Ammonium Salts of Silanethiol and Silaneselenol

By **S. Cradock, E. A. V. Ebsworth,** and **H. F. Jessep** (née Angus), **Department of Chemistry, West Mains Road, Edinburgh EH9 3JJ**

Trisilylamine reacts with H_2Y ($Y = S$ or Se) at room temperature, giving $(SiH_3)_2Y$ and solid equimolar adducts of ammonia and SiH_3Y formulated from their i.r. spectra as $NH_4^+(YSiH_3)^-$; *N*-methyldisilylamine and *N*-dimethylsilylamine react similarly but more rapidly. Reactions of the ammonium salts with MeI, with Me_3SiCl, with GeH_3Br, and with PF_2Br are described. With acetyl chloride, the esters $MeC(O,Y){\cdot}SiH_3$ are formed; n.m.r. spectra indicate that in these compounds there is intramolecular exchange of SiH_3 between O and Y that is rapid at room temperature but slow at temperatures below −50°. When $Y = S$, the predominant isomer is $MeC(\colon S){\cdot}O{\cdot}SiH_3$; when $Y = Se$, the ratio of isomers $CH_3{\cdot}C(\colon O){\cdot}Se{\cdot}SiH_3 : MeC(\colon Se){\cdot}O{\cdot}SiH_3$ is *ca.* 2·5.

TRIORGANOSILYLAMINES have been found to react slowly with thiols or with hydrogen sulphide, giving low yields of triorganosilyl sulphur compounds:[1]

$$Et_3Si{\cdot}NH_2 + H_2S \longrightarrow (Et_3Si)_2S + Et_3Si{\cdot}SH$$

We present in this paper a study of the reactions of trisilylamine and related compounds with hydrogen sulphide and with hydrogen selenide. A preliminary account of some of our results has already appeared.[2]

Trisilylamine reacts slowly with an excess of hydrogen sulphide at room temperature under moderate pressure in the absence of solvent. Disilyl sulphide is produced, together with a white crystalline solid, which on the basis of analysis and of the overall stoicheiometry of the reaction we identify as an equimolar adduct of ammonia and silanethiol; the same solid compound is formed when ammonia and silanethiol are mixed in equimolar proportions at room temperature. Trisilylamine reacts similarly but more rapidly with hydrogen selenide; there are analogous but much

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[1] E. Larson and R. E. I. Marin, *Acta Chem. Scand.*, 1951, **5**, 964.

[2] H. F. Angus, S. Cradock, E. A. V. Ebsworth, and C. Glidewell, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 717.

faster reactions between hydrogen sulphide or selenide and *N*-methyldisilylamine or *N*-dimethylsilylamine:

$$(SiH_3)_3N + 2H_2Y \longrightarrow (SiH_3)_2Y + SiH_3{\cdot}YH,NH_3$$

$$2(SiH_3)_2N{\cdot}CH_3 + 3H_2Y \longrightarrow (SiH_3)_2Y + 2SiH_3{\cdot}YH,NH_2{\cdot}CH_3$$

$$SiH_3{\cdot}N(CH_3)_2 + H_2Y \longrightarrow SiH_3{\cdot}YH,NH(CH_3)_2$$

The adducts are stable at room temperature in the absence of air and moisture for at least 24 h; some sublime slowly *in vacuo*, but in none of the mass spectra is there any trace of parent ions of adduct molecules. Unfortunately, we have not been able to find a solvent that dissolves any of the adducts without decomposing it. We have therefore concentrated our attention on the vibrational spectra of the simplest of these derivatives—the adducts of ammonia—and on their reactions. Our results lead us to regard the adducts as ammonium salts or methylammonium salts of silanethiol or silaneselenol.

In the i.r. spectra of $SiH_3{\cdot}YH,NH_3$ there are broad bands near 3000 and 1400 cm^{-1}, frequencies characteristic of the ammonium ion;[3] as expected, these bands shift when the adduct concerned is prepared from D_2Y. The other bands in the spectra can all be assigned plausibly to vibrations of the SiH_3Y^- ion or to lattice modes or combination bands; in particular, there are no bands that can reasonably be assigned to YH-stretching or deformation modes or to NH_3-rocking vibrations. The bands assigned to vibrations of ammonium ions in the spectra of the adducts are very similar in shape and frequency to those in the spectra of the ammonium halides.[3] The spectra of the adducts of methylamine and of dimethylamine are more complicated, but again it is possible to detect bands that can be assigned to the vibrations of the anions SiH_3Y^-. The spectra, which are discussed in more detail below, imply that there is significant hydrogen bonding in the solids,[3] which may help to explain their insolubility. On the basis of these spectra we formulate all the adducts as salts.

