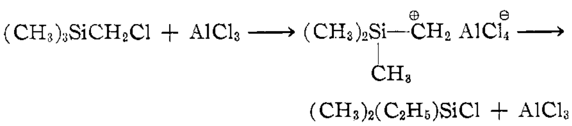
(3) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p. 121.

(4) See, for instance, J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1956, pp. 218–219, and D. J. Cram and G. S. Hammond, "Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1959, pp. 336–337, for a discussion of the direction of addition of polar electrophilic reagents to olefinic double bonds in terms of the stabilities of the possible intermediate carbonium ions.

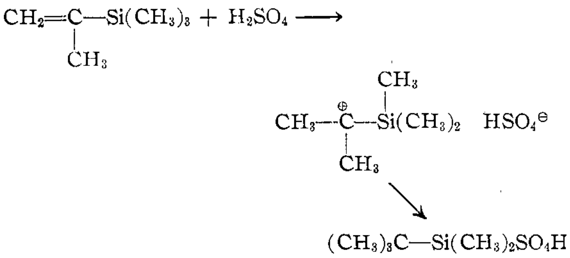
(5) D. Seyferth, "Vinyl Compounds of Metals," in Vol. III of "Progress in Inorganic Chemistry," F. A. Cotton, Ed., Interscience Publishers, New York, N. Y., pp. 132–137.

(6) F. C. Whitmore, L. H. Sommer, and J. R. Gould, *J. Am. Chem. Soc.*, **69**, 1976 (1947).

(7) L. H. Sommer and F. J. Evans, *ibid.*, **76**, 1186 (1954).



$$(CH_3)_3SiCH_2Cl + AlCl_3 \longrightarrow (CH_3)_2\underset{\displaystyle CH_3}{\underset{|}{Si}}-\overset{\oplus}{C}H_2\ AlCl_4^{\ominus} \longrightarrow (CH_3)_2(C_2H_5)SiCl + AlCl_3 \quad (1)$$



$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}-Si(CH_3)_3 + H_2SO_4 \longrightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\oplus}{C}}}-\overset{\displaystyle CH_3}{\overset{|}{Si}}(CH_3)_2\ \ HSO_4^{\ominus} \quad (2)$$

$$\searrow\ (CH_3)_3C-Si(CH_3)_2SO_4H$$

Mikhailov and Shchegoleva[8] have reported the displacement of isobutylene from triisobutylborane by allyltrimethylsilane to give $[(CH_3)_3SiCH_2CH_2CH_2]_3B$ in 62% yield. Such reactions are presumed to proceed by an elimination–addition sequence,[9] hence, in essence the hydroboration of allyltrimethylsilane also is involved in this example. However, these authors assumed, but did not prove, the structure of the product borane.

We have reported the hydroboration of trimethylvinylsilane using an excess of diborane source to produce a mixture of mostly mono- and disubstituted silyl-substituted boranes.[2] We have now used this general procedure in an alternate route to silyl-substituted borazines as shown by the equations

$$(CH_3)_3SiCH{=}CH_2 \xrightarrow{B_2H_6} \xrightarrow{CH_3OH}$$

$$(CH_3)_3Si(C_2H_4)B(OCH_3)_2 \xrightarrow{PCl_5} (CH_3)_3Si(C_2H_4)BCl_2 \xrightarrow{C_6H_5NH_2}$$

$$(CH_3)_3Si(C_2H_4)B(NHC_6H_5)_2 \xrightarrow{340°} [(CH_3)_3Si(C_2H_4)BNC_6H_5]_3$$

Oxidation of a portion of the trimethylsilylethyldimethoxyborane and gas chromatographic analysis of the alcohols produced indicated that a 59:41 mixture of $(CH_3)_3SiCH(CH_3)B(OCH_3)_2$ and $(CH_3)_3SiCH_2CH_2B(OCH_3)_2$ was present. This is in good agreement with previous results.[2] This route to trimethylsilylethyl-substituted borazines is much less practical than the alternate route investigated by us, addition of organosilicon hydrides to B-trivinyl-N-triphenylborazine,[10] and no further work in this direction is contemplated.

