# **971.** *The Reactions of Hexamethyldisilthiane and Ethylthiotrimethylsilane with Alcohols, Thiols, Acids, and Amines.*

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Hexamethyldisilthiane, $S(SiMe_3)_2$, has been prepared in good yield from anhydrous sodium sulphide and chlorotrimethylsilane. The reactions of hexamethyldisilthiane with alcohols, thiols, acids, and amines have been investigated. From these reactions the series of compounds $R{\cdot}SiMe_3$ where R = EtO, $Bu^nO$, $Pr^iO$, $Bu^tO$, $Bu^nS$, Et·CO·O, BzO, $Bu^n_2N$, $Bu^n{\cdot}NH$, Ph·NH was produced. Similarly, reactions of ethylthiotrimethylsilane with the requisite amine and acid have given in each case ethanethiol and $R{\cdot}SiMe_3$ where R = Et·CO·O, BzO, $Bu^n_2N$, $Bu^n{\cdot}NH$, Ph·NH.

PREVIOUSLY, the formation of the alkyldisilthianes from alkylsilicon halides has involved [1-3] the expensive iodides and silver sulphide. It is now found that chlorotrimethylsilane and anhydrous sodium sulphide give almost quantitative yields of hexamethyldisilthiane, $S(SiMe_3)_2$. The reaction did not take place under ordinary conditions of temperature and pressure, but proceeded smoothly in pressure vessels at 250°:

$$2Me_3SiCl + Na_2S \longrightarrow (Me_3Si)_2S + 2NaCl \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

The Si–S bond has been shown [2] to be readily attacked by water; also alcoholysis of the alkythiotrimethylsilanes produced [4] alkoxytrimethylsilanes. A number of these alkoxytrimethylsilanes have now been prepared by alcoholysis of hexamethyldisilthiane:

$$(Me_3Si)_2S + ROH \longrightarrow Me_3Si{\cdot}SH + RO{\cdot}SiMe_3 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$Me_3Si{\cdot}SH + ROH \longrightarrow H_2S + RO{\cdot}SiMe_3 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

The reaction was exothermic in the cases of ethanol and butan-1-ol, and high yields of the corresponding alkoxytrimethylsilanes were obtained. In the cases of propan-2-ol and t-butyl alcohol, however, the reaction required heating and was slow, and yields were not as good. The reaction is written in two stages (2 and 3), with the initial formation of trimethylsilanethiol, as when heating was necessary the temperature of reflux invariably remained at 77—78° for some time. Although the thiol [5] was not isolated as such, this temperature suggested its presence (b. p. 77°), and it would then react with further alcohol.

In the corresponding reactions of hexamethyldisilthiane with thiols, hydrogen sulphide was evolved only slowly upon prolonged refluxing, and owing to the very long times required reactions were not carried to completion. The alkylthiotrimethylsilanes were

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[1] Eaborn, *Nature*, 1950, **165**, 685.
[2] Eaborn, *J.*, 1950, 3077.
[3] Emeléus, Onyszchuk, and Kuchen, *Z. anorg. Chem.*, 1956, **283**, 74.
[4] Abel, *J.*, 1960, 4406.
[5] Larsson and Marin, *Acta Chem. Scand.*, 1951, **5**, 964.

isolated in varying yields. 1,1-Dimethylethanethiol did not react with hexamethyldisilthiane.

The reactions of hydrogen sulphide[5-7] and thiols[4,6] with aminosilanes have been extensively studied for the production of Si–S from Si–N bonds. As a result of the approximately equal replacement tendencies of the alkylthio- and alkylamino-groups in these and similar[8] systems, the reverse procedure has now been used to produce aminosilanes from compounds containing Si–S bonds. Hexamethyldisilthiane, when heated with di-n-butylamine, n-butylamine, or aniline evolved hydrogen sulphide, and produced, respectively, di-n-butylamino-, butylamino-, and anilino-trimethylsilane:

$$2R_2NH + (Me_3Si)_2S \longrightarrow H_2S + 2R_2N{\cdot}SiMe_3 \tag{4}$$

$$2R{\cdot}NH_2 + (Me_3Si)_2S \longrightarrow H_2S + 2R{\cdot}NH{\cdot}SiMe_3 \tag{5}$$