Most of the reactions of the compounds prepared from trisilylamine that we have studied support this formulation. The adducts react very slowly with methyl iodide; the volatile products include silyl methyl sulphide or selenide:

$$NH_4(Y{\cdot}SiH_3) + CH_3I \longrightarrow NH_4I + CH_3{\cdot}YSiH_3$$

Trimethylchlorosilane reacts much more rapidly, and the mixed species silyl trimethylsilyl sulphide or selenide is obtained in up to 50% yield:

$$NH_4(Y{\cdot}SiH_3) + Me_3SiCl \longrightarrow NH_4Cl + Me_3Si{\cdot}Y{\cdot}SiH_3$$

We did not detect the formation of any silylamine, as might have been expected if ammonia as such were present at any stage in the system. Similarly, the reaction between the sulphide and germyl bromide gave high yields of a mixture of digermyl sulphide, disilyl sulphide, and silyl germyl sulphide:

$$NH_4(S{\cdot}SiH_3) + GeH_3Br \longrightarrow NH_4Br + GeH_3{\cdot}S{\cdot}SiH_3$$

$$2GeH_3{\cdot}S{\cdot}SiH_3 \longrightarrow (GeH_3)_2S + (SiH_3)_2S$$

The only reactions of those we have studied that do not fit in with the formulation of the adducts as salts are those with PF_2Br. In each case the reaction is complex. The products do not appear to include $PF_2{\cdot}Y{\cdot}SiH_3$ (whose n.m.r. spectrum we have obtained by means of a different chemical reaction [4]) but consist of a mixture including $(SiH_3)_2Y$, H_2Y, $HPF_2{:}Y$, and $PF_2{\cdot}NH{\cdot}SiH_3$ (whose characterization we shall report elsewhere [4]). The formation of these products can be understood if the adducts are regarded as dissociating into ammonia and silanethiol or silaneselenol:

$$NH_4(Y{\cdot}SiH_3) \longrightarrow SiH_3{\cdot}YH + NH_3$$

$$2SiH_3{\cdot}YH \longrightarrow (SiH_3)_2Y + H_2Y$$

$$PF_2Br + 2NH_3 \longrightarrow PF_2{\cdot}NH_2 + NH_4Br$$

$$3PF_2{\cdot}NH_2 + 2SiH_3Br \longrightarrow PF_2Br + NH_4Br + 2SiH_3{\cdot}NH{\cdot}PF_2$$

$$PF_2Br + H_2Y \longrightarrow HPF_2{:}Y + HBr$$

If the adducts were normal and undissociated salts, however, it is hard to understand the formation of the amine $SiH_3{\cdot}NH{\cdot}PF_2$. It is equally hard to understand why silylamines do not seem to have been formed in any of the other reactions.

The ammonium salts react rapidly with acetyl chloride at room temperature to give a mixture of products, which include $(SiH_3)_2Y$, $(CH_3CO)_2Y$, and substantial proportions of the esters $CH_3{\cdot}C(O,Y){\cdot}SiH_3$. These esters might exist in two isomeric forms: $CH_3{\cdot}C({:}O){\cdot}Y{\cdot}SiH_3$ and $CH_3{\cdot}C({:}Y){\cdot}O{\cdot}SiH_3$. The evidence from the i.r. spectra of the vapours does not establish the isomeric composition of either ester. Both when Y = S and when Y = Se there are bands that could be assigned to ν(C=O), but the spectra are complicated and could be interpreted as showing the presence of both isomers in each system. The presence of impurities makes the assignments still less definite. The ^1H n.m.r. spectra are much more helpful. At room temperature and 100 MHz the spectrum of each ester contains, in addition to peaks assigned to $(SiH_3)_2Y$ and $(CH_3CO)_2Y$, only two resonances; one is assigned to Si*H* and the other to acetyl protons. At room temperature the Si*H* resonance of the monoselenoacetate is broad at 100 MHz, and at low temperatures it splits into two components, one in the region characteristic of SiH_3O-protons and the other near the resonance in $(SiH_3)_2Se$. The latter component has associated satellites due to coupling with ^{77}Se in its natural abundance of 7·5%, whereas the former has not. The peak due to acetyl protons also splits into two components at low tempera-

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[3] T. C. Waddington, *J. Chem. Soc.*, 1958, 4340.

[4] D. E. J. Arnold, J. Dryburgh, E. A. V. Ebsworth, H. F. Jessep, and D. W. H. Rankin, to be published.

[5] E. A. V. Ebsworth, G. Rocktaschel, and J. C. Thompson, *J. Chem. Soc.* (*A*), 1967, 362.

tures. We interpret these observations as showing that there is exchange of SiH_3-groups between O and Se that is rapid at room temperature but slow at low temperatures on the n.m.r. time-scale; the exchange is presumably intramolecular, since the spectrum is not affected by a substantial change in concentration of the ester. If this interpretation is correct, the equilibrium favours the isomer with silicon bound to selenium by a factor of *ca.* 2·5.

