

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Preparation of Organosilicon- and Organotin-substituted Boranes and their Oxidation to Organosilicon- and Organotin-substituted Alcohols<sup>1</sup>

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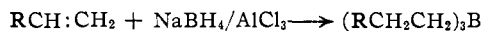
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Organosilicon-substituted boranes of type  $(Me_2RSiCH_2)_3B$  and  $(Me_3SnCH_2)_3B$  have been prepared by the Grignard method. Hydroboration of trimethylvinylsilane with the  $NaBH_4-AlCl_3$  reagent<sup>2</sup> and with  $Me_3N \cdot BH_3$  yielded a borane,  $(Me_3SiC_2H_4)_3B$ , in which the groupings  $Me_3SiCH_2CH_2-B$  and  $Me_3SiCHMe-B$  occurred in about 2:1 molar ratio. Decreasing the trimethylvinylsilane:  $NaBH_4$  ratio gave products where this ratio was about 1:1. Oxidation of the silyl-boranes using the method of Brown and Rao<sup>2</sup> gave the corresponding alcohols in good yield.

The facile oxidation in good yields of triorgano-boranes reported by Brown and Rao<sup>2</sup> has prompted us to investigate the preparation of organosilicon- and organotin-substituted alcohols by this new method.

We have used two methods for preparing the organosilicon- and organotin-substituted boranes which serve as intermediates for the alcohols: (a) addition of the sodium borohydride-aluminum chloride reagent<sup>2,3</sup> and of trimethylamine-borane to trimethylvinylsilane, and (b) the reaction of Grignard reagents derived from chloromethylsilanes and chloromethyltrimethyltin with boron trifluoride diethyl etherate. The latter method proceeded in a straightforward manner and gave high yields of boranes.<sup>4a</sup> The hydroboration reaction, on the other hand, presented considerable complications which require some comment.

It has been reported<sup>2</sup> that terminal addition is usually observed when the  $NaBH_4-AlCl_3$  reagent reacts with a monosubstituted olefin, *i.e.*



Thus, oxidation of the borane resulting from the addition of this reagent to 1-pentene was reported to give 1-pentanol of *ca.* 95% purity. We found that the reaction between the  $NaBH_4-AlCl_3$  reagent and trimethylvinylsilane in diethylene glycol-dimethyl ether solution also gives good yields of a triorgano-borane of composition  $(Me_3SiC_2H_4)_3B$ .<sup>4b,5</sup> Oxidation of this borane yielded a mixture of organosilicon alcohols, b.p. 62–75° at 43 mm. Nuclear magnetic resonance studies<sup>6</sup> showed the mixture to consist of  $\alpha$ -trimethylsilylethanol,  $(CH_3)_3SiCH(CH_3)OH$  and  $\beta$ -trimethylsilylethanol,  $(CH_3)_3SiCH_2CH_2OH$ . The alcohol mixture was also analyzed quantitatively by gas chromatography and it was established that the  $\beta$ -alcohol and the  $\alpha$ -alcohol were present in about 2:1 molar ratio.

(1) Part III of the series "Neopentyl Group Analogs"; for Part II see D. Seyferth, *THIS JOURNAL*, **80**, 1336 (1958). Also Part VIII of the series "Vinyl Derivatives of the Metals"; for Part VII see A. Saitow, E. G. Rochow and D. Seyferth, *J. Org. Chem.*, **23**, 116 (1958).

(2) H. C. Brown and B. C. Subba Rao, *THIS JOURNAL*, **78**, 5694 (1956).

(3) H. C. Brown and B. C. Subba Rao, *ibid.*, **78**, 2582 (1956).

(4a) D. Seyferth, U. S. Patent 2,831,009 (Apr. 15, 1958); *cf. Chem. Abstr.*, **52**, 14653 (1958).

(4b) For a preliminary communication concerning the hydroboration of  $Me_3SiCH:CH_2$  see: D. Seyferth, *J. Inorg. Nucl. Chem.*, **7**, 152 (1958).

(5) Writing the trimethylsilylethyl group as  $Me_3SiC_2H_4$  has no structural implications. This representation is intended to indicate only the aggregate formula, not the arrangement of carbon atoms of the  $C_2H_4$  unit.

(6) D. Seyferth, S. Castellano and J. S. Waugh, report in preparation.

