Reaction of Silyl Bromide with Some Group VI Hydrido-anions

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The reaction of silyl bromide with the products of the reactions of lithium tetrahydridoaluminate with alcohols and thiols, and with metal alkoxides, has been studied. Alcohols react with silylphosphine to give silyl ethers. N.m.r. parameters of a number of silyl ethers are reported and discussed. Attempts to prepare derivatives of silanol are described.

THE reactions of silyl bromide with lithium tetraphosphinoaluminate, lithium tetra-amminoaluminate, and a number of their P- and N-substituted derivatives have been described.[1-3] We have now extended this study to include a number of complex aluminates derived from alcohols and thiols.

Methyl, ethyl, and isopropyl alcohol react readily with lithium tetrahydridoaluminate in the absence of a solvent to yield tetrasubstituted products, $\mathrm{LiAl(OR)_4}$, while t-butyl alcohol gives the tri-substituted aluminate, $\mathrm{LiAlH(OBu^t)_3}$. Methanethiol reacts to give tri-substitution when monoglyme is the solvent, but tetra-substitution when diethyl ether is employed. Such a solvent dependence of the degree of substitution has also been observed for the methylphosphines: methylphosphine and dimethylphosphine give tri- and di-substitution respectively when the solvent is diglyme,[2] but tetra-substitution is observed in each case when monoglyme is employed as solvent. 2,2,2-Trifluoroethyl alcohol did not react with lithium tetrahydridoaluminate in the absence of a solvent, but rapidly gave a tetra-substituted product in the presence of monoglyme.

Silyl bromide reacted with the complexes derived from methyl, ethyl, isopropyl, and t-butyl alcohol to give good yields of the alkyl silyl ethers. The complex derived from methanethiol gave methyl silyl sulphide, but that from 2,2,2-trifluoroethyl alcohol gave only decomposition products.

Hydrogen sulphide and hydrogen selenide react rapidly with lithium tetrahydridoaluminate:

$$\mathrm{LiAlH_4 + 2H_2X \longrightarrow 4H_2 + `\,LiAlX_2\,'} \qquad \mathrm{X = S\ or\ Se}$$

Material of this composition has been postulated[4] as a product in the reduction by lithium tetrahydridoaluminate of dialkyl trisulphides. Whatever the true nature of these phases, they react with methyl iodide and silyl bromide to give quantitative conversion to the dimethyl and disilyl derivatives respectively of sulphur and selenium. Although dimethyl disulphide reacts readily with lithium tetrahydridoaluminate giving $\mathrm{LiAl(SMe)_4}$, as found for other disulphides,[4] dimethyl diselenide shows no reaction.

Whereas sodium phenoxide reacts with silyl bromide to give phenyl silyl ether, sodium alkoxides and lithium, strontium, and tetramethylammonium hydroxides promote rapid base-catalysed decomposition to monosilane and polymeric products. Sodium methanethiolate gives some substitution product accompanied by decomposition, although sodium benzenethiolate[5] and trimethylammonium hydrogen sulphide[6,7] give substitution with no decomposition. The dissociation constants for a number of these weak acids in aqueous solution are[8]: PhSH, 6·5; $\mathrm{H_2S}$, 7·0; PhOH, 10·0; MeSH, 10·2; MeOH, 15·5; and $\mathrm{H_2O}$, 15·7. Although the reactions in question are conducted in non-aqueous media this order of acidity (and hence basicity of the corresponding anions) apparently rationalises their behaviour with silyl bromide: however, the example of phosphine, $K = 27$, the anion of which reacts cleanly with excess of silyl bromide to give trisilylphosphine,[9] indicates that this is not the only factor involved.

Silyl bromide does not react with sodium peroxide in dimethyl ether at −96° but reacts explosively in diglyme at −45°; this may be a solubility effect. Anhydrous hydroxylamine reacts with silyl bromide in dimethyl ether to give a volatile product which ignites spontaneously in the vacuum system. Neither disilyl peroxide nor any silyl hydroxylamines was isolated from these reactions. Dilithium disulphide reacts with silyl bromide to give disilyl sulphide in good yield: on one occasion only, a less-volatile thermally unstable fraction was obtained which decomposed to give disilyl sulphide, sulphur, and a mixture having five peaks in the n.m.r. spectrum in the region associated with $\mathrm{SiH_3S^-}$ groups. Possibly disilyl disulphide is formed initially and then decomposes to a number of disilylsulphanes, $\mathrm{(SiH_3)_2S_n}$.

