

**117. *The Reaction of Methylidisiloxanes and 1:1-Dimethyldisilthiane with Boron and Hydrogen Halides.***

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Boron trifluoride and trichloride do not give stable addition compounds with 1:1'-dimethyl-, 1:1':2:2'-tetramethyl-, or hexamethyl-disiloxane. Cleavage of the Si-O-Si bond occurs, with formation of the methylhalogenosilane and the methylsiloxyboron dihalide. The latter decomposes spontaneously to the methylhalogenosilane, boron trihalide, and boron trioxide. Hydrogen iodide causes cleavage of the Si-O-Si bond, but trimethylboron and methyl iodide do not react. Boron trifluoride or trichloride decomposes 1:1'-dimethyldisilthiane at 100°, whereas trimethylboron and methyl iodide do not react with it and hydrogen iodide cleaves the Si-S-Si bond. The absence of electron-donor activity for oxygen and sulphur in Si-O-Si and Si-S-Si linkages is discussed.

OXYGEN and sulphur atoms in dialkyl ethers and sulphides readily react with acceptor molecules, such as boron trifluoride, boron trichloride, hydrogen iodide, and alkyl halides, to form co-ordination complexes and oxonium or sulphonium compounds. This electron-donor activity of oxygen or sulphur is, however, absent in the disilyl analogues,<sup>1</sup> and this has been attributed in part to the ability of silicon to use its vacant *3d*-orbitals in the formation of  $\pi$ -type bonds with the elements of Groups V, VI, and VII.<sup>2</sup> One method of increasing the electron-donor power of oxygen or sulphur when bonded to silicon might be to replace symmetrically the hydrogen atoms attached to silicon in disiloxane, (SiH<sub>3</sub>)<sub>2</sub>O, and disilthiane, (SiH<sub>3</sub>)<sub>2</sub>S, by electron-releasing methyl groups. The experiments described below were made to examine this possibility with three symmetrically substituted disiloxanes and with 1:1'-dimethyldisilthiane by determining if addition compounds are formed with boron trifluoride, boron trichloride, trimethylboron, hydrogen iodide, and methyl iodide.

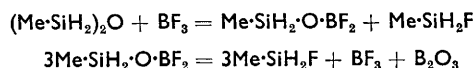
The results showed that, unlike the diethyl ether analogue, 1:1'-dimethyldisiloxane did not form a stable 1:1 addition compound with boron trifluoride. Instead, cleavage of the Si-O-Si bond occurred at -78°. The reaction took place in two stages, but the

<sup>1</sup> Emeléus, MacDiarmid, and Maddock, *J. Inorg. Nuclear Chem.*, 1955, **1**, 194.

<sup>2</sup> Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, **332**; Stone and Seyferth, *J. Inorg. Nuclear Chem.*, 1955, **1**, 112; Aylett, Emeléus, and Maddock, *J. Inorg. Nuclear Chem.*, 1955, **1**, 187.

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methylsiloxyboron difluoride formed in the first was so unstable that it could not be isolated:



The possibility of the formation of a 1 : 1 adduct at low temperatures could not be eliminated, but decomposition at  $-78^\circ$  was rapid and there was no appreciable dissociation into the original reactants. The reactions of 1 : 1' : 2 : 2'-tetramethyldisiloxane and of hexamethyldisiloxane at  $-78^\circ$  were very similar to that of 1 : 1'-dimethyldisiloxane. When, however, a mixture of hexamethyldisiloxane and excess of boron trifluoride was held at  $-78^\circ$  for only 2 hr. and then cooled to  $-96^\circ$ , excess of boron trifluoride could be pumped away, leaving a solid 1 : 1 adduct which was involatile at this temperature. When the temperature was raised to  $-78^\circ$  most of the combined boron trifluoride was recovered unchanged, though a little reacted to form trimethylfluorosilane.