Comparison of the retention times of the alcohols in the mixture and of a sample of pure  $\beta$ -trimethylsilylethanol prepared by the method of Speier<sup>7</sup> served to confirm the structures assigned on the basis of the n.m.r. spectra.

Our yields of the silicon-substituted borane averaged 65–75% in a large number of runs. This is in marked contrast to the results of Wartik and Pearson<sup>8</sup> who found that the action of  $NaBH_4$  on vinyltrichlorosilane caused vinyl-silicon bond cleavage to yield silane as the ultimate product.

Better yields of the silicon-substituted borane could be obtained when trimethylamine-borane,  $(CH_3)_3N \cdot BH_3$ , was used as the boron hydride source. The addition of this reagent to olefins at 100° or over in the absence of solvent has been reported by Köster.<sup>9</sup> We found that diethylene glycol-dimethyl ether serves excellently as a solvent in carrying out this reaction and that 85–93% yields of the borane derived from  $Me_3SiCH:CH_2$  and  $Me_3N \cdot BH_3$  are obtained when the reactants are heated at *ca.* 80° overnight in diethylene glycol-dimethyl ether solution. Oxidation of the borane produced in this reaction followed by gas chromatographic analysis of the resulting alcohols showed that the ratio of  $\beta$ -trimethylsilylethanol to the  $\alpha$ -isomer again was 2:1.

In order to gain some insight into the factors causing this unexpected isomer distribution, attempts were made to limit the reaction to the introduction of only one organic group per boron atom. However, the action of the  $NaBH_4-AlCl_3$  reagent on  $Me_3SiCH:CH_2$ , using a  $NaBH_4:Me_3SiCH:CH_2$  molar ratio of *ca.* 1.6:1, followed by acid hydrolysis of the reaction mixture, did not result in the expected  $Me_3SiC_2H_4B(OH)_2$ . Subsequent experiments carried out in a similar manner, in which the crude hydrolysis products were refluxed with ethanol overnight, yielded three products— $(Me_3SiC_2H_4)_2BOC_2H_5$ ,  $(Me_3SiC_2H_4)_3B$  and  $[(Me_3SiC_2H_4)_2H_4]_2B]_2O$ . The yield of these products varied somewhat from experiment to experiment, but the cause for these variations could not be discovered. It is not possible to say whether the  $[(Me_3SiC_2H_4)_2-BH]_2$ —from which the  $(Me_3SiC_2H_4)_2BOC_2H_5$  and  $[(Me_3SiC_2H_4)_2B]_2O$  must have derived—and the  $(Me_3SiC_2H_4)_3B$  were formed directly in the addition reaction, or whether they resulted from disproportionation of  $(Me_3SiC_2H_4BH_2)_2$  formed in an initial

(7) J. L. Speier, J. A. Webster and G. H. Barnes, *THIS JOURNAL*, **79**, 977 (1957).

(8) T. Wartik and R. K. Pearson, *J. Inorg. Nucl. Chem.*, **5**, 250 (1958).

(9) R. Köster, *Angew. Chem.*, **69**, 684 (1957).

1:1 addition reaction. It is possible that both routes may have contributed to the product yield. It may be noted that Wartik and Pearson<sup>8</sup> were able to isolate some diethyldiborane from the reaction of vinyl bromide with sodium borohydride in 1:1 molar ratio. However, in their experiments it was also apparent that a mixture of products resulting from secondary disproportionation reactions had formed. The three silicon-containing boron compounds obtained in these experiments were oxidized separately in several runs, giving the following ranges of  $\alpha$ -trimethylsilylethanol and  $\beta$ -trimethylsilylethanol yields

$(\text{Me}_3\text{SiC}_2\text{H}_4)_2\text{BOC}_2\text{H}_5$ :  $\alpha$ -alcohol, 61–70%;  $\beta$ -alcohol, 30–39%

$(\text{Me}_3\text{SiC}_2\text{H}_4)_2\text{B}$ :  $\alpha$ -alcohol, 40–50%;  $\beta$ -alcohol, 50–60%

$[(\text{Me}_3\text{SiC}_2\text{H}_4)_2\text{B}]_2\text{O}$ :  $\alpha$ -alcohol, 43–46%;  $\beta$ -alcohol, 54–57%

Calculation of a total  $\alpha$ -trimethylsilylethanol and  $\beta$ -trimethylsilylethanol yield for these experiments gave:  $\alpha$ , 51.5–53.5%;  $\beta$ , 47–48.5%.