In the ^1H resonance spectrum of $CH_3\cdot C(O,S)\cdot SiH_3$, both resonances are sharp at room temperature, suggesting that only one isomer is present. As the temperature is reduced, however, these also broaden, and may split at very low temperatures. If exchange is also responsible for this, the isomer with silicon bound to oxygen is by far the more abundant in this system. We have in the past suggested that intramolecular exchange is responsible[5] for features in the proton resonance spectra of $Me_2N\cdot C(\colon S)\cdot S\cdot SiH_3$ and $Me_2N\cdot C(\colon O)\cdot O\cdot SiH_3$; since in silyl formate in the vapour phase the silyl group is *cis* to the carbonyl oxygen atom,[6] it is not hard to imagine how this intramolecular exchange might take place. Some of the changes in the n.m.r. spectra with temperature that we report here might be accounted for if rotation about the Si–O or Si–Y bonds were restricted at low temperatures. However, the Si*H* chemical shifts are very close to those expected for the different isomers to which they are assigned, and in addition satellites due to ^{77}Se when Y is selenium are only observed with one of the Si*H* resonances (the one we have assigned to the isomer with silicon bound to selenium). For these reasons we prefer the interpretation based on intramolecular exchange. At first sight it is surprising that despite the very strong Si–O bond these equilibria do not overwhelmingly favour the SiH_3O-isomers. However, the changes on isomerization involve the C=Y as well as the Si–O, and the C=O as well as the Si–Y bonds; the strength of Si–O as against Si–Y must be balanced by the weakness of C=Y as against C=O.

EXPERIMENTAL

Compounds were handled in conventional vacuum-systems fitted with greased taps, or under dry nitrogen in an evacuable Mecaplex glove-box or in Polythene bags; some reaction-vessels were closed with Rotaflo Teflon/glass taps. I.r. spectra were recorded by means of Perkin-Elmer 457 or 225 spectrometers, in the range 4000—200 cm^{-1}; solid samples were ground with dried Nujol or hexachlorobutadiene. Raman spectra were recorded using a Cary 81 spectrometer with laser excitation. Mass spectra were obtained with a high-resolution AEI MS902 instrument, and ^1H and ^{19}F n.m.r. spectra with a Varian Associates HA 100 spectrometer.

Silylamines,[7] germyl bromide,[8] hydrogen selenide,[9] and the difluorophosphine halides[10] were prepared by established methods and purified in the vacuum system. Hydrogen sulphide was made using a Kipp's apparatus; other starting materials were obtained commercially. All solvents were thoroughly dried before use. Compounds were identified by i.r. and n.m.r. spectroscopy, and purities checked using measurements of vapour pressure and molecular weight.

Reaction of Trisilylamine.—(a) *With* H_2S. In a typical experiment, trisilylamine (0·116 g., 1·08 mmol) was kept with H_2S (0·102 g., 3·00 mmol) at room temperature (48 hr.) under pressure (2—3 atm.) in a vessel fitted with a Rotaflo tap. White crystals slowly formed all over the walls of the tube, implying that at least some of the product was formed from a vapour-phase reaction. The volatile products were found spectroscopically to consist of $(SiH_3)_2S$, H_2S, and a trace of SiH_4. The involatile *residue* (0·087 g., 1·07 mmol) was identified by analysis as SiH_3SH,NH_3 (Found: H, 8·5; N, 17·2. H_7NSSi requires H, 8·7; N, 17·3%). In a separate experiment, pure $(SiH_3)_2S$ (0·41 mmol; v.p. at 0°, found, 62 mm, lit.[11] 61 mm) was obtained from the reation of trisilylamine (0·50 mmol) and H_2S (2·33 mmol) under the same conditions; excess of H_2S (1·28 mmol) was recovered. The reaction is therefore effectively quantitative; small amounts of SiH_3SH may have been formed.

(b) *With* H_2Se. In a typical experiment, trisilylamine (0·126 g., 1·18 mmol) was kept with H_2Se (0·278 g., 3·48 mmol) at room temperature (48 hr.) under a pressure of 2—4 atm.; white crystals appeared when the system reached room temperature, and on standing crystals appeared all over the walls of the tube. The volatile products consisted of H_2Se (0·086 g., 1·05 mmol) shown spectroscopically to have contained a trace of disiloxane, and crude disilyl selenide (0·161 g., 1·14 mmole; v.p. at 0°, found, 30 mm, lit.[11] 21 mm), from which pure disilyl selenide (1·01 mmole; v.p. at 0°, found, 21 mm) was obtained by fractional condensation. The involatile *residue* (0·1375 g., 1·06 mmol) was identified by analysis as SiH_3SeH,NH_3 (Found: H, 5·3; N, 10·9. H_7NSeSi requires H, 5·6; N, 10·9%).

Reactions of N-*Methyldisilylamine and of* N-*Dimethylsilylamine with* H_2S *and with* H_2Se.—These reactions were allowed to take place as described above. With H_2S, *N*-methyldisilylamine (0·092 g., 1·01 mmol) gave a white solid adduct (0·091 g., 0·96 mmol) on warming to room temperature; *N*-dimethylsilylamine (0·067 g., 0·89 mmol) gave a similar adduct (0·087 g., 0·80 mmol), the reaction starting at a temperature well below that of the room. In the latter reaction no disilyl sulphide was formed. Reactions with H_2Se were similar. The adducts were analysed and the results are set out below:

$CH_3NH_2,HSSiH_3$: Found: C, 12·9; H, 9·1; N, 14·3. CH_9NSSi requires C, 12·6; H, 9·5; N, 14·7%. $(CH_3)_2NH,HSSiH_3$: Found, C, 21·9; H, 9·7; N, 12·9. $C_2H_{11}NSSi$ requires C, 22·0; H, 10·2; N, 12·8%. $CH_3NH_2,HSeSiH_3$: Found, C, 8·8; H, 6·6; N, 10·0. CH_9NSeSi requires C, 8·5; H, 6·4; N, 9·9%. $(CH_3)_2NH,HSeSiH_3$: Found,

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[6] G. M. Sheldrick, personal communication.