Boron trichloride with 1 : 1'-di- or 1 : 1' : 2 : 2'-tetra-methyldisiloxane also failed to form stable 1 : 1 adducts. In the first case the main reaction at  $-78^\circ$  was:  $3(\text{Me}\cdot\text{SiH}_2)_2\text{O} + 2\text{BCl}_3 = 6\text{Me}\cdot\text{SiH}_2\text{Cl} + \text{B}_2\text{O}_3$ , but it was also possible to isolate the intermediate methylsiloxyboron dichloride, though this decomposed readily at room temperature. It was, however, more stable than the difluoride. The reaction of 1 : 1' : 2 : 2'-tetramethyldisiloxane with boron trichloride was similar, though dimethylsiloxyboron dichloride was not isolated. Wiberg and Kruerke<sup>3</sup> showed that an equimolecular mixture of boron tribromide and hexamethyldisiloxane formed an addition compound at  $-40^\circ$ , which decomposed slowly to dimethylbromosilane, boron tribromide, and boron trioxide.

Neither boron trifluoride nor boron trichloride formed an addition compound at low temperatures with 1 : 1'-dimethyldisilthiane, but reaction occurred at  $100^\circ$  with the formation of unidentified complex organosilicon compounds. Thus the sulphur atom, in this case, shows no donor activity, though dimethyl sulphide forms a weak adduct,  $\text{Me}_2\text{S}\cdot\text{BF}_3$ , which is over 90% dissociated at ordinary temperatures.<sup>4</sup> Methyl-substituted disiloxanes and 1 : 1'-dimethyldisilthiane did not react with trimethylboron at  $-78^\circ$ , room temperature or  $100-150^\circ$ : recovery of the reactants was almost quantitative.<sup>5</sup> Dimethyl sulphide forms the compound  $\text{Me}_2\text{S}\cdot\text{BMe}_3$ . The reaction of 1 : 1'-dimethyldisiloxane with hydrogen iodide gave a complex mixture of products, which included methyl iodosilane, but with 1 : 1'-dimethyldisilthiane there was an almost quantitative formation of hydrogen sulphide and methyl iodosilane:  $(\text{Me}\cdot\text{SiH}_2)_2\text{S} + 2\text{HI} = 2\text{Me}\cdot\text{SiH}_2\text{I} + \text{H}_2\text{S}$ . No reaction occurred with methyl iodide.

The failure of the methyl-substituted disiloxanes and disilthiane to form stable co-ordination complexes supports the current theoretical view that silicon uses its vacant 3d-orbitals to form bonds with oxygen and sulphur which have considerable double-bond character. Moreover, it is clear that methyl-substitution of the silicon atom does not appreciably influence the donor properties of the oxygen and sulphur atoms. For boron trifluoride, boron trichloride, and hydrogen iodide the possible formation of adducts of low stability is masked by halogenation in which silicon-oxygen bonds are broken. This occurs more readily than does the cleavage of carbon-oxygen bonds in ethers and is favoured by the larger size of the silicon atom, which favours polar attack, and also by the fact that the silicon-oxygen bond is more polar than the carbon-oxygen bond.

The mechanism which has been proposed for the reaction of alkyl ethers with boron trichloride involves an electrophilic attack by boron trichloride, with transitory formation of a carbonium cation.<sup>6</sup> Organosilicon compounds do not form siliconium ions,<sup>7</sup> and a similar mechanism is therefore unlikely in the reactions of disiloxanes with boron halides.

<sup>3</sup> Wiberg and Kruerke, *Z. Naturforsch.*, 1953, 8b, 608.

<sup>4</sup> Graham and Stone, *Chem. and Ind.*, 1956, 319.

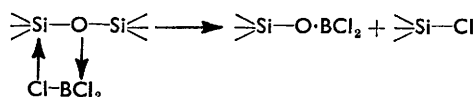
<sup>5</sup> For details of these experiments see Onyszchuk, Ph.D. Thesis, Cambridge, 1956.

<sup>6</sup> Gerrard and Lappert, *J.*, 1951, 1020; 1952, 1486; Gerrard, Lappert, and Silver, *J.*, 1956, 4987.

<sup>7</sup> Swain, Esteve, and Jones, *J. Amer. Chem. Soc.*, 1949, 71, 965; Eaborn, *J.*, 1953, 494.

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A stepwise dehalogenation by a four-centre broadside attack, as suggested for the reaction of alcohols with boron trichloride,<sup>8</sup> would yield the following scheme for the interaction of boron trichloride with disiloxanes:



Since methylsiloxyboron dichlorides and the corresponding methylchlorosilanes are the first products, only the first stage of this scheme need be invoked. There is no evidence about the mechanism of decomposition of the methylsiloxyboron dichlorides. Methoxy- and ethoxy-boron dichloride yield boron oxychloride in their decomposition, and this decomposes at 70° to boron trichloride and boron trioxide.<sup>9</sup> No boron oxychloride was, however, isolated in the experiments described below.