Thus with a 1.6:1  $\text{NaBH}_4$ - $\text{Me}_3\text{SiCH}:\text{CH}_2$  ratio, conditions under which complete substitution to give a triorgano-borane is diminished, the boron atom is as likely to become attached to the  $\alpha$ -carbon atom of the vinyl group as to the  $\beta$ -carbon. Yet when complete substitution is sought, attachment of the boron atom to the  $\beta$ -carbon atom of the vinyl group is now preferred by a factor of two. These results seem to reflect a steric influence, the presence of one  $\text{Me}_3\text{SiCH}(\text{CH}_3)$  group on a boron atom making further substitution in this direction difficult because of the steric requirements of trimethylsilyl- and methyl groups attached to the carbon atom bearing the boron substituent; there would be less hindrance to the introduction of a  $\text{Me}_3\text{SiCH}_2\text{CH}_2$  group into the molecule. The mechanism whereby the addition reaction occurs is not known, hence a discussion of possible causes for the direction of addition observed would have little meaning at this time.

The yields of the  $\alpha$ - and  $\beta$ -alcohols resulting from oxidation of the two disubstituted boron compounds  $(\text{Me}_3\text{SiC}_2\text{H}_4)_2\text{BOC}_2\text{H}_5$  and  $[(\text{Me}_3\text{SiC}_2\text{H}_4)_2\text{B}]_2\text{O}$ , provide another example of steric effects. Both compounds undoubtedly derived from  $(\text{Me}_3\text{SiC}_2\text{H}_4)_2\text{BOH}$  resulting in the hydrolysis of the reaction mixture. Heating of the residue containing this borinic acid to fairly high temperatures probably caused condensation of some of those borinic acid molecules with at least one  $\text{Me}_3\text{SiCH}_2\text{CH}_2$  group per molecule and very likely of all bearing two  $\text{Me}_3\text{SiCH}_2\text{CH}_2$  groups per molecule. Those with two  $\text{Me}_3\text{SiCH}(\text{CH}_3)$  groups and the remainder of those bearing one  $\text{Me}_3\text{SiCH}(\text{CH}_3)$  group per molecule probably did not condense because of steric hindrance to this bimolecular condensation. Those borinic acid molecules which did not react to form the anhydride could, however, undergo condensation with ethanol, giving  $(\text{Me}_3\text{SiC}_2\text{H}_4)_2\text{BOC}_2\text{H}_5$ . Hence the distributions of  $\alpha$ - and  $\beta$ -alcohols mentioned earlier—61–70%  $\alpha$ -trimethylsilylethanol from  $(\text{Me}_3\text{SiC}_2\text{H}_4)_2\text{BOC}_2\text{H}_5$  and only 43–46%  $\alpha$ -alcohol from  $[(\text{Me}_3\text{SiC}_2\text{H}_4)_2\text{B}]_2\text{O}$ —are obtained.

The oxidation of the silicon-substituted boranes prepared in this study proceeded smoothly to give the corresponding alcohols in yields of 75–92%. This method of preparing particularly those

alcohols of structure  $\text{R}_3\text{SiCH}_2\text{OH}$  is perhaps more practical in the laboratory than the method used heretofore<sup>10</sup> which required the conversion of the corresponding chloromethylsilane to the acetoxy-methylsilane at high temperatures in an autoclave, followed by hydrolysis of the acetoxy-methylsilane to the alcohol. It is apparent that the hydroboration reaction, which gives both  $\alpha$ - and  $\beta$ -addition with trimethylvinylsilane, is not practical as a preparative method for pure silyl-substituted alcohols.

The oxidation procedure which worked so well with silicon-containing boranes was not successful in the preparation of organotin-substituted alcohols. Oxidation of  $(\text{Me}_3\text{SnCH}_2)_3\text{B}$  gave only a 13% yield of trimethylstannylmethanol. A 35% yield of dimethyltin oxide also resulted in the oxidation reaction. Furthermore,  $\text{Me}_3\text{SnCH}_2\text{OH}$  was not stable even after it had been distilled. Within 48 hours this alcohol had decomposed, giving a yellow liquid and a white solid. This is in agreement with the observations of van der Kerk, Luijten and Noltes, who note that  $\alpha$ -organofunctional organotin compounds are rather unstable.<sup>11</sup>