[7] A. Stock and C. Somieski, *Ber.*, 1921, **54**, 740; H. J. Emeléus and N. Miller, *J. Chem. Soc.*, 1939, 817; S. Sujishi and S. Witz, *J. Amer. Chem. Soc.*, 1954, **76**, 4631.

[8] L. M. Dennis and P. R. Judy, *J. Amer. Chem. Soc.*, 1929, **51**, 2321.

[9] G. R. Watkins and R. Shutt, *Inorg. Synth.*, 1959, **2**, 184.

[10] R. G. Cavell, *J. Chem. Soc.*, 1964, 1992.

[11] H. J. Emeléus, A. G. Maddock, and A. G. MacDiarmid, *J. Inorg. Nuclear Chem.*, 1956, **2**, 194.

C, 15·3; H, 6·9; N, 8·9. $C_2H_{11}NSeSi$ requires C, 15·4; H, 7·1; N, 9·0%.

Reaction of Silanethiol with Ammonia.—Ammonia (0·25 mmol) was allowed to warm to room temperature with SiH_3SH (0·25 mmol). A white solid formed immediately; its i.r. spectrum was identical to that of the adduct SiH_3SH,NH_3 prepared as described above. Volatile products, shown spectroscopically to consist mainly of $(SiH_3)_2S$, amounted to *ca.* 0·01 mmol.

Vibrational Spectra.—Infrared and Raman spectra of the adducts SiH_3YH,NH_3 are given in Table 1, with proposed assignments based on the formulation of the compounds as $NH_4(YSiH_3)$. The modes associated with the anions are readily assigned; the SiH_3 deformation and rocking modes appear at frequencies very close to those associated with SiH_3Y-groups in other compounds.[12] It is interesting that ν(Si–Y) is somewhat higher in these compounds even than is $\nu_{as}(Si_2Y)$ in $(SiH_3)_2Y$, an observation that is consistent with delocalization of negative charge in the anions from Y to Si by (π-*d*)π-interaction, thus strengthening the Si–Y bonds. The fundamental modes of the ammonium ion are also easily identified.[3] The bands due to NH stretching modes are very broad, which is consistent with significant hydrogen bonding in the crystal.[3] The appearance of weak bands near 1800 cm^{-1}, assigned to combinations of NH_4^+ deformation modes with lattice modes, also suggests that hydrogen bonding is quite strong in these systems. Bands at frequencies below 400 cm^{-1} are assigned to lattice modes; a weak band in the Raman spectrum of the sulphide at 425 cm^{-1} has been assigned similarly. The frequencies of these lattice modes are in reasonable agreement with those for lattice modes in the ammonium halides.[3] Frequencies of $ND_4(S{\cdot}SiH_3)$ are given below, with those for the methylammonium and dimethylammonium salts; frequencies from these spectra that have been assigned to modes of the anions are given in Table 2.

TABLE 1

Vibrational frequencies (cm^{-1}) for $NH_4^+(YSiH_3)^-$, with assignments

$NH_4^+(SSiH_3)^-$		$NH_4^+(SeSiH_3)^-$		
I.r.	Raman	I.r.	Raman	Assignment
3100sh		3080sh		ν(NH_4) and combinations
2920br		2920br		
2780br		2780sh		
2470sh		2470sh		
2340brsh		2360w		
2100m	2124s	2120m	2123s	ν(SiH)
1960brsh		1950br		?$\nu_2(NH_4^+)$ + 350
1810w,br		1770br		?$\nu_2(NH_4^+)$ + 200
1740w,br		1700br		1420 + 350
1420m		1415m		$\delta(NH_4^+)$
930m,br	926m	930m,br	900m	$\delta(SiH_3)$
635m		615m		$\rho(SiH_3)$
550m	551m	425m	425m	ν(SiY)
	425w			?Lattice mode
350w	350w	325w	330w	
	200w		190w	Lattice modes

Assignments of the bands between 1400 and 2000 cm^{-1} are based on modes of the ammonium ion because the bands are very broad and look like those in the spectra of other ammonium salts. Alternative assignments involving anion frequencies are also possible.