Stepwise defluorination of boron trifluoride by methylidisiloxanes, yielding in the first stage a methylsiloxyboron difluoride, will also account for the reactions involving boron trifluoride. The methylsiloxyboron difluoride is less stable than the chloro-compound but the exact mechanism of its decomposition is again uncertain since no evidence was obtained in these reactions for the formation or the presence of the volatile cyclic trimeric boron oxyfluoride.<sup>10</sup>

## EXPERIMENTAL

1 : 1'-Dimethyl-disiloxane and -disilthiane were prepared by reaction of methylidiodisilane with water and mercuric sulphide<sup>11</sup> (Found: *M*, 106.3; v. p. 190.5 mm. at 0°. Calc. for C<sub>2</sub>H<sub>10</sub>Si<sub>2</sub>O: *M*, 106.2; v. p. 189.1 mm. at 0°) (Found: *M*, 122.7; v. p. 9.0 mm. at 0°. Calc. for C<sub>2</sub>H<sub>10</sub>Si<sub>2</sub>S: *M*, 122.3; v. p. 8.5 mm. at 0°). 1 : 1' : 2 : 2'-Tetramethylidisiloxane was made by hydrolysis of dimethylidiodisilane<sup>12</sup> (Found: *M*, 134.5; v. p. 44.5 mm. at 0°. Calc. for C<sub>4</sub>H<sub>14</sub>Si<sub>2</sub>O: *M*, 134.0; v. p. 44.0 mm. at 0°). Hexamethylidisiloxane was prepared by the hydrolysis of trimethylchlorosilane<sup>13</sup> (Found: *M*, 161. Calc. for C<sub>6</sub>H<sub>18</sub>Si<sub>2</sub>O: *M*, 162). Trimethylboron was prepared by a Grignard reaction between methyl iodide and boron trichloride<sup>14</sup> (84% yield) (Found: *M*, 56.7; v. p. 31.3 mm. at -78°. Calc. for C<sub>3</sub>H<sub>9</sub>B: *M*, 55.9; v. p. 32.5 mm. at -78°). Hydrogen iodide was made from phosphorus iodide and water. Commercial boron trifluoride and trichloride and methyl iodide were purified by fractional condensation and distillation and checked tensimetrically before use.

*Reaction of 1 : 1'-Dimethylidisiloxane with Boron Trifluoride.*—Boron trifluoride (0.0829 g.) and 1 : 1'-dimethylidisiloxane (0.151 g.), held for 12 hr. at -78°, gave on distillation at -132° methylfluorosilane (0.157 g.) (Found: Si-H, by alkaline hydrolysis, 3.15; F, 29.5%; *M*, 64.7. CH<sub>5</sub>FSi requires Si-H, 3.14; F, 29.6%; *M*, 64.1), and a white solid which contained 81.4% of boron trioxide. Methylfluorosilane had vapour pressures (-99° to -56°) given by the equation log<sub>10</sub> *p* (mm.) = 7.830 - 1133/*T*. The extrapolated b. p. was -44.0° ± 0.5°, the latent heat of vaporization 5190 cal./mole, and Trouton's constant 22.6. The vapour pressure at -78° was 103 mm. The m. p. was -125.0° ± 0.5°. A sample was unchanged after storage in a glass bulb at 20° in daylight for 8 weeks.

With a different ratio of reactants, boron trifluoride (0.167 g.) and 1 : 1'-dimethylidisiloxane (0.400 g.) were kept at -78° overnight and methylfluorosilane (0.274 g.) (Found: *M*, 64.8. Calc. for CH<sub>5</sub>FSi: *M*, 64.1) was recovered by distillation at -96°. The amount recovered was 12% in excess of that for the equation (Me·SiH<sub>2</sub>)<sub>2</sub>O + BF<sub>3</sub> = Me·SiH<sub>2</sub>F + Me·SiH<sub>2</sub>·O·BF<sub>2</sub>. The decomposition of methylsiloxyboron difluoride (3Me·SiH<sub>2</sub>·O·BF<sub>2</sub> = 3Me·SiH<sub>2</sub>F + BF<sub>3</sub> + B<sub>2</sub>O<sub>3</sub>) was confirmed by the fact that on completion of the distillation at room temperature the total recovery of methylfluorosilane (0.449 g.), which was probably contaminated with boron trifluoride, was 93%, and the yield of boron trioxide was 93% of that for the reaction

<sup>8</sup> Gerrard and Lappert, *J.*, 1951, 2545.