The reactions were slow, and yields of aminosilanes were not good. Although expressions (4) and (5) are written to represent the overall reaction, again trimethylsilanethiol appeared to be present, and possibly as a result of its slightly acidic nature, formed compounds with the amines present. Similar reactions between these amines and ethylthiotrimethylsilane gave ethanethiol and the same aminosilanes:

$$R_2NH + Me_3Si{\cdot}SEt \longrightarrow EtSH + R_2N{\cdot}SiMe_3 \tag{6}$$

$$R{\cdot}NH_2 + Me_3Si{\cdot}SEt \longrightarrow EtSH + R{\cdot}NH{\cdot}SiMe_3 \tag{7}$$

Propionic acid and hexamethyldisilthiane did not react in the cold but, on warming, hydrogen sulphide was evolved and trimethylsilyl propionate was formed in good yield. The ester was also produced by the action of the acid on ethylthiotrimethylsilane:

$$R{\cdot}CO_2H + (Me_3Si)_2S \longrightarrow H_2S + 2R{\cdot}CO_2{\cdot}SiMe_3 \tag{8}$$

$$R{\cdot}CO_2H + Me_3Si{\cdot}SEt \longrightarrow EtSH + R{\cdot}CO_2{\cdot}SiMe_3 \tag{9}$$

Reactions (8) and (9) were also carried out with benzoic acid, giving good yields of trimethylsilyl benzoate.

In general, it may be concluded that compounds containing Si–S bonds react smoothly with alcohols and acids to give good yields of the products, but reactions with thiols and amines are not undergone so readily and yields of the resulting compounds are not always good.

## EXPERIMENTAL

The reactions were carried out under anhydrous conditions with dried materials. The use of wet reagents produced hexamethyldisiloxane as a major by-product. Ethylthiotrimethylsilane was prepared as previously described,[4] and sodium sulphide was dried at 200°/0·01 mm.

*Preparation of Hexamethyldisilthiane.*—Anhydrous sodium sulphide (18·0 g., 1 mol.) and chlorotrimethylsilane (50·2 g., 2 mols.) were heated (20 hr.) in a heavy-walled sealed glass tube at 240°. Subsequent distillation yielded hexamethyldisilthiane (39·4 g., 96%), b. p. 163°, $n_D^{20}$ 1·4572 (Found: C, 40·1; H, 10·6. Calc. for $C_6H_{18}SSi_2$: C, 40·4; H, 10·2%), and a dark residue of sodium chloride.

*Interaction of Hexamethyldisilthiane with Alcohols.*—The alcohol (0·2 mole) was added to the hexamethyldisilthiane (0·1 mole) with shaking. With ethanol and butan-1-ol, the mixture became warm and hydrogen sulphide was immediately evolved; no observable reaction took place with propan-2-ol or t-butyl alcohol. The mixture was refluxed and hydrogen sulphide was evolved in all cases. Subsequent fractionation gave varying yields of the alkoxytrimethylsilanes (see Table). These were characterised by b. p., *n*, and identity of the infrared spectra with those previously reported.[4]

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[6] Larsson and Marin, Swed. P., 138,357/1952 (*Chem. Abs.*, 1954, **48**, 2761).

[7] Larsson and Mjörne, *Acta Chem. Scand.*, 1951, **5**, 64.

[8] Aubrey and Lappert, *Proc. Chem. Soc.*, 1960, 148.

| R in $Me_3Si{\cdot}OR$ | Yield (%) | Reaction time (hr.) | B. p. | $n_D^{20}$ | R in $Me_3Si{\cdot}OR$ | Yield (%) | Reaction time (hr.) | B. p. | $n_D^{20}$ |
|---|---|---|---|---|---|---|---|---|---|
| Et | 92 | 1 | 75° | 1·3745 | $Pr^i$ | 78 | 15 | 88° | 1·3788 |
| $Bu^n$ | 94 | 1 | 125 | 1·3930 | $Bu^t$ | 58 | 400 | 105 | 1·3910 |

*Interaction of Hexamethyldisilthiane with Butane*-1-*thiol.*—No evolution of gas occurred when the thiol (5·48 g., 2 mol.) was mixed with the hexamethyldisilthiane (5·43 g., 1 mol.) in the cold. On warming, hydrogen sulphide was evolved for 20 hr. Fractionation of the resulting oil gave n-butylthiotrimethylsilane (7·24 g., 76%), b. p. 169°, $n_D^{20}$ 1·4553, having an authentic infrared spectrum.[4]

In a similar experiment involving hexa-1,1-dimethylethanethiol no evolution of hydrogen sulphide was noted after three days' heating, and subsequent distillation gave virtually complete recovery of the reactants.