TABLE 2

Frequencies (cm^{-1}) from the spectra of deuterioammonium, methylammonium, and dimethylammonium salts of the anions SiH_3Y that are assigned to anion modes

	Cation				
	Y = S			Y = Se	
Assignment	ND_4^+	$MeNH_3^+$	$Me_2NH_2^+$	$MeNH_3^+$	$Me_2NH_2^+$
ν(SiH)	2100m	2100m	2050m	2090m	2050m
$\delta(SiH_3)$	935br	940br	930br	940br	935br
$\rho(SiH_3)$	635m	635m	635m	430m	430m
ν(SiY)	550m	550m	550m	430m	430m

Observed Infrared Frequencies.—(*a*) $ND_4(S{\cdot}SiH_3)$: 2980w, 2920w, 2850w, 2760w, 2360sh, 2280br, 2220br, 2100m, 1420w, 1370w, 1310w, 1170w, 1080s, 935br, 635m, 550m.

(*b*) $MeNH_3(S{\cdot}SiH_3)$: 3120sh, 2920br, 2850sh, 2740sh, 2520sh, 2460m, 2240w, 2110m, 2090m, 1920br, 1570m, 1460m, 1420m, 1300m, 1265m, 1170w, 1160w, 1000sh, 940br, 855sh, 810sh, 635m, 550m, 470w.

(*c*) $MeNH_3(Se{\cdot}SiH_3)$: 3120sh, 3060sh, 2920br, 2780sh, 2720sh, 2660sh, 2430m, 2160sh, 2090m, 1850br, 1550br, 1460m, 1415m, 1300w, 1265m, 1170w, 1160w, 1090m, 1000sh, 940br, 875sh, 820sh, 770m, 600m, 450w, 430m, 395w.

(*c*) $Me_2NH_2(S{\cdot}SiH_3)$: 3120sh, 2920br, 2840sh, 2700br, 2380br, 2080sh, 2050m, 1850br, 1750br, 1670br, 1580br, 1460m, 1415m, 1300sh, 1250m, 1025m, 930br, 880sh, 635m, 550m.

(*d*) $Me_2NH_2(Se{\cdot}SiH_3)$: 2920br, 2840sh, 1760sh, 2700sh, 2380br, 2100sh, 2050m, 1460m, 1410m, 1370w, 1330w, 1160w, 1070w, 1025w, 935br, 880sh, 600m, 465w, 430m.

Mass spectra.—The *m/e* values for peaks observed in the mass spectra of the ammonium salts are given below, with assignments in terms of groups of peaks. Patterns due to successive loss of hydrogen atoms from SiH_3-groups and to the different isotopes of S and Se were observed; the *m/e* values given are for ^{28}Si, and ^{32}S or ^{80}Se, with the maximum number of hydrogen atoms. (*a*) $NH_4(SSiH_3)$: 94, $(SiH_3)_2S^+$; 78, $(SiH_3)_2O^+$; 64, SiH_3SH^+; 34, H_2S^+; 31, SiH_3^+. (*b*) $NH_4(SeSiH_3)$: 142, $(SiH_3)_2Se^+$; 111, SiH_3Se^+; 82, H_2Se^+; 78, $(SiH_3)_2O^+$; 31, SiH_3^+.

Reactions of MeI.—(a) *With* $NH_4(SSiH_3)$. The ammonium salt (0·5 mmol) was prepared as described above during 48 h, and volatile products were removed. Methyl iodide (0·5 mmol) was then added, and the system was kept at room temperature for several days. After removal of volatile material, the solid residue was shown spectroscopically to consist of ammonium iodide containing a trace of SiH. Fractional condensation of the volatile products gave silyl methyl sulphide (0·1 mmol; identified by its i.r. and n.m.r. spectra [13]).

(b) *With* $NH_4(Se{\cdot}SiH_3)$. The ammonium salt (0·5 mmol), prepared as described above, was treated with methyl iodide (0·5 mmol) for several days; the involatile solid residue was shown to consist of ammonium iodide. From the volatile products, *silyl methyl selenide* (0·25 mmol) was obtained (parent ion in mass spectrum: *m/e*, found, for ^{80}Se, 125·940377; $CH_6{}^{80}SeSi$ requires 125·940072). In a capillary tube relative to Me_4Si external standard, τ(SiH) = 5·94, τ(CH) = 8·45; ^4J(HSiSeCH) = 0·4 Hz. It should be noted that chemical shifts measured in this way may differ by as much as 0·5 p.p.m. from those

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[12] E. A. V. Ebsworth, R. Taylor, and L. A. Woodward, *Trans. Faraday Soc.*, 1959, **55**, 211.

[13] B. Sternbach and A. G. MacDiarmid, *J. Inorg. Nuclear Chem.*, 1961, **23**, 225.

measured under normal conditions relative to an internal standard. Infrared bands were observed at (cm^{-1}): 2940w and 2840w (ν CH), 2160s (ν SiH), 1280w (δ_s CH_3), 950s (δ SiH_3), 910m (δ SiH_3), 600m (ρ SiH_3), and 405m (ν SiSe).

