854. *The Alkylthiotrimethylsilanes: Preparations and Some Properties.*

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The alkylthiotrimethylsilanes, $RS{\cdot}SiMe_3$ (R = Et, Pr^n, Pr^i, Bu^n, Bu^t) have been prepared by interaction of chlorotrimethylsilane with the appropriate lead mercaptide. The higher homologues may also be obtained by displacement reactions with the higher thiols. The alkylthiotrimethylsilanes reacted with alcohols to produce the corresponding alkoxytrimethylsilanes in excellent yield. The infrared spectra of the alkylthiotrimethylsilanes and alkoxytrimethylsilanes have been measured over the range 400—4000 cm.$^{-1}$, and are discussed.

For an investigation of the properties of organosilicon compounds, it has been necessary to prepare a series of alkylthiotrimethylsilanes.

Chlorotrimethylsilane and alkanethiols did not react, and were recovered unchanged after prolonged heating. The lead salts of the thiols, however, with chlorotrimethylsilane produce the alkylthiotrimethylsilanes in good yield (Table 1):

$$Pb(SR)_2 + 2SiClMe_3 \longrightarrow PbCl_2 + 2SiMe_3{\cdot}SR \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$
$$(R = Et, Pr^n, Pr^i, Bu^n, Bu^t)$$

This reaction has previously been used [1] to afford ethylthiotriethylsilane, and similarly sodium butyl sulphide was used [2] in the preparation of n-butylthiotrimethylsilane from chlorotrimethylsilane.

The lead salts of ethane-, propane-1-, and butane-1-thiol underwent reaction (1) quite rapidly on warming, but reaction of the propane-2-analogue was considerably slower, and the t-butyl salt required 25 hr. for complete reaction. There was presumably a steric hindrance to the reaction of the branched-chain thiols.

The products are colourless liquids, which smell strongly of thiol, as a result of their rapid hydrolysis in moist air. Quantitative hydrolysis produced the thiol and hexamethyldisiloxane:

$$2SiMe_3{\cdot}SR + H_2O \longrightarrow (SiMe_3)_2O + 2R{\cdot}SH \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

The alkylthiotrimethylsilanes may be converted into higher homologues, on careful fractionation with a higher thiol:

$$SiMe_3{\cdot}SR + R'{\cdot}SH \qquad\qquad SiMe_3{\cdot}SR' + R{\cdot}SH \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (3)$$

Similarly the alkylthiotrimethylsilanes may also be prepared by careful fractionation of diethylaminotrimethylsilane and a thiol:

$$SiMe_3{\cdot}NEt_2 + R{\cdot}SH \longrightarrow SiMe_3{\cdot}SR + NHEt_2 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (4)$$

In this preparation, however, only thiols of higher boiling point than the amine produced are suitable; *e.g.*, fractionation of the aminosilane and ethanethiol gave only the starting materials. This approximately equal replacement tendency of alkoxythio- and dialkylamino-groups has also been observed [3] in the corresponding boron system.

The interaction of exactly equimolar quantities of an alcohol and the alkylthiotrimethylsilanes was in all cases exothermic, and distillation of the resulting mixture produced the thiol and the alkoxytrimethylsilane, irrespective of the relative boiling points of alcohol and thiol:

$$SiMe_3{\cdot}SR + R'OH \longrightarrow R{\cdot}SH + SiMe_3{\cdot}OR' \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (5)$$

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[1] Schmeisser and Müller, *Angew. Chem.*, 1957, **69**, 781.
[2] Langer, Connell, and Wender, *J. Org. Chem.*, 1958, **23**, 50.
[3] Aubrey and Lappert, *Proc. Chem. Soc.*, 1960, 148.

The alkoxytrimethylsilanes are often difficult and tedious to prepare and purify by other methods, owing to formation of troublesome alcohol–alkoxysilane azeotropes.[4,5]

Alkyl halides, although reacting with dialkyl sulphides to produce trialkylsulphonium halides, are reported not to react at all with disilyl sulphide.[6] As the alkylthiotrimethylsilanes, with C–S–Si linkages, lie between the alkyl (C–S–C) and silyl (Si–S–Si) sulphides, it is interesting that, although no sulphonium compounds have as yet been isolated, possible evidence for their formation as intermediates is obtained by the presence of iodotrimethylsilane in the reaction products of alkylthiotrimethylsilanes and alkyl iodides:

$$SiMe_3{\cdot}SR + R'I \longrightarrow SiMe_3{\cdot}SRR'I \longrightarrow SiMe_3I + R{\cdot}SR'$$

Further work on this and other aspects of the co-ordination reactions of the alkylthiotrimethylsilanes is proceeding.