<sup>9</sup> Wiberg and Sutterlin, *Z. anorg. Chem.*, 1931, 202, 1.

<sup>10</sup> Baumgarten and Bruns, *Ber.*, 1939, 72, 1753.

<sup>11</sup> Emeléus, Onyszchuk, and Kuchen, *Z. anorg. Chem.*, 1956, 283, 74.

<sup>12</sup> Emeléus and Smythe, following paper.

<sup>13</sup> Sauer, *J. Amer. Chem. Soc.*, 1944, 66, 1707.

<sup>14</sup> Brown, *ibid.*, 1945, 67, 374.

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$3(\text{Me}\cdot\text{SiH}_2)_2\text{O} + 2\text{BF}_3 = 6\text{Me}\cdot\text{SiH}_2\text{F} + \text{B}_2\text{O}_3$ . In a further experiment with 1 : 1'-dimethyldisiloxane (0.429 g.) and boron trifluoride (0.182 g.), kept for 12 hr. at  $-78^\circ$ , methylfluorosilane (0.394 g.) (Found:  $M$ , 64.8) was obtained by distillation at  $-98^\circ$  for 1 hr. Further distillation at  $20^\circ$  gave 0.116 g. of a product with  $M$ , 72.5, which gave a white deposit of boron trioxide in the molecular-weight bulb. This probably contained some of the unstable methylsiloxyboron difluoride. Measurements of the vapour pressure of an equimolar mixture of boron trifluoride and 1 : 1'-dimethyldisiloxane at  $-132^\circ$  to  $-63^\circ$  showed an initial v. p. of ca. 30 mm. at  $-132^\circ$ , which decreased almost to zero in 2 min. The v. p. of boron trifluoride is 32 mm. at  $-132^\circ$  and this therefore reacts rapidly with the siloxane at  $-132^\circ$ . The vapour pressure curve of the mixture at higher temperatures was identical with that for methylfluorosilane.

*Reaction of 1 : 1'-Dimethyldisiloxane with Boron Trichloride.*—Boron trichloride (0.277 g.) and 1 : 1'-dimethyldisiloxane (0.206 g.) were kept at  $-78^\circ$  for 12 hr. Distillation of the product at  $-78^\circ$  gave methylchlorosilane (0.142 g.) (Found:  $M$ , 81.0. Calc. for  $\text{CH}_3\text{ClSi}$ :  $M$ , 80.4), a 91% recovery for the reaction  $3(\text{Me}\cdot\text{SiH}_2)_2\text{O} + 2\text{BCl}_3 = 6\text{Me}\cdot\text{SiH}_2\text{Cl} + \text{B}_2\text{O}_3$ . Further distillation at  $20^\circ$  gave a small fraction of  $M$  130–150, which decomposed in the molecular-weight bulb and was probably the dichloro-compound,  $\text{Me}\cdot\text{SiH}_2\cdot\text{O}\cdot\text{BCl}_2$  ( $M$ , 143). Boron trioxide (0.0375 g.) was also recovered. A 5 : 1 molar mixture of boron trichloride (1.675 g.) and 1 : 1'-dimethyldisiloxane (0.208 g.), after reaction at  $-78^\circ$  for 12 hr., gave, on fractional condensation of the mixed products, a fraction condensing at  $-78^\circ$ , which was impure methylsiloxyboron dichloride (Found: Si-H, 1.19; Cl, 46.7%;  $M$ , 146. Calc. for  $\text{CH}_3\text{OCl}_2\text{BSi}$ : Si-H, 1.41; Cl, 49.6%;  $M$ , 142.6). The v. p. at  $0^\circ$  gradually increased owing to decomposition. The material not condensed at  $-78^\circ$  was a mixture of methylchlorosilane with excess of boron trichloride which could not be separated.