Reactions of Me_3SiCl.—(a) *With* $NH_4(S{\cdot}SiH_3)$. The ammonium salt (1·07 mmol), prepared as described above, was allowed to react at room temperature with Me_3SiCl (1·31 mmol, 24 h); the involatile solid residue was shown spectroscopically to be ammonium chloride, and contained no SiH. The volatile products consisted of a mixture of disilyl sulphide, excess of Me_3SiCl, and *silyl trimethylsilyl sulphide*, a pure sample of which was obtained by fractional condensation (Found: C, 27·3; H, 8·9. $C_3H_{12}SSi_2$ requires C, 26·4; H, 8·9%). The compound melted at -104 to $-106°$, and had v.p. at 0° of 4 mm; the ^1H n.m.r. spectrum (rel. to cyclopentane as solvent and internal standard) gave $\tau(SiH) = 5{\cdot}72$, $\tau(CH) = 9{\cdot}64$; $^1J(^{29}SiH) = 218{\cdot}6$ Hz, $^3J(^{29}SiSSiH) = 2{\cdot}5$ Hz. In the i.r. spectrum of the vapour, bands were observed at (cm^{-1}) 2960m and 2900w (ν CH), 2160s (ν SiH), 1450w and 1405w (δ_{as} CH_3), 1325w (?690 + 640), 1255s (δ_s CH_3), 1070w (?Si_2O impurity or 640 + 440), 935s (δ SiH)$_3$, 845vs (ρ CH_3), 750 m (ν_{as} C_3Si), 690m (ν_s C_3Si), 640m (ρ SiH_3), 525m (ν_{as} Si_2S), and 440m (ν_s Si_2S). In the mass spectrum, groups of peaks were observed at *m/e* values associated with the molecular ion and with loss of methyl groups and hydrogen and silicon atoms.

(b) *With* $NH_4(Se{\cdot}SiH_3)$. The ammonium salt (1·01 mmol), prepared as described above, was allowed to react with Me_3SiCl (1·31 mmole) at room temperature (24 h.); the solid residue was identified spectroscopically as ammonium chloride, and contained no SiH. The volatile products consisted of a trace of SiH_4, Me_3SiCl, disilyl selenide, and *silyl trimethylsilyl selenide*, a pure sample of which was isolated by fractional condensation (Found: C, 20·3; H, 6·6. $C_3H_{12}SeSi_2$ requires C, 19·7; H, 6·6%). The compound was involatile at $-46°$; at 22° it had v.p. 5 mm. It disproportionated slowly at room temperature, giving disilyl selenide and (presumably) $(Me_3Si)_2Se$. The ^1H n.m.r. spectrum (in cyclopentane as solvent and internal standard) gave $\tau(SiH) = 5{\cdot}99$, $\tau(CH) = 9{\cdot}54$; $^1J(^{29}SiH) = 218{\cdot}5$, $^2J(^{77}SeSiH) = 14{\cdot}9$, $^3J(^{29}SiSeSiH) = 2{\cdot}1$ Hz. In the i.r. spectrum of the vapour, bands were observed at (cm.$^{-1}$) 2960m and 2900w (ν CH), 2170s (ν SiH), 1450w and 1410w (δ_{as} CH_3), 1325w (925 + 400), 1250m (δ_s CH_3), 1070w (?Si_2O impurity), 950sh, 925vs, and 890vs (δ SiH_3), 850vs (ρ CH_3), 755m (ν_{as} C_3Si), 700w (ν_s C_3Si), 630m (ρ SiH_3), 400m (ν_{as} Si_2Se), and 360m (ν_s Si_2Se). In the mass spectrum, groups of peaks were observed with the general isotope pattern expected for a selenium compound at *m/e* values associated with the molecular ion and with loss of methyl groups and hydrogen and silicon atoms, as well as smaller fragments.

Reaction of Germyl Bromide with $NH_4(S{\cdot}SiH_3)$.—The ammonium salt (0·5 mmol), prepared as described above, was allowed to warm to room temperature with germyl bromide (0·5 mmol); a vigorous reaction occurred. Fractional distillation of the volatile products gave a trace of germane, some disilyl sulphide (both identified spectroscopically), and a less volatile fraction whose i.r. spectrum showed that it contained both GeH_3S- and SiH_3S-groups; it was not possible to tell whether any silyl germyl sulphide were present. Repeated fractionation did not lead to the isolation of any of this compound. In a second experiment, the reactants were held at $-20°$ (30 min); the volatile products were then transferred without fractional distillation to an n.m.r. tube. In CCl_4 containing Me_4Si standard, peaks were observed due to $(GeH_3)_2S$ ($\tau = 5{\cdot}32$, lit.,[14] 5·33), $(SiH_3)_2S$ ($\tau = 5{\cdot}62$, lit.,[15] 5·65), and $GeH_3{\cdot}S{\cdot}SiH_3$ ($\tau = 5{\cdot}41$, 5·59; lit.,[16] 5·36, 5·60; $J = 0{\cdot}8$ Hz., lit.,[15] 0·8 Hz). On standing, silyl chloride was formed. In cyclopentane as solvent and standard, the spectrum was unchanged over several hours at room temperature.