The infrared spectra of the alkylthiotrimethylsilanes and the corresponding alkoxytrimethylsilanes have been measured over the range 400—4000 cm.$^{-1}$. In general, the assignments made by previous workers have been confirmed. A very strong absorption band at 1253—1260 cm.$^{-1}$ is extremely constant in position in all the compounds measured, and has been assigned by Young, Koehler, and McKinney[7] as the symmetric methyl deformation frequency. The strong bands observed herein at 842—849 and 752—758 cm.$^{-1}$ have also been observed[8,9] in many polysiloxanes, and are assigned to vibrations of the $SiMe_3$ grouping. A band observed by Richards and Thompson[9] at about 700 cm.$^{-1}$ in straight-chain and cyclic siloxanes, and believed by them to be associated with the $SiMe_2$ group, has been found to be present in all the compounds examined.

The major difference between the spectra of the analogous oxygen and sulphur compounds is the presence of a very strong absorption in the former at 1037—1104 cm.$^{-1}$, which is completely absent for the sulphur compounds. Two bands at 639—641 and 486—498 cm.$^{-1}$ are, however, present in the sulphur compounds, with no corresponding bands in the oxygen analogues. The strong band at 1037—1104 cm.$^{-1}$ for the oxygen compounds has been assigned[8,9] to the Si–O–C and Si–O–Si linkages. There appears to be no change in position of the band in going from C–O to Si–O despite the considerable change in mass. This has been ascribed to a compensating increase in the Si–O force constant, and this view is reasonable in view of the highly probable partial double-bond character of the SiO bond due to $p\pi$–$d\pi$ bonding.[10] From a simple reduced-mass calculation, based on the known C–S frequency at 650 cm.$^{-1}$, the Si–S stretcing frequency would be expected to absorb at about 430 cm.$^{-1}$. It is probable again, however, that the increase in bond order in going from C–S to Si–S would produce a larger force constant with a consequent absorption shift to higher frequency. In view of this, the bands present in the alkylthiotrimethylsilanes at 639—641 and 486—498 cm.$^{-1}$ may be tentatively assigned to the stretching modes of the C–S–Si linkage. These compare with the combined Raman and infrared measurements of the symmetrical and antisymmetric stretching vibrations of the Si–S–Si linkage in disilyl sulphide, which have been assigned frequencies of 480 and 517 cm.$^{-1}$, respectively.[11]

The bands observed by Wright and Hunter[8] at 435—450 cm.$^{-1}$ and assigned to the Si–O valency bend vibration were not confirmed in the present work.

EXPERIMENTAL

Preparations and Techniques.—Lead salts of thiols[12] were prepared from the thiol and lead acetate in aqueous alcohol, and after copious washing with distilled water were dried in a

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[4] Gerrard and Kilburn, *J.*, 1956, 1536.
[5] Sauer, *J. Amer. Chem. Soc.*, 1944, **66**, 1707.
[6] Emeléus, MacDiarmid, and Maddock, *J. Inorg. Nuclear Chem.*, 1955, **1**, 194.
[7] Young, Koehler, and McKinney, *J. Amer. Chem. Soc.*, 1947, **69**, 1410.
[8] Wright and Hunter, *J. Amer. Chem. Soc.*, 1947, **69**, 803.
[9] Richards and Thompson, *J.*, 1949, 124.
[10] Stone and Seyferth, *J. Inorg. Nuclear Chem.*, 1955, **1**, 112.
[11] Ebsworth, Taylor, and Woodward, *Trans. Faraday Soc.*, 1959, **55**, 211.
[12] Borgstrom, Ellis, and Emmet Reid, *J. Amer. Chem. Soc.*, 1929, **51**, 3649.

vacuum-desiccator. Infrared spectra were measured on a Unicam S.P. 100 instrument, sodium chloride and potassium bromide optics being used.