Silyl bromide reacts with hydrated lead(II) oxide, either when streamed over the solid or in monoglyme, to give disilyl ether almost quantitatively. When di-iodosilane is streamed over this oxide, prosiloxane[10] is formed: the mass spectrum suggested that the tetramer $\mathrm{(SiH_2O)_4}$ is formed almost exclusively. Dibromogermane, however, when pumped through a column of the lead oxide was recovered unchanged except for traces of monogermane. If progermoxane is produced under these conditions, it is involatile.

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Silyl trifluoroacetate is completely decomposed by sodium methoxide but its reaction with sodium phenoxide affords phenyl silyl ether quantitatively: with lithium tetrahydridoaluminate, the silyl groups are reduced quantitatively to monosilane. These observations suggest that displacement of trifluoroacetate is faster than nucleophilic attack on the carbonyl groups, as has been observed with a number of organo-silicon derivatives.[11]

Silylphosphine has been shown [12] to react with water yielding phosphine and disilyl ether. Phenol and 2,2,2-trifluoroethyl alcohol react rapidly with silylphosphine to give the corresponding silyl ethers:

$$ROH + SiH_3PH_2 \longrightarrow ROSiH_3 + PH_3$$

In the reaction of silylphosphine with benzyl alcohol, the stoicheiometry and the n.m.r. spectrum of the involatile product suggest that this is benzyl silyl ether, although it was not isolated.

N.m.r. parameters of silyl ethers

Compound	Solvent	τ SiH_3	$^1J^{29}SiH$/Hz	τ CH_α	τ CH_β	τ CH_γ	
SiH_3OSiH_3	C_6H_{12} [a]	5·39 ± 0·01	221·5 ± 0·2				
	Me_4Si	5·39 ± 0·01	221·6 ± 0·5				
SiH_3OMe	C_6H_{12} [a]	5·51 ± 0·01	216·2	6·58 ± 0·01			
	Me_4Si	5·52 ± 0·01	216·0 ± 0·5	6·56 ± 0·01			
SiH_3OEt	Me_4Si	5·52 ± 0·01	218·1 ± 0·5	6·40 ± 0·01	8·87 ± 0·01		$^3J(H_\alpha H_\beta)$ = 7·1 ± 0·4
SiH_3OPr^i	Me_4Si	5·52 ± 0·01	216·0 ± 0·5	6·13 ± 0·01	8·87 ± 0·01		$^3J(H_\alpha H_\beta)$ = 6·1 ± 0·4
SiH_3OBu^t	Me_4Si	5·50 ± 0·01	216·6 ± 0·5		8·77 ± 0·01		
$SiH_3OCH_2CF_3$	Me_4Si	5·39 ± 0·01	223·1 ± 0·5	6·17 ± 0·01			$^3J(H_\alpha F_\beta)$ = 8·4 ± 0·2
	CS_2	5·40 ± 0·01	224·0 ± 0·5	6·18 ± 0·01			$^3J(H_\alpha F_\beta)$ = 8·3 ± 0·2
	CCl_3F	5·39 ± 0·01	223·0 ± 0·5	6·16 ± 0·01			$^3J(H_\alpha F_\beta)$ = 8·3 ± 0·2
SiH_3OPh	C_6H_{12} [b]	5·27 ± 0·01	223·6 ± 0·5	3·24 ± 0·01	2·92 ± 0·01	3·18 ± 0·01	
	Me_4Si	5·23 ± 0·01	223·2 ± 0·5	Complex absorption			
SiH_3OCH_2Ph	Me_4Si	5·46 ± 0·01	219·0 ± 0·5	5·41 ± 0·01	All aromatic protons at 2·82 ± 0·02		
SiH_3OBCl_2	Me_4Si	5·36 ± 0·01	232·4 ± 0·3				

[a] H. J. Campbell-Ferguson, E. A. V. Ebsworth, A. G. MacDiarmid, and T. Yoshioka, *J. Phys. Chem.*, 1967, **71**, 723. [b] C. Glidewell, D. W. H. Rankin, and G. M. Sheldrick, *Trans. Faraday Soc.*, 1969, **65**, 2801.