Reactions of PF_2Br.—(a) *With* $NH_4(S{\cdot}SiH_3)$. Equimolar amounts of the ammonium salt, prepared as described above, and of PF_2Br were allowed to warm to room temperature together. An immediate reaction occurred and the solid turned yellow. The system was kept at $-22°$ (1 h); volatile products were removed. The solid residue contained no SiH bonds, but in addition to the peaks due to the ammonium salt there were weak bands below 1000 cm^{-1}. The volatile products were very complex. The fraction volatile at $-120°$ contained SiH_3F,PF_3, and perhaps H_2S; the fraction volatile at $-96°$ consisted mainly[17] of SPF_2H; that involatile at $-96°$ consisted mainly of $(SiH_3)_2S$ and $PF_2{\cdot}NH{\cdot}SiH_3$ (all identified spectroscopically[4]). No evidence was found in any of the spectra for the presence of $SiH_3{\cdot}S{\cdot}PF_2$. The reaction with PF_2Cl was similar.

(b) *With* $NH_4(Se{\cdot}SiH_3)$. Under similar conditions the ammonium salt reacted with PF_2Br to give a yellow involatile solid and a complex mixture of volatile products. The most volatile fraction consisted of a mixture of PF_3, SiH_3F, PF_2Br, and H_2Se. The material volatile at $-78°$ but not at $-96°$ contained $SePF_2H$ (mass spectrum: for ^{80}Se, observed, 149·894157. HF_2PSe^+ requires 149·894893. Typical Se isotope pattern observed for molecular ion peaks. In CCl_3F/Me_4Si, $\tau = -1{\cdot}54$; $^1J(PH) = 687{\cdot}7$, $^2J(HPF) = 92{\cdot}4$ Hz; $\phi_F = 43 \pm 0{\cdot}2$, $^1J(PF) = 1182 \pm 3$, $^2J(^{77}SePF) = 118{\cdot}7 \pm 0{\cdot}7$ Hz). The i.r. spectrum of the vapour showed that SiH and perhaps other impurities were present; for this reason we cannot assign fundamental frequencies to this molecule. The least volatile fraction contained $(SiH_3)_2Se$ and $SiH_3{\cdot}NH{\cdot}PF_2$. The mass spectrum of the combined products gave no peak at *m/e* 181 ($PF_2{\cdot}Se{\cdot}SiH_3$).

Reactions of Acetyl Chloride.—(a) *With* $NH_4(S{\cdot}SiH_3)$. Acetyl chloride was found to react with the ammonium salt at room temperature. With any excess of acetyl chloride, large amounts of silyl chloride were formed, so rather less than an equimolar proportion of acetyl chloride was taken in most experiments. After removal of the volatile products, the i.r. spectrum of the pale yellow solid residue contained no peaks due to SiH, but there were weak bands below 1000 cm^{-1} in addition to those due to NH_4Br. The volatile products consisted of silyl chloride (volatile at $-96°$; identified by its i.r. spectrum), diacetyl sulphide (parent ion *m/e* = 118, calc. 118. Infrared spectrum consistent), disilyl sulphide, and *silyl monothioacetate* (*m/e*, found, 105·990727. C_2H_6OSSi requires 105·990860). It proved impossible to separate this compound completely from diacetyl and disilyl sulphides.

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[14] C. Glidewell, D. W. H. Rankin, and G. M. Sheldrick, *Trans. Faraday Soc.*, 1969, **65**, 1409.

[15] E. A. V. Ebsworth and J. J. Turner, *J. Phys. Chem.*, 1963, **67**, 805.

[16] J. E. Drake and C. Riddle, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 713.

[17] T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, 1967, **6**, 2204.

In the i.r. spectrum of the vapour, peaks were observed at (cm^{-1}) 2190s (ν SiH), 1750w (ν C=O in diacetyl sulphide), 1720br (ν C=O), 1440w (δ_{as} CH_3), 1370m (δ_s CH_3), 1265vs (ν C–O), 1235vs (?), 1130m (?ν C=S), 1015m (ρ CH_3), 930s (δ SiH_3), 820m (?), 720m (?), 700m (ρ SiH_3O), 635m (?ρ SiH_3S), and 510w (ν SiS). Some of these assignments are tentative, since we do not know the isomeric composition of the vapour. The n.m.r. spectrum (CCl_4/Me_4Si) at room temperature gave weak/very weak peaks at τ 5·63 (disilyl sulphide) and 7·47 (diacetyl sulphide), and in addition two peaks of equal intensity, at τ 5·39 (SiH) and 7·43 (acetyl) with $^1J(^{29}SiH) = 234$, $^1J(^{13}CH) = 129{\cdot}4$ Hz. The small amounts of impurity hampered the study of the spectrum at low temperatures. When a sample of the compound in cyclopentane was cooled to 0°, both main resonances broadened; this broadening was more pronounced at $-20°$, but at $-35°$ the resonances became sharper, and were found to have shifted to τ 5·36 and 7·41. We assign these sharp resonances to the isomer $CH_3{\cdot}C(:S){\cdot}O{\cdot}SiH_3$, since the SiH chemical shift is in the region associated with SiH_3O-groups and some 0·3 p.p.m. to low field of that associated with SiH_3S-systems. There was some evidence for the appearance at very low temperatures ($-45°$) of a weak peak at $\tau = 5{\cdot}63$ but the presence of traces of $(SiH_3)_2S$ makes it difficult to identify this peak with certainty. Splitting of the peak at τ 7·43 could not be confirmed because of the presence of diacetyl sulphide. However, the peak at $\tau = 5{\cdot}63$ may well be due to the isomer $CH_3{\cdot}C(:O){\cdot}S{\cdot}SiH_3$. The broadening in the resonances between 0 and $-25°$ is not due to changes in viscosity of the solvent, because the peaks due to diacetyl and disilyl sulphides remained very sharp. If our interpretation is correct, and if the chemical shifts of the isomers do not change between room temperature and $-35°$, the ratio of the two isomers at room temperature must be at least $7[CH_3{\cdot}C(:S){\cdot}O{\cdot}SiH_3] : 1[CH_3{\cdot}C(:O){\cdot}S{\cdot}SiH_3]$.