*Attempted Interaction of Butane-*1*-thiol and Chlorotrimethylsilane.*—The chlorosilane (5·49 g., 1 mol.) and butane-1-thiol (4·54 g., 1 mol.) were refluxed together for 2 hr., during which no evolution of hydrogen chloride occurred. Fractionation of the mixture yielded chlorotrimethylsilane (5·12 g., 93%), b. p. 57—60°, n_D^{20} 1·3924, and butane-1-thiol (4·17 g., 82%), b. p. 96—98°, n_D^{20} 1·4428. No residue remained after the distillation.

Interaction of Lead Mercaptides and Chlorotrimethylsilane.—The carefully dried mercaptide (1 mol.) and chlorotrimethylsilane (2·2 mol.) were heated under reflux on a steam-bath until all the bright yellow mercaptide had been converted into white lead chloride. The mixture was then filtered, and the residue washed with chlorotrimethylsilane (2 × 10 c.c.). Distillation of the combined filtrate and washings yielded, first, unchanged chlorotrimethylsilane, and then the required alkylthiotrimethylsilane (Table 1) as a colourless liquid.

TABLE 1.

R in $SiMe_3 \cdot SR$	Yield (%)	B. p.	Reaction time (hr.)	d_4^{20}	n_D^{20}	Found (%)		Required (%)	
						C	H	C	H
Et	76	130°	0·3	0·832	1·4512	45·3	10·8	44·8	10·5
Pr^n	92	151	1·0	0·844	1·4524	48·4	10·1	48·6	10·8
Pr^i	73	142	2·0	0·824	1·4497	48·6	10·3	48·6	10·8
Bu^n	81	168	1·0	0·854	1·4550	51·7	10·9	51·8	11·1
Bu^t	70	157	25	0·834	1·4570	51·4	10·8	51·8	11·1

All preparations were carried out on ~0·1-molar scale, and yields are based on lead mercaptide taken.

Attempted Interaction of NN-*Diethylaminotrimethylsilane and Ethanethiol.*—The aminosilane (7·81 g., 1 mol.) and thiol (3·34 g., 1 mol.) were refluxed together for 10 hr. and the resultant mixture was carefully fractionated. Ethanethiol (3·17 g., 95%), b. p. 35°, n_D^{20} 1·4300, a middle fraction (0·52 g.), b. p. 36—126°, and *NN*-diethylaminotrimethylsilane (7·22 g., 92%) (infrared spectrum identical with that of starting material) were recovered.

Interaction of NN-*Diethylaminotrimethylsilane and Butane-*1*-thiol.*—The aminosilane (7·25 g., 1 mol.) and thiol (4·50 g., 1 mol.) were refluxed together for 1 hr., and the mixture was distilled to yield diethylamine (3·45 g., 94%), b. p. 54—56°, n_D^{20} 1·3877, and n-butylthiotrimethylsilane (7·14 g., 88%), b. p. 166—169°, n_D^{20} 1·4549 (Found: C, 52·0; H, 10·8%).

*Interaction of Ethylthiotrimethylsilane and Butane-*1*-thiol.*—The silane (6·71 g., 1 mol.) and the thiol (5·4 g., 1·2 mol.) were refluxed together for 1 hr. and the mixture was distilled to yield ethanethiol (2·61 g., 84%), b. p. 36°, n_D^{20} 1·4315, unchanged butanethiol, and n-butylthiotrimethylsilane (6·4 g., 78%), b. p. 166—169°, n_D^{20} 1·4542.

Alcoholysis of Alkylthiotrimethylsilanes.—The silane (1 mol.) and alcohol (1 mol.) were mixed, and a temperature rise noted each time. Distillation of the products gave the alkoxytrimethylsilane and thiol (Table 2).

TABLE 2.

$SiMe_3 \cdot SR$	R′ in R′OH	Yield (%) $SiMe_3 \cdot OR'$	B. p.	n_D^{20}
Bu^n	Me	76	57°	1·3685
Et	Bu^n	93	125	1·3934
Et	Pr^n	82	99	1·3822
Et	Bu^t	79	105	1·3915
Et	Pr^i	81 *	87	1·3782

* Found: C, 54·3; H, 10·3. $C_6H_{16}OSi$ requires C, 54·6; H, 12·1%.

Each alcoholysis was carried out on ~0·5M scale.

