

1011. *Reaction of Dichlorotrimethylsiloxyaluminium with Dialkylcyclosiloxanes.*

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The reaction between dichlorotrimethylsiloxyaluminium and four dialkylcyclosiloxanes has been studied. From methylsiloxanes, a crystalline substance $C_8H_{16}Al_3Cl_2O_6Si_4$ and an amorphous substance of formula $[Me_2Si^*O-AlClO]_n$ have been isolated from ethylsiloxanes, only a crystalline substance $C_{16}H_{32}Al_3Cl_2O_6Si_4$ was found.

IN the preparation of polyaluminium-organosiloxanes, we studied the reaction between dichlorotrimethylsiloxyaluminium and dialkylcyclosiloxanes. It is known¹ that dichlorotrimethylsiloxyaluminium decomposes when heated into chlorotrimethylsilane and

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¹ M. G. Voronkov, B. N. Dolgov, and N. A. Dmitrieva, *Doklady Akad. Nauk S.S.S.R.*, 1952, **84**, 959.

contains

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bonds.

In addition to the chlorosilane, various sulphur–nitrogen compounds

have been isolated from these reactions. A novel method for the preparation

of *NN*-diethylaminotrimethylsilane is also reported.

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ALTHOUGH many covalent halides are known to cause the fission of silicon–nitrogen bonds,¹ only one report has been made of the reaction of aminosilanes and disilazanes with covalent compounds containing sulphur–chlorine bonds. Sulphuryl chloride and ethyl chlorosulphonate cause fission of one of the silicon–nitrogen bonds in hexamethyldisilazane, to give *N*-silylsulphonamides.² It is also noted, however, that ethyl chlorosulphonate and chlorosulphonic acid can react with the labile hydrogen atoms in hexamethyldisilazane and *N*-methylaminotrimethylsilane, respectively, without fission of the Si–N bond.² Although not involving fission of Si–N bonds, a number of reactions between *N*-metallated hexamethyldisilazane and sulphur halides have been recorded as producing *N*-silylated sulphur–nitrogen compounds, with metal halide as by-product.^{3,4}

In all the reactions considered below, we treated the aminosilanes and disilazanes with sufficient of the covalent sulphur–chlorine compound to allow fission of all Si–N bonds. Yields of trimethylchlorosilane were very good, and some of the reactions were extremely vigorous, even when carried out at greatly reduced temperature.

¹ Fessenden and Fessenden, *Chem. Rev.*, 1961, **61**, 361.

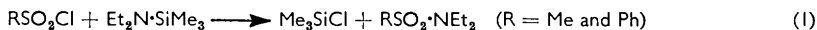
² Becke-Goehring and Wunsch, *Annalen*, 1958, **618**, 43.

³ Wannagat and Kuckertz, *Angew. Chem.*, 1962, **74**, 117.

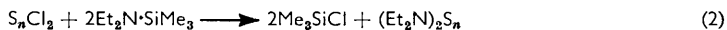
⁴ Scherer and Schmidt, *Angew. Chem.*, 1963, **75**, 139.

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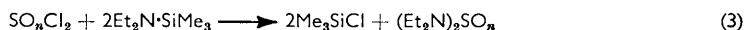
Both methane- and benzene-sulphonyl chloride reacted with *NN*-diethylaminotrimethylsilane to evolve trimethylchlorosilane and form, respectively, methane- and benzene-sulphonyl *NN*-diethylamide (reaction 1).



Sulphur dichloride, when treated with 2 moles of *NN*-diethylaminotrimethylsilane, produced bis(diethylamino)sulphane (reaction 2; $n = 1$). The corresponding reaction with disulphur dichloride (reaction 2; $n = 2$) gives an almost quantitative evolution of trimethylchlorosilane, and bis(diethylamino)disulphane. In this case, however, we were unable to distil the high-boiling product without slight decomposition to the monosulphane and sulphur.



NN-Diethylaminotrimethylsilane and thionyl chloride react to produce sulphinyl di-*NN*-diethylamide (reaction 3; $n = 1$). Sulphuryl chloride underwent a similar reaction to give sulphonyl di-*NN*-diethylamide (reaction 3; $n = 2$).

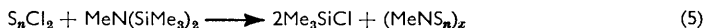


When thionyl chloride reacted with the *N*-substituted hexamethyldisilazanes, the corresponding sulphinyl alkylimides were formed (reaction 4).



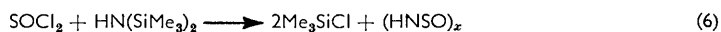
The corresponding reactions of sulphur dichloride and sulphuryl chloride with *N*-phenylhexamethyldisilazane, whilst producing trimethylchlorosilane, gave only black, charred solids as the other products.