Experimental[11]

Hydroboration of Allyltrimethylsilane.—To a mixture of 18.9 g. (0.165 mole) of allyltrimethylsilane and 1.25 g. (0.033 mole) of $NaBH_4$ in 80 ml. of tetrahydrofuran (THF) at 0° was added slowly with stirring 6.23 g. (0.044 mole) of $BF_3 \cdot O(C_2H_5)_2$ in 10 ml. of THF. The reaction mixture was stirred at room temperature for 3 hr., then 150 ml. of pentane and 60 ml. of water were added. The organic layer was separated, dried, and distilled to remove volatiles at a bath temperature of 50° (0.1 mm.). The colorless liquid residue was separated from a small amount of solid. Eleven grams (70%) of air-sensitive liquid was obtained in this manner. This product, assumed to be $[(CH_3)_3SiCH_2CH_2CH_2]_3B$, was characterized by oxidation to the organosilicon alcohol.

To 10.7 g. of the liquid obtained above in 150 ml. of THF was added 0.031 mole of NaOH (as a 3 M solution) and subsequently 12.6 g. of 30% H_2O_2. The temperature was maintained at 20–30°. The resulting mixture was stirred at room temperature for 1 hr. and then 200 ml. of ether was added. The organic layer was dried and distilled to give 11.0 g. (92.5%) of $(CH_3)_3SiCH_2CH_2CH_2OH$, b.p. 82° (21 mm.), $n^{25}D$ 1.4273; lit.[12] b.p. 82° (24 mm.), $n^{20}D$ 1.4290. Gas chromatography (20% Dow Corning 550 silicone fluid on Chromosorb P, jacket temperature 70°, 15 p.s.i. He) showed that only one component (retention time 15 min.) was present.

Anal. Calcd. for $C_6H_{16}OSi$: C, 54.48; H, 12.19. Found: C, 54.52; H, 12.42.

The other possible isomeric trimethylsilylpropanol, $(CH_3)_3SiCH_2CH(OH)CH_3$, was prepared,[13] and its retention time and n.m.r. spectrum compared with the alcohol obtained above. Under comparable conditions the retention time of $(CH_3)_3SiCH_2CH(OH)CH_3$ was 6.4 min. The n.m.r. spectra[14] proved the difference in structure conclusively.

$(CH_3)_3SiCH_2CH(OH)CH_3$ (56 mg./200 μl.): singlet at *ca.* 0 p.p.m. $[(CH_3)_3Si]$; doublets (1 H each) at 0.75 and 0.86 p.p.m. (CH_2 adjacent to Si); doublet (3 H) at 1.15 p.p.m. (J = 6.0 c.p.s.) (terminal CH_3 split by adjacent CH); singlet (1 H) at 2.97 p.p.m. (OH, as shown by shift downfield on addition of a few drops of pyridine); complex multiplet (1 H) centered at 3.93 p.p.m. (CH bearing OH substituent).

$(CH_3)_3SiCH_2CH_2CH_2OH$ (oxidation product obtained above) (100 mg./250 μl.): singlet at *ca.* 0 p.p.m. $[(CH_3)_3Si]$; complex multiplet from 0.3 to 0.8 p.p.m. (2 H) (CH_2 adjacent to Si); complex multiplet (2 H) from 1.20 to 1.80 p.p.m. (middle CH_2); triplet (2 H) at 3.48 p.p.m. (CH_2 adjacent to OH); singlet (1 H) at 4.13 p.p.m. (OH, as shown by shift downfield on addition of pyridine).