No insertion occurs when disilyl ether or methyl silyl ether is treated with sulphur dioxide: the ethers rapidly decompose, as do trisilylamine and *N*-silyldimethylamine on treatment with sulphur dioxide.[13]

N.m.r. Spectra.—The n.m.r. parameters of the new silyl ethers are set out in the Table together with those of several other *O*-silyl compounds. Studies of silylamines [3,14] indicate that their n.m.r. parameters are rather insensitive to changes of solvent: this appears from the data in the Table also to be the case for silyl ethers. The variations in the parameters are similar to those found with the analogous silylamines: thus ethers containing electron-donating groups have higher chemical shifts than does disilyl ether, whereas *O*-dichloroboryl silyl ether and phenyl silyl ether have lower shifts, probably dominated by the diamagnetic anisotropy of BCl_2– and C_6H_5– groups. The unusually low SiH_3–chemical shift, 5·28, in monofluorodisilyl ether has been commented on by Kifer and Van Dyke.[15]

In the silylamines, small Si–H coupling constants are associated with electron-donating substituents and short Si–N bonds.[3,14,16] Although the coupling constants in silyl ethers generally decrease on substitution of electron-donating groups, no correlation is found with Si–O bond length: *r*(Si–O) in $(SiH_3)_2O$, 1·634 ± 0·002 Å;[17] SiH_3-OMe, 1·640 ± 0·003 Å;[18] SiH_3OPh, 1·648 ± 0·007 Å.[19] Since electronic effects may be expected to be similar in silyl ethers and amines, the values of *J*(Si–H) and *r*(Si–O) in the ethers suggest that the trend observed in the amines may be merely fortuitous.

EXPERIMENTAL

The apparatus and techniques employed have been described previously:[3] reactions between alcohols or thiols and lithium tetrahydridoaluminate were monitored by the evolution of hydrogen. When no further hydrogen was evolved during 3 h, the mixture was used with no attempt to isolate or purify the complexes.

Methyl, ethyl, and isopropyl alcohol were dried by distillation from sodium; t-butyl, 2,2,2-trifluoroethyl, and benzyl alcohol were dried over flamed-out molecular sieve. Phenol was twice sublimed *in vacuo*.

O-Dichloroboryl silyl ether was isolated from the reaction of disilyl ether and boron trichloride.[20] All attempts to obtain *O*-difluoroboryl silyl ether from the corresponding reaction with boron trifluoride yielded, besides silyl fluoride, a mixture of volatile products the n.m.r. spectrum of which in dilute solution in tetramethylsilane, showed the following peaks (p.p.m.): τ 5·33 (*J* 228·3 Hz), 5·36 (*J* 223·0 Hz), and 5·41 (*J* 237·0 Hz). The only difference between samples was the relative intensity of these peaks. It is possible that these products are of the type $(SiH_3O)_xBF_{3-x}$. From the reaction of boron tribromide with an excess of disilyl ether, the only volatile products were silyl bromide and dibromosilane.

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Reactions of Hydrides with Lithium Tetrahydridoaluminate, followed by Silyl Bromide.—(a) *Methyl alcohol*. Lithium tetrahydridoaluminate (84 mg, 2·2 mmol) was set aside at room temperature overnight with excess of methyl alcohol. After removal of hydrogen (8·5 mmol), the excess of methyl alcohol was pumped off and silyl bromide (8·0 mmol) and monoglyme (*ca*. 5 ml) were added. After 30 min. at −64°, fractionation afforded methyl silyl ether (7·4 mmol) together with traces of monosilane and silyl bromide.

(b) *Ethyl alcohol*. Lithium tetrahydridoaluminate (111 mg, 2 mmol) and excess of ethyl alcohol were held at room temperature for 10 h: hydrogen (11·0 mmol) was evolved. After removal of all the volatiles, diglyme (*ca*. 5 ml) and silyl bromide (10·5 mmol) were added and the mixture was held at −45° for 30 min. Fractionation gave traces of monosilane and an almost quantitative yield of ethyl silyl ether (Found: v.p. at 0°, 430 ± 1 mmHg; M = 76·3. Calc.: M = 76·2); i.r. (vapour); 2936m, 2882m, 2149s, 1445vw, 1384w, 1115vs, 970vs, 939sh, 730sh, 712ms, 552vw, 545w, and 530vw cm^{-1}.

(c) *Isopropyl alcohol*. Lithium tetrahydridoaluminate (76 mg, 2·0 mmol) was set aside overnight with excess of isopropyl alcohol: after removal of hydrogen (7·8 mmol), the unreacted alcohol was pumped off. Silyl bromide (8·0 mmol) and diglyme (*ca*. 5 ml) were added: after 1 h at −45°, fractionation gave a trace of monosilane and, volatile at −64° and involatile at −96°, isopropyl silyl ether. The yield was almost quantitative (Found: v.p. at 0°, 291 ± 1 mmHg; M = 90·4. Calc.: M = 90·2); i.r.; 2960m, 2936m, 2872sh, 2180sh, 2147s, 1452w, 1372m, 1163sh, 1131s, 1039s, 967vs, 951vs, 934sh, 752ms, 724ms, 556w, 548w, and 532w cm^{-1}.