*Reaction of 1 : 1'-Dimethyldisiloxane with Hydrogen Iodide.*—Hydrogen iodide (0.040 g.) and 1 : 1'-dimethyldisiloxane (0.170 g.) at  $-78^\circ$  (12 hr.) gave no hydrogen. No hydrogen iodide was recovered by distillation at  $-132^\circ$ . Fractional distillation at higher temperatures gave inseparable mixtures, probably containing the reactants, methyliodosilane, and water  $[(\text{Me}\cdot\text{SiH}_2)_2\text{O} + 2\text{HI} \rightleftharpoons 2\text{Me}\cdot\text{SiH}_2\text{I} + \text{H}_2\text{O}]$ .

*Reaction of 1 : 1' : 2 : 2'-Tetramethyldisiloxane with Boron Trifluoride.*—Boron trifluoride (0.343 g.) and tetramethyldisiloxane (0.226 g.) were kept at  $-78^\circ$  for 12 hr. The white solid product when distilled at  $-96^\circ$  gave a volatile fraction (0.399 g.) which was further separated into boron trifluoride (0.204 g.) (Found:  $M$ , 67.2. Calc. for  $\text{BF}_3$ :  $M$ , 67.8) and dimethylfluorosilane (0.170 g.) (Found: Si-H 1.29%;  $M$ , 78.6.  $\text{C}_2\text{H}_7\text{SiF}$  requires Si-H, 1.28%;  $M$ , 78.1). The v. p. ( $-30^\circ$  to  $-12^\circ$ ) was given by the equation  $\log_{10} p \text{ (mm.)} = 7.500 - 1219/T$ . The extrapolated b. p. was  $-9.0^\circ \pm 0.5^\circ$ , the latent heat of vaporization was 5580 cal./mole, and Trouton's constant 21.1. The m. p. was  $-115^\circ \pm 0.5^\circ$ .

The yield in the above reaction was 64% of that for the equation  $3(\text{Me}_2\text{SiH})_2\text{O} + 2\text{BF}_3 = 6\text{Me}_2\text{SiHF} + \text{B}_2\text{O}_3$ , and 28% greater than that for the reaction  $(\text{Me}_2\text{SiH})_2\text{O} + \text{BF}_3 = \text{Me}_2\text{SiH}\cdot\text{O}\cdot\text{BF}_2 + \text{Me}_2\text{SiHF}$ . The white solid residue from the distillation at  $-96^\circ$  gave further volatile material at room temperature consisting of dimethylfluorosilane (0.0478 g.), boron trifluoride (0.0594 g.), and a very small fraction of  $M$  124, which was probably dimethylsiloxyboron difluoride. The final white solid residue contained 97.4% of boron trioxide.

*Reaction of 1 : 1' : 2 : 2'-Tetramethyldisiloxane with Boron Trichloride.*—Boron trichloride (0.148 g.) and tetramethyldisiloxane (0.170 g.) formed a colourless solution after 20 hr. at  $-78^\circ$ . The volatile products on fractionation gave hydrogen chloride (0.0045 g.) (Found:  $M$ , 41.3; v. p. 19.0 mm. at  $-132^\circ$ . Calc. for  $\text{HCl}$ :  $M$ , 36.5; v. p. 14.0 mm. at  $-132^\circ$ ), dimethylchlorosilane (0.0563 g.) (Found:  $M$ , 95.0. Calc. for  $\text{C}_2\text{H}_7\text{SiCl}$ :  $M$ , 94.6), and a fraction (0.0146 g.) with  $M$  126. The last fraction, when redistilled at  $-23^\circ$ , gave a product with  $M$  163 and v. p. 7.4 mm. at  $0^\circ$ , which was probably dimethylsiloxyboron dichloride ( $M$ , 156.8) contaminated with bis(dimethoxyboron) chloride ( $M$ , 196). When 0.356 g. of tetramethyldisiloxane reacted at room temperature with 0.207 g. of boron trichloride the yield of dimethylchlorosilane was 63% based on the boron trichloride used in the reaction  $(\text{Me}_2\text{SiH})_2\text{O} + \text{BCl}_3 = \text{Me}_2\text{SiHCl} + \text{Me}_2\text{SiH}\cdot\text{O}\cdot\text{BCl}_2$ . Fractions which probably contained dimethylsiloxyboron dichloride and bis(dimethoxyboron) chloride were again obtained but could not be further separated. The following new physical properties of dimethylchlorosilane were measured: the v. p. ( $-17^\circ$  to  $10^\circ$ ) was given by  $\log_{10} p \text{ (mm.)} = 7.322 - 1370/T$ , the extrapolated b. p. being  $34.7^\circ \pm 0.5^\circ$ . The latent heat of vaporization was 6270 cal./mole, Trouton's constant 20.4 and the m. p.  $-111^\circ \pm 1^\circ$ .