### Experimental<sup>12</sup>

**Starting Materials.**— $\text{Me}_3\text{SiCH}_2\text{Cl}$ ,  $\text{Me}_2\text{EtSiCH}_2\text{Cl}$ ,  $\text{Me}_2$ -(*n*- $\text{C}_4\text{H}_7$ ) $\text{SiCH}_2\text{Cl}$  and  $\text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{CH}_2\text{Cl}$ , all known compounds, were prepared by the reaction of the appropriate Grignard reagent with  $\text{Me}_2(\text{CH}_2\text{Cl})\text{SiCl}$  in diethyl ether solution. The method of Nagel and Post<sup>13</sup> was used for the synthesis of trimethylvinylsilane, while trimethylvinyltin was prepared by treating  $\text{Me}_3\text{SnCl}$  with vinylmagnesium bromide in tetrahydrofuran.<sup>14</sup>

Sodium borohydride was a product of Metal Hydrides, Inc. and the trimethylamine-borane was obtained from Calvery Chemical Company. Reagent grade aluminum chloride (Baker and Adamson) was used without further purification. Diethylene glycol-dimethyl ether (Ansul Ether 141) was purchased from the Ansul Chemical Company.

**Preparation of  $(\text{Me}_3\text{RSiCH}_2)_3\text{B}$  and of  $(\text{Me}_3\text{SnCH}_2)_3\text{B}$  by the Grignard Method.**—The preparation of tris(trimethylsilylmethyl)-borane<sup>15</sup> is given as an example of the procedure used. All operations involving the preparation and handling of organoboron compounds were carried out in an atmosphere of prepurified nitrogen.

Trimethylsilylmethylmagnesium chloride was prepared from 61.5 g. (0.5 mole) of  $\text{Me}_3\text{SiCH}_2\text{Cl}$  and 12.2 g. (0.5 g. atom) of magnesium turnings in 200 ml. of diethyl ether. The Grignard reagent was cooled with an ice-bath and 31 ml. (ca. 0.17 mole) of boron trifluoride diethyl etherate diluted with 30 ml. of ether was added slowly with vigorous stirring. The reaction mixture was stirred overnight and subsequently was refluxed for 4 hr. Hydrolysis of the mixture, cooled in an ice-bath, with 75 ml. of saturated  $\text{NH}_4\text{Cl}$  solution was followed by separation and distillation of the organic layer to give 38 g. (83%) of  $(\text{Me}_3\text{SiCH}_2)_3\text{B}$ , b.p. 55–56° (0.4 mm.).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{33}\text{Si}_3\text{B}$ : C, 52.89; H, 12.21; B, 3.97; Si, 30.93. Found: C, 52.54; H, 12.09; B, 3.9; Si, 31.28.

Similarly prepared were the following compounds.

Tris-(trimethylstannylmethyl)-borane,  $(\text{Me}_3\text{SnCH}_2)_3\text{B}$ , b.p. 90–91° (0.15 mm.), 58% yield.

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{33}\text{Sn}_3\text{B}$ : C, 26.48; H, 6.11; Sn, 65.42. Found: C, 26.40; H, 6.02; Sn, 65.62.

Tris-(dimethylethylsilylmethyl)-borane,  $(\text{Me}_2\text{EtSiCH}_2)_3\text{B}$ , b.p. 87–89° (0.3 mm.), 71% yield.

(10) J. L. Speier, B. F. Daubert and R. R. McGregor, *THIS JOURNAL*, **70**, 1117 (1948).

(11) G. J. M. van der Kerk, J. G. A. Luijten and J. G. Noltes, *Angew. Chem.*, **70**, 298 (1958).

(12) Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by Dr. S. M. Nagy and his associates at the Microchemical Laboratory at this Institute.

(13) R. Nagel and H. W. Post, *J. Org. Chem.*, **17**, 1379 (1952).

(14) D. Seyferth and F. G. A. Stone, *THIS JOURNAL*, **79**, 515 (1957).

*Anal.* Calcd. for  $C_{15}H_{39}Si_3B$ : C, 57.27; H, 12.5. Found: C, 56.88; H, 12.33.

Tris-(dimethyl-*n*-propylsilylmethyl)-borane,  $(Me_2PrSiCH_2)_3B$ , b.p. 111–113° (0.3 mm.), 80% yield.