(d) *t-Butyl alcohol*. Excess of t-butyl alcohol and lithium tetrahydridoaluminate (114 mg, 3·0 mmol) were set aside for 24 h at 50°: hydrogen (8 mmol) was evolved. After prolonged pumping, silyl bromide (12·0 mmol) and diglyme (*ca*. 5 ml) were added and the mixture was kept for 1 h at −45°. Fractionation gave monosilane (3·0 mmol) and t-butyl silyl ether, volatile at −45° and involatile at −64° (Found: v.p. at 0°, 88 ± 1 mmHg; M = 104·0. Calc.: M = 104·2); i.r.: 2966m, 2872m, 2162s, 1452vw, 1367m, 1253w, 1194ms, 1095sh, 1052ms, 959s, 922vs, 738ms, and 412vw cm^{-1}.

(e) 2,2,2-*Trifluoroethyl alcohol*. Lithium tetrahydridoaluminate (115 mg, 3·0 mmol) was set aside with excess of the alcohol at room temperature for 5 days; no permanent gas was evolved. Monoglyme (*ca*. 4 ml) was frozen into a ring above the slurry of alcohol and lithium tetrahydridoaluminate which was then thawed. The monoglyme was then allowed to melt: vigorous gas evolution occurred as soon as the two phases mixed. After 5 min, 11·7 mmol of hydrogen had been evolved. The volatiles were removed, and monoglyme (*ca*. 5 ml) and silyl bromide (13·0 mmol) were added. The mixture was maintained at −45° and the reaction was monitored by i.r. spectroscopy. The amount of monosilane increased and that of silyl bromide decreased with time; no silyl ether was detected. After removal of all the volatiles, treatment of the solid residue with excess of hydrogen chloride yielded di- and tri-chlorosilanes.

(f) *Methanethiol*. (*i*) Lithium tetrahydridoaluminate (145 mg, 3·8 mmol) and methanethiol (28 mmol) were set aside overnight in monoglyme (*ca*. 8 ml). After removal of hydrogen (11·3 mmol), the volatiles were pumped away, and diglyme (4 ml) and silyl bromide (14·1 mmol) were added. After 3 h at −45° fractionation gave monosilane (4·0 mmol) and methyl silyl sulphide (9·9 mmol). (*ii*) Lithium tetrahydridoaluminate (198 mg, 5·2 mmol) and methanethiol (30 mmol) were set aside overnight in diethyl ether (*ca*. 10 ml). Hydrogen (20·1 mmol) was evolved. Silyl bromide (16 mmol) was added and after 1 h at −45°, methyl silyl sulphide was obtained almost quantitatively.

(g) *Hydrogen sulphide and hydrogen selenide*. Typically, hydrogen sulphide (17·2 mmol) and lithium tetrahydridoaluminate (110 mg, 2·9 mmol) were set aside overnight in monoglyme (*ca*. 4 ml). Hydrogen (11·6 mmol) was removed and 11·3 mmol of hydrogen sulphide were recovered. After removal of all the volatiles, the solid product was treated with methyl iodide (7 mmol) for 20 h at room temperature: quantitative conversion to dimethyl sulphide was found.

Attempted Reaction of Dimethyl Diselenide with Lithium Tetrahydridoaluminate.—To lithium tetrahydridoaluminate (91 mg, 2·4 mmol) was added dimethyl diselenide (*ca*. 1·5 ml) and the mixture was set aside for 8 weeks at room temperature. No permanent gas was evolved. After 7 days at 70° no hydrogen had been evolved but selenium had begun to precipitate.

Reaction of Silyl Bromide with Hydroxides.—Typically, lithium hydroxide (18·7 mmol) and silyl bromide (5·0 mmol) were allowed to react at −64° in monoglyme (5 ml). After 10 min, hydrogen (2·0 mmol) and monosilane (1·3 mmol) had been evolved. Treatment of the solid residue with methyl bromide at room temperature yielded no volatile silyl compound, but excess of hydrogen chloride gave di- and tri-chlorosilanes.

Reaction of Silyl Bromide with Sodium Methanethiolate.—Silyl bromide (19·0 mmol) and sodium methanethiolate (18·7 mmol) were shaken in diglyme (10 ml) at −64° for 10 min. Fractionation of the volatile products gave methyl silyl sulphide (6·7 mmol) and monosilane: the solid product yielded di- and tri-chlorosilanes on treatment with hydrogen chloride.

Reaction of Silyl Bromide with Sodium Phenoxide.—Silyl bromide (7·0 mmol) and sodium phenoxide (6·8 mmol) reacted in diethyl ether (*ca*. 5 ml) during 1 h at −64° to give phenyl silyl ether in almost quantitative yield.