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**Reaction of Hexamethyldisiloxane with Boron Trifluoride.**—Boron trifluoride (0.298 g.) and hexamethyldisiloxane (0.237 g.) were mixed at  $-78^{\circ}$  and kept for 12 hr. Unchanged boron trifluoride (0.184 g.) (Found:  $M$ , 68.5. Calc. for  $\text{BF}_3$ :  $M$ , 67.8) was recovered by distillation at  $-96^{\circ}$ . Trimethylfluorosilane (0.146 g.) (Found:  $M$ , 90.0. Calc. for  $\text{C}_3\text{H}_9\text{SiF}$ :  $M$ , 92.1) was isolated by distillation at  $-78^{\circ}$ . These amounts are respectively 12 and 11% in excess of those calculated for the equation  $(\text{Me}_3\text{Si})_2\text{O} + \text{BF}_3 = \text{Me}_3\text{Si}\cdot\text{O}\cdot\text{BF}_2 + \text{Me}_3\text{SiF}$ . A white solid residue from these distillations, when distilled at room temperature, gave trimethylfluorosilane (0.105 g.) (Found: v. p. 134 mm. at  $-21.5^{\circ}$ . Calc. for  $\text{C}_3\text{H}_9\text{SiF}$ : v. p. 138 mm. at  $-21.5^{\circ}$ ). This was 77% of the amount for the decomposition  $3\text{Me}_3\text{Si}\cdot\text{O}\cdot\text{BF}_2 = 3\text{Me}_3\text{SiF} + \text{BF}_3 + \text{B}_2\text{O}_3$ . A second fraction (0.0146 g.;  $M$ , 113) probably contained trimethylsiloxyboron difluoride (Calc.:  $M$ , 138), but this was not isolated because of its ready decomposition. The residue was boron trioxide. The total yield of trifluoromethylsilane isolated was 96% based on the hexamethyldisiloxane used in the reaction  $3(\text{Me}_3\text{Si})_2\text{O} + 2\text{BF}_3 = 6\text{Me}_3\text{SiF} + \text{B}_2\text{O}_3$ . When hexamethyldisiloxane (0.296 g.) and boron trifluoride reacted at room temperature (12 hr.) the products were trimethylfluorosilane (0.321 g.) (Found:  $M$ , 92.5. Calc. for  $\text{C}_3\text{H}_9\text{SiF}$ :  $M$ , 92.1) and an involatile residue (0.0425 g.) which contained 95.8% of boron trioxide. These yields were 95.6 and 97.4% respectively for the reaction:  $3(\text{Me}_3\text{Si})_2\text{O} + 2\text{BF}_3 = 6\text{Me}_3\text{SiF} + \text{B}_2\text{O}_3$ . To obtain information about the initial stages of this reaction a 3:1 molar excess of boron trifluoride (0.399 g.) was taken with hexamethyldisiloxane (0.318 g.) and held at  $-78^{\circ}$  for only 2 hr. Excess of boron trifluoride (0.277 g.) was distilled out at  $-96^{\circ}$ . 0.92 Mole of boron trifluoride was consumed per mole of hexamethyldisiloxane. The temperature of the white residue was then raised to  $-78^{\circ}$  and a further 0.105 g. of boron trifluoride (Found:  $M$ , 68.0. Calc. for  $\text{BF}_3$ :  $M$ , 67.8) was recovered with 0.0236 g. of trimethylfluorosilane (Found:  $M$ , 92.8. Calc. for  $\text{C}_3\text{H}_9\text{SiF}$ :  $M$ , 92.1). The boron trifluoride recovered was 97% of that taken, showing that a relatively stable 1:1 adduct was formed at  $-78^{\circ}$ , which was readily dissociated at this temperature but not at  $-96^{\circ}$ . The fluorosilane arose from the decomposition.