*Anal.* Calcd. for  $C_{18}H_{45}Si_3B$ : C, 60.61; H, 12.72. Found: C, 60.33; H, 12.69.

All four boranes were clear, colorless liquids that oxidized fairly slowly in air without bursting into flame.

Tris-(2,2,4,4-tetramethyl-2,4-disilapentyl)-borane,  $(Me_3SiCH_2SiMe_2CH_2)_3B$ , was prepared using the procedure described above but was not isolated in the pure state before oxidation to the corresponding alcohol.

**Oxidation of  $(Me_2RSiCH_2)_3B$ .**—The method used to prepare dimethyl-*n*-propylsilylmethanol,  $Me_2PrSiCH_2OH$ , is given as an example of the procedure used.

To a mixture of 28.6 g. (0.08 mole) of  $(Me_2PrSiCH_2)_3B$  and 4 g. of sodium hydroxide dissolved in 70 ml. of 95% ethanol was added with stirring 34.4 g. of 30% hydrogen peroxide at such a rate that a gentle reflux was maintained. The reaction mixture was then stirred until it had cooled to room temperature. Fifty ml. of distilled water and 50 ml. of diethyl ether were added and the mixture was agitated vigorously. The organic layer was separated and the aqueous phase was extracted with three 30-ml. portions of ether. The combined organic layer and ether extracts were dried over anhydrous magnesium sulfate and distilled to give 29.1 g. (92%) of the new compound,  $Me_2PrSiCH_2OH$ , b.p. 161–162° at atmospheric pressure,  $n_D^{25}$  1.4320.

*Anal.* Calcd. for  $C_6H_{16}OSi$ : C, 54.47; H, 12.19. Found: C, 54.79; H, 12.21.

A similar procedure was used in the preparation of the following.

Trimethylsilylmethanol, 79% yield, b.p. 122–123° at 768 mm.,  $n_D^{25}$  1.4174. Speier<sup>10</sup> reports b.p. 121.7–121.9° at 751 mm.,  $n_D^{25}$  1.4169.

Dimethylethylsilylmethanol,  $Me_2EtSiCH_2OH$ , 91% yield, b.p. 143–144° at atmospheric pressure,  $n_D^{25}$  1.4291. Petrov, *et al.*,<sup>15</sup> report b.p. 144°,  $n_D^{25}$  1.4307.

Dimethyl-(trimethylsilylmethyl)-silylmethanol,  $Me_3SiCH_2SiMe_2CH_2OH$ , b.p. 80–82° (10 mm.),  $n_D^{25}$  1.4440.

*Anal.* Calcd. for  $C_7H_{20}OSi_2$ : C, 47.65; H, 11.43. Found: C, 48.26; H, 11.66.

**Oxidation of  $(Me_3SnCH_2)_3B$ .**—To a mixture of 22.5 g. (0.041 mole) of  $(Me_3SnCH_2)_3B$  and 2.5 g. of NaOH in 40 ml. of 95% ethanol was added 21.5 g. of 30% hydrogen peroxide in the manner described above. During the reaction a white solid deposited. Filtration of the reaction mixture after addition of 40 ml. each of distilled water and diethyl ether gave about 8.0 g. of amorphous white solid which was insoluble in all common solvents. Separation of the organic layer of the filtrate and extraction of the aqueous phase with ether was followed by drying of the combined organic layer and ether extracts. Distillation yielded 3.5 g. (13%) of  $Me_3SnCH_2OH$ , colorless liquid, b.p. 58–59° (6.5 mm.), and a yellow high-boiling residue. The distillate decomposed within 48 hr. to a yellow liquid and a white solid.

*Anal.* Calcd. for  $C_4H_{12}OSn$ : C, 24.66; H, 6.21. Found: C, 24.37; H, 5.97.

The white solid formed in the original reaction was found to be dimethyltin oxide.

*Anal.* Calcd. for  $C_2H_6OSn$ : C, 14.57; H, 3.67. Found: C, 15.27; H, 3.55.