Reaction of Silyl Trifluoroacetate with Sodium Phenoxide.—Silyl trifluoroacetate (10·2 mmol) and sodium phenoxide (10·6 mmol) reacted in diethyl ether (*ca*. 5 ml) during 10 min at −64° to give an almost quantitative yield of phenyl silyl ether: no volatile Si–H species was obtained from the solid residue by treatment with excess of either methyl iodide or hydrogen chloride.

Reaction of Silyl Trifluoroacetate with Lithium Tetrahydridoaluminate.—Lithium tetrahydridoaluminate (106 mg, 2·8 mmol) and silyl trifluoroacetate (5·7 mmol) were shaken in diglyme (*ca*. 4 ml) at −45° for 5 min: fractionation gave monosilane (5·6 mmol). Treatment of the solid residue with methyl iodide or hydrogen chloride gave no volatile Si–H species.

Reactions of Hydrated Lead(II) *Oxide with Halides*.—(a) *Silyl bromide*. Silyl bromide (5·0 mmol) was shaken at −64° for 1 h with a suspension of hydrated lead oxide (2·4 g) in monoglyme (*ca*. 10 ml). Fractionation of the volatiles yielded disilyl ether (2·4 mmol).

(b) *Di-iodosilane*. Di-iodosilane was pumped through a short column of the oxide; the only volatile product was prosiloxane. Its mass spectrum, recorded on an AEI MS9 spectrometer, contained the following peaks, given with their relative intensities: 233, 1; 232, 1; 231, 1;

230, 1; 229, 4; 228, 1; 227, 2; 226, 1; 225, 1; 187, 1; 186, 2; 185, 16; 184, 22; 183, 100; 182, 9; 181, 27; 180, 2; 179, 4; 178, 2; 177, 1; 140, 2; 139, 4; 138, 4; 137, 27; 136, 2; 135, 12; 134, 1; 95, 4; 94, 2; 93, 11; 92, 2; 91, 1; 90, 4; 89, 8; and 88, 2.

Reaction of Silyl Bromide with Lithium Disulphide.—Lithium disulphide (13·5 mmol) and silyl bromide (28·0 mmol) were set aside at −96° for 6 h in dimethyl ether (10 ml). Fractionation gave unchanged silyl bromide, disilyl sulphide, and a fraction involatile at −45°. This fraction decomposed on attempted further fractionation to give disilyl sulphide, sulphur, and a mixture the n.m.r. spectrum of which showed peaks at 5·54, 5·55, 5·57, 5·59, and 5·63 (solution in tetramethylsilane, all in p.p.m. ±0·01). In three subsequent experiments, no fraction involatile at −45° was obtained.

Reaction of Silylphosphine with 2,2,2-*Trifluoroethyl Alcohol.*—A mixture of 2·8 mmoles of each reagent was set aside at 0° for 30 min. Fractionation yielded phosphine (2·7 mmol) and silyl 2,2,2-trifluoroethyl ether (2·8 mmol), which passes very slowly through a trap at −96° (Found: v.p. at 0°, 199 ± 1 mmHg; $M = 130{\cdot}8$. Calc.: $M = 130{\cdot}1$); i.r.; 2941mw, 2900w, 2172, 1459vw, 1418m, 1380w, 1296s, 1168vs, 1080br, 978vs, 955s, 983w, 785sh, 720m, 667vw, 550m, 542m, and 390w cm^{-1}.

Reaction of Silylphosphine with Benzyl Alcohol.—The reagents (0·3 mmol each) were held at 0° for 30 min in an n.m.r. tube. Phosphine (0·3 mmol) was removed and tetramethylsilane added to the involatile liquid remaining. The n.m.r. spectrum showed only peaks assignable to benzyl silyl ether.

Reactions of Silyl Ethers with Hydrogen Iodide.—All reactions were carried out at room temperature for 10—20 min. Ethyl silyl ether (1·42 mmol) and hydrogen iodide (1·41 mmol) gave ethanol (1·42 mmol) and silyl iodide (1·40 mmol); isopropyl silyl ether (1·90 mmol) and hydrogen iodide (1·89 mmol) gave isopropyl alcohol (1·89 mmol) and silyl iodide (1·88 mmol); t-butyl silyl ether (1·25 mmol) and hydrogen iodide (1·26 mmol) gave t-butyl alcohol (1·24 mmol) and silyl iodide (1·26 mmol); 2,2,2-trifluoroethyl silyl ether (2·01 mmol) and hydrogen iodide (2·03 mmol) gave 2,2,2-trifluoroethyl alcohol (1·98 mmol) and silyl iodide (2·02 mmol).

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