Sulphur dichloride and *N*-methylhexamethyldisilazane gave a 96% yield of trimethylchlorosilane (reaction 5; $n = 1$), the other product being an orange gel similar to that obtained by Stone and Nielsen from the interaction of methylamine and sulphur dichloride.^{5,6} The gel decomposed on standing to deposit sulphur. Similarly, disulphur dichloride gave trimethylchlorosilane and an insoluble yellow polymeric solid (reaction 5, $n = 2$), which analysed, considering the intractable nature of the product, quite closely to $(\text{MeNS}_2)_x$.



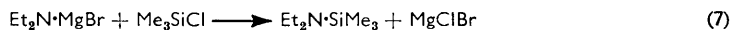
Both sulphur dichloride and disulphur dichloride reacted with hexamethyldisilazane to give excellent yields of trimethylchlorosilane, but the other products were very complex, including sulphur, ammonium chloride, and tetrasulphur tetranitride, presumably formed by secondary reactions, as with ammonia and the sulphur chlorides.⁷

In the absence of solvent, thionyl chloride and hexamethyldisilazane reacted violently, even at liquid-air temperature, to produce a cream coloured solid. After warming, trimethylchlorosilane was removed in 93% yield (reaction 6). The polymeric sulphinyl



imide decomposed upon standing, as has been previously observed for the product from the reaction of ammonia with thionyl chloride.⁸

For use in this work, *NN*-diethylaminotrimethylsilane was prepared in excellent yield



⁵ Stone and Nielsen, *J. Amer. Chem. Soc.*, 1957, **79**, 1264.

⁶ Stone and Nielsen, *J. Amer. Chem. Soc.*, 1959, **81**, 3580.

⁷ Valkenburgh and Bailar, *J. Amer. Chem. Soc.*, 1925, **47**, 2134.

⁸ Schenk, *Ber.*, 1942, **75**, 94.

by a novel method involving the reaction (7) between *NN*-diethylaminomagnesium bromide and trimethylchlorosilane.

EXPERIMENTAL

Hexamethyldisilazane and *N*-methylhexamethyldisilazane were prepared by known methods,⁹ as also were *N*-*n*-butylhexamethyldisilazane¹⁰ and *N*-phenylhexamethyldisilazane.¹¹ The sulphur-containing halides were redistilled to constant b. p. before use. It was necessary to distil sulphur dichloride in the presence of 10% of phosphorus trichloride, which inhibits the disproportionation to disulphur dichloride and chlorine during distillation;^{5,6} the distillate was used promptly. Care was taken throughout to ensure absence of moisture.

Light petroleum had b. p. 100–120°. Trimethylchlorosilane was identified by b. p. and refractive index.

NN-Diethylaminotrimethylsilane.—Bromoethane (316 g., 1 mol.) was slowly added to dry magnesium (75 g., 1 mol.) in dry ether (500 ml.), reaction being initiated by a few drops of bromine. After stirring for 1 hr., diethylamine (224 g., 1 mol.) was carefully added; this resulted in the steady evolution of ethane. Trimethylchlorosilane (325 g., 1 mol.) was carefully added after 2 hr. and the mixture set aside. Volatile matter was distilled off, and fractionation gave the required silane (155 g., 75%), b. p. 126–127°, n_D^{20} 1.4108. This method is analogous to that reported for *NN*-diethylaminotrimethyltin.¹²

Reaction of Methanesulphonyl Chloride with NN-Diethylaminotrimethylsilane (reaction 1; R = Me).—Methanesulphonyl chloride (5.03 g., 1 mol.) was slowly added to *NN*-diethylaminotrimethylsilane (6.37 g., 1 mol.) cooled in a bath of solid carbon dioxide and acetone. A vigorous reaction occurred, and, after 24 hr. at room temperature, distillation gave trimethylchlorosilane (87%). Vacuum-distillation of the residue gave methanesulphonyl *NN*-diethylamide (5.48 g., 83%), b. p. 110°/8 mm., n_D^{20} 1.4480 (Found: C, 40.0; H, 9.0; N, 9.6. Calc. for $C_5H_{13}NO_2S$: C, 39.7; H, 8.65; N, 9.25%).

Reaction of Benzenesulphonyl Chloride with NN-Diethylaminotrimethylsilane (reaction 1; R = Ph).—Benzenesulphonyl chloride (11.22 g., 1 mol.) was added dropwise to *NN*-diethylaminotrimethylsilane (9.23 g., 1 mol.) at –78°. After standing for 24 hr. at room temperature, the trimethylchlorosilane formed was removed at reduced pressure (0.1 mm.) and collected at –78° (92%). The residual cream solid gave crystals of benzenesulphonyl *NN*-diethylamide (9.80 g., 73%), m. p. 41–42° (from ethanol) (Found: C, 56.7; H, 7.0; N, 7.0. Calc. for $C_{10}H_{15}NO_2S$: C, 56.4; H, 7.1; N, 6.6%).