**Reaction of Hexamethyldisiloxane with Boron Trichloride.**—Hexamethyldisiloxane (0.455 g.) and boron trichloride (0.987 g.) gave a clear solution when left overnight at room temperature. Unchanged boron trichloride (0.668 g.) (Found:  $M$ , 117. Calc. for  $\text{BCl}_3$ :  $M$ , 117) was distilled off at  $-78^{\circ}$ . The molar ratio for the reaction was thus almost 1:1. Repeated fractionation of the product gave trimethylchlorosilane (0.372 g.) (Found:  $M$ , 115; v. p. 63.5 mm. at  $0^{\circ}$ . Calc. for  $\text{C}_3\text{H}_9\text{SiCl}$ :  $M$ , 108.6; v. p. 74 mm. at  $0^{\circ}$ ) and trimethylsiloxyboron dichloride (0.371 g.) (Found:  $\text{Cl}$ , 41.8%;  $M$ , 171; v. p. 10.5 mm. at  $0^{\circ}$ .  $\text{C}_3\text{H}_9\text{OCl}_2\text{BSi}$  requires  $\text{Cl}$ , 41.4%;  $M$ , 170.8). The yield was 77% of that calculated for the equation  $(\text{Me}_3\text{Si})_2\text{O} + \text{BCl}_3 = \text{Me}_3\text{Si}\cdot\text{O}\cdot\text{BCl}_2 + \text{Me}_3\text{SiCl}$ . The compound decomposed slowly at room temperature.

**Reaction of 1:1'-Dimethyldisilthiane with Boron Trifluoride.**—There was no reaction between 1:1'-dimethyldisilthiane (0.327 g.) and boron trifluoride (0.182 g.) at  $-78^{\circ}$  or  $20^{\circ}$ , and the unchanged reactants were recovered quantitatively by distillation at  $-96^{\circ}$ . Heating the mixture on a steam-bath for 2 hr. gave hydrogen (17.8 ml. at S.T.P.), a viscous liquid, and white crystals. The liquid product, which had the odour of a sulphide, was not fully separated and characterized. A fraction (0.298 g.) had  $M$ , 57.9 and a second fraction (0.0055 g.) had  $M$ , 151. The first would contain any residual boron trifluoride, also methylsilane and methylfluorosilane. The white crystals melted above  $350^{\circ}$ , with some decomposition. Positive tests were obtained for silicon, hydrogen bonded to silicon, and sulphur. Boron was absent. The quantities of solid and liquid were too small for a detailed examination.

**Reaction of 1:1'-Dimethyldisilthiane with Boron Trichloride.**—Boron trichloride (0.194 g.) and 1:1'-dimethyldisilthiane (0.202 g.) formed a white solid and a clear liquid when warmed to room temperature. The mixture was kept at  $100^{\circ}$  for 16 hr. for complete reaction. The products identified were hydrogen (18.2 ml. at S.T.P.), hydrogen chloride (0.0033 g.), and boron trichloride (0.136 g.) (Found:  $M$ , 117; v. p. 133.5 mm. at  $-23^{\circ}$ . Calc. for  $\text{BCl}_3$ :  $M$ , 117.2; v. p. 167 mm. at  $-23^{\circ}$ ). A small fraction of  $M$  106 may have been a mixture of boron trichloride and methylchlorosilane. The solid and viscous liquid products, which had the odour of a sulphide, were too small in amount for further separation.

**Reaction of 1:1'-Dimethyldisilthiane with Hydrogen Iodide.**—The volatile products from the reaction of 1:1'-dimethyldisilthiane (0.294 g.) and hydrogen iodide (0.509 g.) at room temperature during 16 hr. were hydrogen sulphide (0.0728 g.) (Found:  $M$ , 34.8. Calc. for  $\text{H}_2\text{S}$ :  $M$ , 34.0) and methyl iodide (0.719 g.) (Found:  $M$ , 170. Calc. for  $\text{CH}_3\text{SiI}$ :  $M$ , 172). Droplets of a viscous liquid remained in the reaction vessel.

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*Reaction of 1 : 1'-Dimethyldisilthiane with Methyl Iodide.*—Methyl iodide (0.309 g.) and 1 : 1'-dimethyldisilthiane (0.134 g.) at 100° during 16 hr. gave a small amount of transparent polymer. Methyl iodide was recovered quantitatively (Found: v. p. 141 mm. at 0°. Calc. for CH<sub>3</sub>I: v. p. 141 mm. at 0°). The remaining volatile material was unchanged 1 : 1'-dimethyldisilthiane (0.105 g., 78%). There was no evidence for the formation of a sulphonium complex.

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