Preparation of Trimethylsilylethyldimethoxyborane.—A solution of diborane in 600 ml. of THF was prepared under nitrogen from 0.4 mole of $NaBH_4$ and 0.9 mole of $BF_3 \cdot O(C_2H_5)_2$ by the procedure of Brown.[15] To this solution was added dropwise 12 g. (0.12 mole) of trimethylvinylsilane in 50 ml. of THF at 0°. The reaction mixture was maintained at 45° for 4 hr., cooled to 0° again, and treated cautiously with 100 ml. of CH_3OH. Distillation of the solvent left a liquid residue, which was fractionally distilled to give: (a) 8.6 g. (41%), b.p. 65–79° (21 mm.); (b) 2.7 g., boiling range 87° at 21 mm. to 89° at 6 mm.; (c) 3.7 g., residue. Fraction (a) was the desired $(CH_3)_3Si(C_2H_4)B(OCH_3)_2$.

Anal. Calcd. for $C_7H_{19}O_2BSi$: C, 48.28; H, 11.00; B, 6.21. Found: C, 48.04; H, 10.72; B, 5.86.

Oxidation with alkaline hydrogen peroxide, using essentially the procedure described above, and gas chromatographic analysis of the alcohols produced showed the presence of a mixture containing 59% $(CH_3)_3SiCH(OH)CH_3$ and 41% $(CH_3)_3SiCH_2CH_2OH$. Gas chromatographic analyses of mixtures of these alcohols have been described by us previously.[2]

Preparation of B-Tris-trimethylsilylethyl-N-triphenylborazine. To 8.1 g. (0.047 mole) of mixed α- and β-trimethylsilylethyldimethoxyborane was added under nitrogen in small portions 19 g. (0.093 mole) of PCl_5. The resulting mixture was stirred at room temperature for a short while and then refluxed gently for 3 hr. Distillation gave: (a) 13.4 g., boiling range 34–44° (30–40 mm.); (b) 5.4 g. of liquid of b.p. 60–63° (30 mm.). Fraction b was not

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[8] B. M. Mikhailov and T. A. Shchegoleva, *Izvest. Akad. Nauk SSSR, Otd. Khim. Nauk*, 546 (1959).

[9] Reference 3, p. 150.

[10] D. Seyferth and M. Takamizawa, *Inorg. Chem.*, **2**, 731 (1963).

[11] All reactions were carried out in an atmosphere of prepurified nitrogen. Analyses by Dr. S. M. Nagy (M.I.T.) and the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[12] L. H. Sommer, R. E. Van Strien, and F. C. Whitmore, *J. Am. Chem. Soc.*, **71**, 3056 (1949).

[13] F. C. Whitmore, L. H. Sommer, J. R. Gould, and R. E. Van Strien, *ibid.*, **69**, 1551 (1947).

[14] N.m.r. spectra were recorded in carbon tetrachloride solution using a Varian Associates A60 n.m.r. spectrometer. Chemical shifts are given in p.p.m. downfield from tetramethylsilane.

[15] Reference 3, p. 94.

analyzed, but its ready flammability on exposure to air suggested that it was the desired $(CH_3)_3Si(C_2H_4)BCl_2$ (63.3% yield).

To 5.3 g. of this chloroborane (0.029 mole) in 25 ml. of toluene under nitrogen at −40° was added slowly during 1 hr. 10.8 g. (0.108 mole) of aniline in 40 ml. of toluene. Subsequently 2 ml. of triethylamine was added. The reaction mixture was allowed to warm to room temperature, then was stirred for 1 hr. and for another hour at 70°. The precipitated solids (9.0 g.) were filtered, and the filtrate was distilled to give: (a) 4.5 g., b.p. 128–132° (0.03 mm.), presumed to be $(CH_3)_3Si(C_2H_4)B(NHC_6H_5)_2$; (b) 0.65 g., b.p. 160–170° (0.02 mm.); (c) 1.10 g., residue. Fraction (a) was pyrolyzed at 320–340° under nitrogen in a Claisen distilling flask during 8 hr. A highly viscous liquid residue remained. Methanol was added. After this mixture had stood overnight, 0.82 g. of white, crystalline solid had formed. Several recrystallizations from ether–methanol gave crystalline fractions melting at 132–133° and at 139–146°. The former fraction was analyzed.

Anal. Calcd. for $C_{33}H_{54}N_3B_3Si_3$: C, 65.02; H, 8.93. Found: C, 65.35; H, 8.94.