A sample of this solid was dissolved in dilute hydrochloric acid solution. Addition of a solution of potassium acid phthalate in water gave a microcrystalline precipitate. The infrared spectrum of the phthalate precipitate (KBr pellet) was identical with that of an authentic sample of dimethyltin phthalate.<sup>16</sup>

**Hydroboration of Trimethylvinylsilane Using the  $NaBH_4-AlCl_3$  Reagent.** A.  $Me_3SiCH:CH_2$  and  $NaBH_4-AlCl_3$  Reagent ( $Me_3SiCH:CH_2$  and  $NaBH_4$  in 2:1 Molar Ratio).—Trimethylvinylsilane, 37.5 g. (0.375 mole), was added slowly with stirring to the  $NaBH_4-AlCl_3$  reagent<sup>3</sup> prepared from 7.0 g. (0.1875 mole) of  $NaBH_4$  and 8.4 g. (0.063 mole) of  $AlCl_3$  in 200 ml. of diethylene glycol-dimethyl ether (diglyme) cooled in an ice-bath. The reaction mixture was

stirred at room temperature for 3 hr., then at ca. 90° for 1 hr. A white solid formed in the reaction vessel during this time. The reaction mixture, cooled in an ice-bath, was hydrolyzed *cautiously* with 50 ml. of cold saturated ammonium chloride solution. The organic layer was filtered from the coagulated salts, and the salts were washed with diethyl ether. The combined organic layer and ether washings were distilled—the ether at atmospheric pressure, the diglyme at reduced pressure (ca. 50° at 1.5–2.0 mm.). Fractional distillation of the residue gave 29.1 g. (75% yield) of colorless liquid, boiling range 65–72° (0.12 mm.), which did not ignite or fume in air.

*Anal.* Calcd. for  $C_{15}H_{39}Si_3B$ : C, 57.27; H, 12.50; B, 3.44. Found: C, 57.15; H, 12.66; B, 3.28.

A light brown viscous oil remained in the still pot.

Varying the reaction conditions did not appear to affect yield very much. Thus yields of 65–75% were obtained when the reaction mixture was stirred for 20 hr. at room temperature and hydrolyzed with dilute hydrochloric acid. Keeping the reaction mixture at 150° for 8 hr. did appear to cause a small decrease in borane yield. In most runs the organoborane was not isolated in the pure state. Instead the residue remaining after removal of all volatiles was used as such in the oxidation experiments.

B.  $Me_3SiCH:CH_2$  and  $NaBH_4-AlCl_3$  Reagent ( $Me_3SiCH:CH_2$  and  $NaBH_4$  in 1:1.6 Molar Ratio).—Trimethylvinylsilane, 37.5 g. (0.375 mole), was added dropwise with vigorous stirring to the  $NaBH_4-AlCl_3$  reagent prepared from 22.8 g. (0.6 mole) of  $NaBH_4$  and 26.8 g. (0.2 mole) of  $AlCl_3$  in 900 ml. of diglyme cooled in an ice-bath. The reaction mixture was allowed to warm to room temperature very slowly and was then stirred for 20 hr. Subsequently it was cooled in an ice-bath and hydrolyzed *very cautiously* with dilute hydrochloric acid (60 ml. of concd. HCl diluted to 500 ml. with distilled water). The organic layer was separated and the aqueous phase was extracted with three 100-ml. portions of diethyl ether. The organic layer and the ether washings were combined and distilled. The residue remaining after removal of all solvents was refluxed with 100 ml. of absolute ethanol for 12 hr. Distillation of the excess of ethanol was followed by fractional distillation of the residue to give: (1)  $(Me_3SiC_2H_4)_2BOC_2H_5$ , b.p. 69–72° (1.2 mm.), 12.8 g.

*Anal.* Calcd. for  $C_{12}H_{31}OSi_2B$ : C, 55.78; H, 12.10; mol. wt. 258.4. Found: C, 55.88; H, 12.09; mol. wt. 248. Analyses of this fraction in other runs gave: C, 55.87; H, 12.14 and C, 55.92; H, 11.95.

(2) Impure  $(Me_3SiC_2H_4)_3B$ , b.p. 80° (0.3 mm.) to 100° (0.2 mm.), 8.8 g.

(3)  $[(Me_3SiC_2H_4)_2B]_2O$ , b.p. 110° (0.12 mm.) to 120° (0.15 mm.), 6.3 g.

*Anal.* Calcd. for  $C_{20}H_{52}OSi_4B_2$ : C, 54.26; H, 11.84; B, 4.89. Found: C, 54.17; H, 11.60; B, 4.67. This fraction obtained in another run gave: C, 54.43; H, 11.75.