Hydrolysis of Ethylthiotrimethylsilane.—The silane (5·61 g., 2 mol.) was added to water (0·377 g., 1 mol.) and set aside. Slight warming took place, and subsequent distillation gave ethanethiol (2·21 g., 87%), b. p. 34—36°, n_D^{20} 1·4291, and hexamethyldisiloxane (2·75 g., 81%), b. p. 97—101°, n_D^{20} 1·3771.

Interaction of n-Butylthiotrimethylsilane and n-Butyl Iodide.—The silane (2·58 g., 1 mol.) and the iodide (2·92 g., 1 mol.) were refluxed together for 25 hr., and then the mixture was carefully fractionated to give: iodotrimethylsilane (2·41 g., 76%), b. p. 107°, n_D^{20} 1·4742 (Found: I, 62·8.

Calc. for C_3H_9ISi: I, 63·5%), a fraction (0·6 g.), b. p. 107—181°, and di-n-butyl sulphide (1·93 g., 83%), b. p. 181—183°, n_D^{20} 1·4534 (Found: C, 65·4; H, 11·4. Calc. for $C_8H_{18}S$: C, 65·8; H, 12·3%).

Infrared Spectra.—Spectra were measured of thin liquid films of each compound. Samples were checked to be better than 99% pure by vapour-phase chromatography. The main bands were as follows:

$SiMe_3$·SEt: 2970vs, 2905s, 1456m, 1412m, 1379m, 1254vs(A), 978m, 845vs(B), 754s(C), 700s(D), 666s, 638s(E), 486s(F).

$SiMe_3$·SPr^n: 2964vs, 2878s, 1458m, 1410w, 1382w, 1296w, 1254vs(A), 1063m, 844vs(B), 792w, 757s(C), 730w, 700s(D), 654sh, 640s(E), 490s(F).

$SiMe_3$·SPr^i: 2960vs, 1875s, 1452m, 1410w, 13087w, 1369m, 1253vs(A), 1160m, 1057m, 845vs(B), 755s(C), 701s(D), 641s(E), 498s(F), 422m.

$SiMe_3$·SBu^n: 2963vs, 2880s, 1468m, 1440m, 1409w, 1382w, 1359w, 1298w, 1253vs(A), 1229m, 1193w, 1100w, 1072w, 1025w, 846vs(B), 756s(C), 731w, 701s(D), 656s, 639s(E), 490s(F).

$SiMe_3$·SBu^t: 2973vs, 2902vs, 1457s, 1461s, 1409m, 1366vs, 1330w, 1256vs(A), 1218m, 1173s, 1162s, 849vs(B), 755vs(C), 701s(D), 641s(E), 592s, 493s(F), 416m.

$SiMe_3$·OMe: 2976vs, 2839s, 1468s, 1260vs(A), 1203s, 1104vs(G), 873vs, 847vs(B), 758vs(C), 725s, 698s(D), 606m.

$SiMe_3$·OEt: 2973vs, 2911s, 1486w, 1447w, 1393m, 1298w, 1258vs(A), 1173m, 1117vs, 1086vs(G), 953vs, 845vs(B), 752s(C), 726w, 695s(D), 622w, 614w.

$SiMe_3$·OPr^n: 2983vs, 2915s, 1460m, 1394m, 1256vs(A), 1115sh, 198vs(G), 1016vs, 875sh, 845vs(B), 754s(C), 689s(D).

$SiMe_3$·OPr^i: 2985vs, 2900s, 1470w, 1456w, 1386m, 1370m, 1258vs(A), 1178s, 1136s, 1037vs(G), 890s, 842vs(B), 758s(C), 715m, 691s(D), 615w, 440s.

$SiMe_3$·OBu^n: 2984vs, 2907s, 1467m, 1390m, 1303w, 1266vs(A), 1126sh, 1104vs(G), 1045m, 987m, 901s, 875s, 846vs(B), 751s(C), 691s(D), 617w.

$SiMe_3$·OBu^t: 2980vs, 2921s, 1464m, 1393s, 1367vs, 1256vs(A), 1206vs, 1060vs(G), 1029vs, 939vs, 847vs(B), 756vs(C), 685s(D), 620m, 600w, 474s.

(A) = Symmetric methyl deformation; (B) and (C) = $SiMe_3$ group vibrations; (D) $SiMe_2$ group vibrations; (E) and (F) = C–S–Si group stretching modes; (G) = C–O–Si group stretching mode.

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