The infrared spectrum of this fraction was almost identical with that of $[(CH_3)_3SiCH_2CH_2BNC_6H_5]_3$,[10] showing bands due to the trimethylsilyl group at 1250, 832, 860, and 740 cm.$^{-1}$ and to the borazine ring around 1385 cm.$^{-1}$.

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CONTRIBUTION FROM NOYES CHEMICAL LABORATORY,
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Infrared and Nuclear Magnetic Resonance Spectra of Methyltin Compounds

BY THEODORE L. BROWN AND GEORGE L. MORGAN

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The infrared and n.m.r. spectra of a number of methyltin compounds containing tin–tin bonds have been studied. Polydimethyltin, $[Sn(CH_3)_2]_x$, prepared from the reaction of dimethyltin dichloride and sodium in liquid ammonia, consists of linear chains containing from 12 to 20 catenated tin atoms. A second form of polydimethyltin has been characterized as possessing a cyclic, six-membered ring of tin atoms (dodecamethylcyclohexatin). Observation of the ^{117}Sn and ^{119}Sn–proton couplings reveals that increasing catentation results in a decrease in J_{Sn-CH_3} and an increase in $J_{Sn-Sn-CH_3}$. An empirical relationship between J_{Sn-CH_3} and both the symmetric and asymmetric tin–carbon stretching modes for a series of methyltin compounds is proposed, employing data taken from the literature. The infrared and n.m.r. data for hexamethylditin and linear polydimethyltin fit the empirical relationship.

This paper reports the results of an investigation of some methyltin compounds containing tin–tin bonds. Although catenated organotin compounds have been known since the early work of Löwig and Frankland more than a century ago,[1,2] neither their chemical nor physical properties are well known. The report by Kraus and Sessions[3] that hexamethylditin is largely dissociated in solution has not been substantiated by more recent work on this simplest member of the series,[3,4] but the possibility of a facile dissociation has nevertheless been described recently as still a matter of uncertainty.[5]

The dehydrogenation of dialkyl- or diaryltin dihydrides to yield the corresponding dialkyl- or diaryltin recently has been developed and exploited for synthetic purposes.[6,7] Diethyltin prepared in this manner is reported to be a cyclic heptamer in benzene solution; the proton n.m.r. spectrum reveals an apparent equivalence of the ethyl groups.[8] Dimethyltin, obtained as a yellow solid from the decomposition of hexamethylditin in the presence of diborane,[9] possesses an empirical formula $(CH_3)_3Sn[Sn(CH_3)_2]_{7-8}Sn(CH_3)_3$ based on elemental analysis.

Experimental

Materials.—Trimethyltin chloride and dimethyltin dichloride were purchased from Metal and Thermit Co., Rahway, N. J. Although usually employed without further purification, they occasionally were sublimed before use. Anhydrous liquid ammonia was obtained from the Matheson Co. Reagent grade benzene was stored over sodium wire, and diethyl ether was dried with Linde Type 4A Molecular Sieve before use. All procedures in the syntheses were carried out under an inert atmosphere of nitrogen or argon. Preparation of samples for spectral analysis and other operations involving the purification and handling of the compounds were conducted in an inert atmosphere box under a nitrogen atmosphere.[10]

Tetramethyltin was prepared as described by Edgell and Ward.[11]

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(1) C. Löwig, *Ann.*, **84**, 308 (1852).

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(7) W. P. Neumann and K. König, *Angew. Chem.*, **74**, 215 (1962).

(8) W. P. Neumann, *ibid.*, **74**, 122 (1962). NOTE ADDED IN PROOF.– In a recent paper, *Angew. Chem.*, **75**, 225 (1963), Neumann concludes that the product commonly obtained from $(C_2H_5)_2SnH_2$ is a cyclic hexamer.

(9) A. B. Burg and J. R. Spielman, *J. Am. Chem. Soc.*, **83**, 2667 (1961).

(10) T. L. Brown, D. W. Dickerhoof, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instr.*, **33**, 491 (1962).

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