*Interaction of Hexamethyldisilthiane and Di-n-butylamine.*—The amine (12·8 g., 2 mol.) and hexamethyldisilthiane (8·80 g., 1 mol.) did not evolve hydrogen sulphide when mixed, but did so when heated. After refluxing (3 days), distillation gave a large forerun of unchanged amine and the disilthiane, followed by *di-n-butylaminotrimethylsilane* (9·80 g., 49%), b. p. 200°, $n_D^{20}$ 1·4291 (Found: C, 65·9; H, 13·7; N, 7·0. $C_{11}H_{27}NSi$ requires C, 65·7; H, 13·4; N, 7·0%).

*Interaction of Hexamethyldisilthiane and n-Butylamine.*—Adding the amine (8·97 g., 2 mol.) to hexamethyldisilthiane (10·95 g., 1 mol.) produced slight heating and a yellow colour. Subsequent refluxing (25 hr.) caused steady but slow evolution of hydrogen sulphide. Careful fractionation of the resulting mixture produced mainly unchanged amine and hexamethyldisilthiane, but a small quantity of butylaminotrimethylsilane[9] (2·3 g., 13%), b. p. 135°, $n_D^{20}$ 1·4097 (Found: N, 9·71. Calc. for $C_7H_{19}NSi$: N, 9·66%), was obtained.

*Interaction of Aniline and Hexamethyldisilthiane.*—The amine (5·43 g., 2 mol.) and the silthiane (5·19 g., 1 mol.) did not react in the cold, but hydrogen sulphide was evolved on warming. Refluxing (25 hr.) gave hydrogen sulphide, and subsequent fractionation gave anilinotrimethylsilane[10] (8·18 g., 85%), b. p. 208°, $n_D^{20}$ 1·5222 (Found: N, 8·6. Calc. for $C_9H_{15}NSi$: N, 8·5%).

*Interaction of Hexamethyldisilthiane and Propionic Acid.*—Addition of the acid (4·35 g., 2 mol.) to hexamethyldisilthiane caused neither heating nor evolution of hydrogen sulphide. On warming, a steady stream of the gas was evolved for 10 hr., and subsequent distillation gave *trimethylsilyl propionate* (7·30 g., 85%), b. p. 122°, $n_D^{20}$ 1·3939 (Found: C, 49·8; H, 10·3. $C_6H_{14}O_2Si$ requires C, 49·3; H, 9·6%).

In a similar reaction benzoic acid produced trimethylsilyl benzoate (83%), b. p. 221°, $n_D^{20}$ 1·4860.

*Interaction of Di-n-butylamine and Ethylthiotrimethylsilane.*—The amine (14·30 g., 1 mol.) and ethylthiotrimethylsilane (14·88 g., 1 mol.) underwent no apparent reaction in the cold. Heating under reflux (50 hr.) and subsequent fractionation gave ethanethiol (4·29 g., 62%), b. p. 35°, $n_D^{20}$ 1·4300, a middle fraction of unchanged reactants, and finally di-n-butylaminosilane (15·1 g., 68%), b. p. 200°, $n_D^{20}$ 1·4291 (Found: N, 6·9%).

Similar reactions of ethylthiotrimethylsilane with n-butylamine and aniline gave, respectively, butylaminotrimethylsilane (58%), b. p. 134°, $n_D^{20}$ 1·4100 (Found: N, 9·5%), and anilinotrimethylsilane (71%), b. p. 207°, $n_D^{20}$ 1·5222 (Found: N, 8·7%).

*Interaction of Ethylthiotrimethylsilane and Propionic Acid.*—The acid (3·22 g., 1 mol.) and ethylthiotrimethylsilane (5·83 g., 1 mol.) were heated together under reflux (5 hr.). Subsequent fractionation gave ethanethiol (2·29 g., 85%), b. p. 34°, $n_D^{20}$ 1·4297, and trimethylsilyl propionate (5·72 g., 90%), b. p. 122°, $n_D^{20}$ 1·3941 (Found: C, 49·1; H, 10·1%).

Similar use of benzoic acid gave trimethylsilyl benzoate (83%), b. p. 220°, $n_D^{20}$ 1·4858.

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[9] Langer, Connell, and Wender, *J. Org. Chem.*, 1958, **23**, 50.

[10] Osthoff and Kantor, *Inorg. Synth.*, 1957, **5**, 55.