(b) *With* $NH_4(Se{\cdot}SiH_3)$. When the ammonium salt was treated with slightly less than an equimolar proportion of acetyl chloride, a yellow liquid formed immediately the system reached room temperature. Fractional distillation of the volatile products gave silyl chloride (volatile at $-96°$), a fraction volatile at $-46°$ that was shown spectroscopically to consist of disilyl selenide with a trace of impurity containing C=O groups, and a bright yellow liquid, involatile at $-46°$. This was shown by its i.r. and mass spectra to consist of a mixture of disilyl selenide (*m/e* for ^{80}Se, found, 142; calc., 142), diacetyl selenide (*m/e* for ^{80}Se, found, 166, calc. 166), and *silyl monoselenoacetate* (*m/e* for peaks associated with Se isotopes of mass numbers 76, 78, and 80 agreed with those required for C_2H_6OSeSi to 6, 13, and 5 p.p.m. respectively). This compound could not be separated completely from diacetyl and disilyl selenides. In the i.r. spectrum of the vapour, bands were observed at (cm^{-1}) 2180s (ν SiH), 1730s (ν C=O), 1420w (δ_{as} CH_3), 1360w (δ_s CH_3), 1270s (?ν C–O), 1190m (?), 1100s (?ν Si–O), 1010w, 930s and 890vs (δ SiH_3), 790w (?ρ CH_3), 575s (ρ SiH_3Se), and 390m (ν SiSe). Some of these bands may be due to the selenide impurities. In the n.m.r. spectrum (CCl_4/Me_3Si) at room temperature there were sharp peaks at $\tau = 5{\cdot}90$ (assigned to disilyl selenide [15]) and 7·45 (assigned to diacetyl selenide); there was also a broad peak at $\tau = 5{\cdot}80$ and a somewhat sharper one at $\tau = 7{\cdot}55$. At 0° both these peaks showed signs of splitting and at $-15°$ both had clearly split into two components of comparable intensity. At $-46°$ the broad peak (τ 5·80) had split into a sharp peak at $\tau = 5{\cdot}935$ with sharp singlet satellites due to coupling with ^{29}Si-$[^1J(^{29}SiH) = 229{\cdot}8$ Hz] and $^{77}Se[^2J(^{77}SeSiH) = 16{\cdot}5$ Hz], and a rather weaker but equally sharp peak at $\tau = 5{\cdot}20$ with sharp singlet satellites due to $^{29}Si(J = 237{\cdot}8$ Hz). There were no ^{77}Se satellites associated with this peak. The peak at higher field (τ 7·55) had similarly split into a sharp peak at $\tau = 7{\cdot}46$ and a rather weaker peak at $\tau = 7{\cdot}62$. The peaks at τ 5·20 and τ 7·62 were of equal intensity, as were those at τ 5·935 and τ 7·46. Neither of the peaks assigned to impurity was significantly affected either in shape or position by the change in temperature from 27° to $-46°$; the satellites due to ^{77}Se in disilyl selenide were sharp at room temperature and the ^{29}SiH satellites retained their quartet structure, so that disilyl selenide is not involved in any fast exchange of SiH_3-groups. The spectra of samples differing in concentration by at least a factor of 5 were effectively identical at corresponding temperatures; changing the solvent from CCl_4 to Me_4Si did not appear to affect the spectrum. We assign the stronger pair of peaks to the isomer $CH_3C(O)SeSiH_3$ [$\tau(SiH) = 5{\cdot}395$, $\tau(CH) = 7{\cdot}46$], and the weaker pair to the isomer $CH_3{\cdot}C(:Se){\cdot}O{\cdot}SiH_3$ [$\tau(SiH) = 5{\cdot}20$, $\tau(CH) = 7{\cdot}62$]; from peak heights at $-50°$ the equilibrium constant (SiH_3Se-isomer : SiH_3O-isomer) was estimated to be $2{\cdot}5 \pm 0{\cdot}5$. Assuming that the chemical shifts do not change significantly with temperature, the equilibrium constant at room temperature is also *ca.* 2·5.

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