Yields of these substances varied from run to run. For example, in two other experiments with the same quantities of reactants the following fractions were collected

$(Me_3SiC_2H_4)_2BOC_2H_5$	10.5	and	8.0 g.
$(Me_3SiC_2H_4)_3B$	9.0	and	14.5 g.
$[(Me_3SiC_2H_4)_2B]_2O$	8.8	and	7.3 g.

**Hydroboration of  $Me_3SiCH:CH_2$  Using Trimethylamine-Borane.**—Trimethylamine-borane, 7.5 g. (0.102 mole), was dissolved in 100 ml. of diglyme and the solution was heated to ca. 80°. Trimethylvinylsilane, 37.5 g. (0.375 mole), was then added in small portions over a period of 1 hr. The reaction mixture was heated at 70–80° for 22 hr., cooled and hydrolyzed with 180 ml. of dilute hydrochloric acid. The organic layer was separated and the aqueous portion was extracted with diethyl ether. The combined organic phase and ether extracts were dried over anhydrous magnesium sulfate. Distillation of the solvents gave 30.0 g. (93.5%) of a colorless liquid residue of  $(Me_3SiC_2H_4)_3B$ .

**Oxidation of Hydroboration Products.**—The method of Brown and Rao<sup>3</sup> as described above was used. Yields of  $\alpha$ -trimethylsilylethanol and  $\beta$ -trimethylsilylethanol were determined by means of gas chromatography of the crude, undistilled alcohol mixtures on a 170 by 0.5 cm. column filled with 30% by weight Dow Corning 550 silicone fluid on 48–100 mesh firebrick. The column temperature was maintained at ca. 140°, the flow rate at 40 ml. per min. Samples

(15) A. D. Petrov, V. F. Mironov and N. A. Pogonkina, *Doklady Akad. Nauk S.S.S.R.*, **100**, 81 (1955).

(16) E. G. Rochow, D. Seyferth and A. C. Smith, Jr., *THIS JOURNAL*, **75**, 3099 (1953).

of 0.005 ml. were used. The  $\beta$ -alcohol had a longer retention time than the  $\alpha$ -isomer.

A.  $(\text{Me}_2\text{SiC}_2\text{H}_4)_2\text{B}$ .—In one run the alcohol mixture resulting from the oxidation of the triorganoborane was distilled, giving an 88% yield of mixed  $\alpha$ - and  $\beta$ - $\text{Me}_2\text{Si}(\text{C}_2\text{H}_4)\text{OH}$ , b.p. 62–75° (42 mm.).

Anal. Calcd. for  $\text{C}_8\text{H}_{14}\text{OSi}$ : C, 50.78; H, 11.93. Found: C, 50.83; H, 12.06.

The results of a number of representative runs are summarized below

Conditions of hydroboration	$\alpha$ -Alcohol, mole %	$\beta$ -Alcohol, mole %
$\text{NaBH}_4\text{-AlCl}_3$ , 20 hr. at room temp.	37	63
$\text{NaBH}_4\text{-AlCl}_3$ , 2 hr. at room temp., 1 hr. at 60°	33	67
$\text{NaBH}_4\text{-AlCl}_3$ , 3 hr. at room temp., 8 hr. at 150°	37	63
$\text{Me}_2\text{N}\cdot\text{BH}_3$ , 22 hr. at 70–80°	34	66

The similar ratios of  $\alpha$ - to  $\beta$ -trimethylsilylethanol obtained in these reactions, in which the thermal history of the reactions covers a fairly wide range, makes the possibility that thermal rearrangements occurred in the direction  $\text{Me}_2\text{SiCHMe-B} \rightarrow \text{Me}_2\text{SiCH}_2\text{CH}_2\text{-B}$ , similar to those reported by Hennion, *et al.*,<sup>17</sup> and by Brown and Rao<sup>18</sup>, seem unlikely.

B. 1:1.6 Hydroboration Reaction Products.—Oxidation of the products of the 1:1.6 hydroboration reaction described above are summarized below.

The  $(\text{Me}_2\text{SiC}_2\text{H}_4)_2\text{BOC}_2\text{H}_5$  obtained, 12.8 g. (0.0495 mole), was oxidized in the usual manner using 1.6 g. NaOH in 50

(17) G. F. Hennion, P. A. McCusker, E. C. Ashby and A. J. Rutkowski, *THIS JOURNAL*, **79**, 5190 (1957).