Reaction of Sulphur Dichloride with NN-Diethylaminotrimethylsilane (reaction 2; n = 1).—Sulphur dichloride (6.00 g., 1 mol.) was added to *NN*-diethylaminotrimethylsilane (16.82 g., 2 mol.) in dry petroleum at –78°. Slow addition produced a steady reaction, and subsequent distillation after 24 hr. gave trimethylchlorosilane (82%). After pumping off the petroleum, vacuum-distillation gave bis(diethylamino)sulphane (6.50 g., 64%), b. p. 75°/10 mm., n_D^{20} 1.4625 (Found: C, 54.8; H, 11.5; N, 15.85. Calc. for $C_8H_{20}N_2S$: C, 54.6; H, 11.4; N, 15.9%); a charred residue remained after distillation.

Reaction of Disulphur Dichloride with NN-Diethylaminotrimethylsilane (reaction 2; n = 2).—Disulphur dichloride (5.94 g., 1 mol.) was slowly added to *NN*-diethylaminotrimethylsilane (12.75 g., 2 mol.) at –78°. After leaving at 20° for 3 hr. all volatile material was pumped off, giving trimethylchlorosilane (97%) on redistillation. The residue, bis(diethylamino)disulphane, remained as a red liquid, n_D^{20} 1.514 (Found: C, 43.1; H, 9.4. Calc. for $C_8H_{20}N_2S_2$: C, 46.0; H, 9.6%), but could not be distilled owing to decomposition. After 2 days decomposition was complete, and distillation gave bis(diethylamino)sulphane, b. p. 32°/0.5 mm., n_D^{20} 1.4636.

Reaction of Thionyl Chloride with NN-Diethylaminotrimethylsilane (reaction 3; n = 1).—Thionyl chloride (5.98 g., 1 mol.) was added to *NN*-diethylaminotrimethylsilane (14.58 g., 2 mol.) in dry petroleum at –78°. Distillation gave trimethylchlorosilane (97%). Vacuum-distillation of the residue gave sulphinyl di-(*NN*-diethylamide) as a pale yellow liquid (6.80 g., 71%), b. p. 58°/0.1 mm., n_D^{20} 1.4640 (Found: C, 50.2; H, 10.4; N, 14.75. Calc. for $C_8H_{20}N_2OS$: C, 49.9; H, 10.5; N, 14.6%).

⁹ Osthoff and Kantor, *Inorg. Synth.*, 1957, **5**, 56.

¹⁰ Ruhlmann, *Chem. Ber.*, 1961, **94**, 2311.

¹¹ Abel and Willey, unpublished work.

¹² Sisido and Kozima, *J. Org. Chem.*, 1963, **27**, 4051.

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Reaction of Sulphuryl Chloride with NN-Diethylaminotrimethylsilane (reaction 3; n = 2).—Sulphuryl chloride (8.15 g., 1 mol.) was slowly added to *NN*-diethylaminotrimethylsilane (17.62 g., 2 mol.) at -78° in dry petroleum. Distillation, after standing at room temperature for a day, gave trimethylchlorosilane (78%). Vacuum-distillation of the residue gave sulphonyl di-*(NN)*-diethylamide as a colourless liquid (5.50 g., 44%), b. p. $70^{\circ}/4$ mm., n_D^{20} 1.4434 (Found: C, 43.6; H, 8.4. Calc. for $C_8H_{20}N_2O_2S$: C, 46.1; H, 9.7%). This compound appeared to undergo slight decomposition during distillation, which may account for the rather low analysis figures obtained.

Reaction of Thionyl Chloride with N-Methylhexamethylidisilazane (reaction 4; R = Me).—The dropwise addition of thionyl chloride (15.44 g., 1 mol.) to *N*-methylhexamethylidisilazane (22.72 g., 1 mol.) in dry petroleum at -78° produced a vigorous reaction. A liquid was distilled from this (36.00 g., 94%), b. p. $57-60^{\circ}$, which contained trimethylchlorosilane (b. p. 57°) and sulphinyl methylimide (b. p. 58°). Attempts to separate the two proved unsuccessful.