(18) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957).

ml. of ethanol and 14 g. of 30% hydrogen peroxide to give 10 g. of mixed alcohols. Gas chromatographic analysis showed the mixture to consist of 70.4%  $\alpha$ -trimethylsilylethanol and 29.7%  $\beta$ -trimethylsilylethanol. The  $(\text{Me}_2\text{SiC}_2\text{H}_4)_2\text{B}$ , 8.8 g. (0.028 mole), was oxidized using 1.5 g. of NaOH in 50 ml. of ethanol and 13 g. of 30%  $\text{H}_2\text{O}_2$  to give 8.1 g. of a mixture containing 42.8% of the  $\alpha$ -alcohol and 57.1% of the  $\beta$ -alcohol. Similarly, the  $[(\text{Me}_2\text{SiC}_2\text{H}_4)_2\text{B}]_2\text{O}$ , 6.3 g. (0.014 mole), was oxidized in solution with 1.0 g. of NaOH in 35 ml. of ethanol by 8 g. of 30%  $\text{H}_2\text{O}_2$ , yielding 5 g. of mixed alcohols (40.5%  $\alpha$ -alcohol and 59.4%  $\beta$ -alcohol).

Thus the boron compounds obtained in this experiment contained a total of 0.128 mole of  $\text{Me}_2\text{SiCHMe}$ - groups and 0.112 mole of  $\text{Me}_2\text{SiCH}_2\text{CH}_2$ - groups, giving an over-all distribution of 53.4%  $\alpha$ -trimethylsilylethyl groups and 46.6% of the  $\beta$ -isomer.

Hydroboration of Trimethylvinyltin.—Attempted hydroboration of trimethylvinyltin with the  $\text{NaBH}_4\text{-AlCl}_3$  reagent gave a product having a characteristic organoborane-like odor that caused ignition when poured on cloth or paper. Attempted distillation resulted in decomposition. Oxidation of the crude trimethylvinyltin hydroboration product by the usual procedure also resulted in decomposition and no organotin-alcohol could be isolated.

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## The Hammett Acidity Function $H_0$ for Trifluoroacetic Acid Solutions of Sulfuric and Hydrofluoric Acids<sup>1</sup>

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The  $H_0$  values of mixtures of  $\text{H}_2\text{SO}_4$  and trifluoroacetic acid, as well as HF and trifluoroacetic acid, have been measured over the entire range of compositions. The values found are related to those found for aqueous systems, displaced as expected due to the higher acid strength of trifluoroacetic acid.

### Introduction

Some interest has been shown in this and other laboratories in non-aqueous highly acid media. Trifluoroacetic acid has rather good solvent properties for many organic molecules, is readily available as a rather pure anhydrous chemical and is completely miscible in all proportions with some stronger acids such as  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$  and HF. The Hammett acidity function has been correlated with other phenomena of interest involving proton mobility.<sup>2</sup> The  $\text{H}_2\text{SO}_4$ -trifluoroacetic acid system has been used to investigate the effect of increasing acidity on the hexamethylbenzene spectrum, and values were given for a Hammett function  $H_0$  calculated using hexamethylbenzene as the indicator.<sup>3</sup> This hydrocarbon is a different type of proton acceptor than is usually used as a Hammett

indicator and as would be true of any indicator, is useful only in a narrow acidity range. This paper gives the acidity of the entire trifluoroacetic acid, sulfuric acid system obtained by using the conventional Hammett indicators. Since systems exist in which the sulfonating behavior of sulfuric acid systems is undesirable, the HF-trifluoroacetic acid system was also investigated. Mixtures containing high concentrations of perchloric acid are too oxidizing to be useful as simple acidic solvents and were not investigated.

The data of Dallinga and Kok discussed by Mackor, *et al.*,<sup>4</sup> were not known to us at the time this program was initiated. Over the range of concentrations reported, the results are in good agreement.

### Experimental

Materials.—The indicators used were Aldrich Chemical Company products sold for use as Hammett indicators. They were used as received. Trifluoroacetic acid is now

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) L. P. Hammett, *Chem. Revs.*, **16**, 67 (1935); "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940.

(3) M. Kilpatrick and H. H. Hyman, *THIS JOURNAL*, **80**, 77 (1958).

(4) E. L. Mackor, P. J. Smit and J. H. van der Waals, *Trans. Faraday Soc.*, **53**, 1309 (1957).