Reaction of Thionyl Chloride with N-n-Butylhexamethylidisilazane (reaction 4; R = Buⁿ).—Thionyl chloride (5.13 g., 1 mol.) was slowly added to *N*-*n*-butylhexamethylidisilazane (9.33 g., 1 mol.) at -78° . A white gel was produced which on distillation yielded trimethylchlorosilane (91%) and sulphinyl *n*-butylimide (3.20 g., 62%), b. p. $50^{\circ}/36$ mm., n_D^{20} 1.4367 (Found: C, 39.9; H, 7.5; N, 12.2. C_4H_9NOS requires C, 40.3; H, 7.6; N, 11.75%) as a colourless liquid.

Reaction of Thionyl Chloride with N-Phenylhexamethylidisilazane (reaction 4; R = Ph).—The slow addition of thionyl chloride (9.28 g., 1 mol.) to the disilazane (18.49 g., 1 mol.) at -78° produced a vigorous reaction. Distillation gave trimethylchlorosilane (86%), and subsequent vacuum-distillation of the residual liquid yielded sulphinyl phenylimide (9.75 g., 90%), b. p. $48^{\circ}/2$ mm., n_D^{25} 1.6247 (Found: C, 51.9; H, 3.5; N, 10.05. Calc. for C_6H_5NOS : C, 51.8; H, 3.6; N, 10.05%), as a bright yellow liquid.

Reaction of Sulphur Dichloride with N-Phenylhexamethylidisilazane.—Sulphur dichloride (8.00 g., 1 mol.) was added to *N*-phenylhexamethylidisilazane (18.40 g., 1 mol.) at -78° in petroleum. The vigorous reaction gave a brown solid, and, after 24 hr., distillation gave trimethylchlorosilane (91%). The residue was an intractable, black, cinder-like solid.

Reaction of Sulphuryl Chloride with N-Phenylhexamethylidisilazane.—Sulphuryl chloride (5.47 g., 1 mol.) was slowly added to the disilazane (9.59 g., 1 mol.) at -78° . A vigorous reaction occurred and an orange solid was formed. On warming to room temperature, this darkened to a black solid with the evolution of heat. Distillation gave trimethylchlorosilane (54%), but the black residue was involatile.

Reaction of Sulphur Dichloride with N-Methylhexamethylidisilazane (reaction 5; n = 1).—Sulphur dichloride (13.20 g., 1 mol.) was slowly added to *N*-methylhexamethylidisilazane (22.41 g., 1 mol.) at -78° in dry petroleum. A slow reaction ensued, with the precipitation of a brown solid which redissolved on standing. Fractionation gave trimethylchlorosilane (96%), and an orange polymeric gel remained after pumping off the solvent. This gel decomposed upon standing, to deposit sulphur.

Reaction of Disulphur Dichloride with N-Methylhexamethylidisilazane (reaction 5; n = 2).—The addition of disulphur dichloride (6.12 g., 1 mol.) to *N*-methylhexamethylidisilazane (7.93 g., 1 mol.) at -78° in dry petroleum produced a slow reaction. A cream solid was precipitated, and subsequent distillation gave trimethylchlorosilane (95%). Pumping off the solvent left a yellow solid (4.14 g., 99%), m. p. 129° . This was insoluble in all common solvents and analysed well for polymeric methylamino disulphide [Found: C, 11.0; H, 3.7; N, 15.1. $(CH_3NS_2)_x$ requires C, 12.9; H, 3.2; N, 15.05%].

Reaction of Sulphur Dichloride with Hexamethylidisilazane.—Addition of sulphur dichloride (14.4 g., 1 mol.) to hexamethylidisilazane (22.47 g., 1 mol.) at -78° in dry petroleum produced a violent reaction. Much coloured material was produced, and, after leaving for a day, distillation gave trimethylchlorosilane (85%). The solvent was pumped off, leaving a yellow solid. Continuous extraction with acetone gave ammonium chloride (1.5 g.).

Reaction of Disulphur Dichloride with Hexamethylidisilazane.—Disulphur dichloride (8.02 g., 1 mol.) was slowly added to hexamethylidisilazane (9.54 g., 1 mol.) in dry petroleum. The vigorous reaction caused precipitation of red and black solids. Distillation yielded trimethylchlorosilane (90%), and filtration, washing, and recrystallisation from the light petroleum gave small amounts of sulphur (yellow crystals), ammonium chloride, and tetrasulphur tetranitride (orange crystals), m. p. ca. 180° (with explosive decomposition) (Found: N, 30.7. Calc. for S_4N_4 : N, 30.4%), and with the same infrared spectrum as pure S_4N_4 .

Reaction of Thionyl Chloride with Hexamethyldisilazane (reaction 6).—The slow addition of thionyl chloride (6.17 g., 1 mol.) to hexamethyldisilazane (8.36 g., 1 mol.) at liquid-air temperature resulted in the formation of a cream precipitate. Distillation yielded trimethylchlorosilane (93%) and an intractable brown solid residue.

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