Structure of Silylated Sulphonamides; a Silicon-29 Nuclear Magnetic Resonance Investigation

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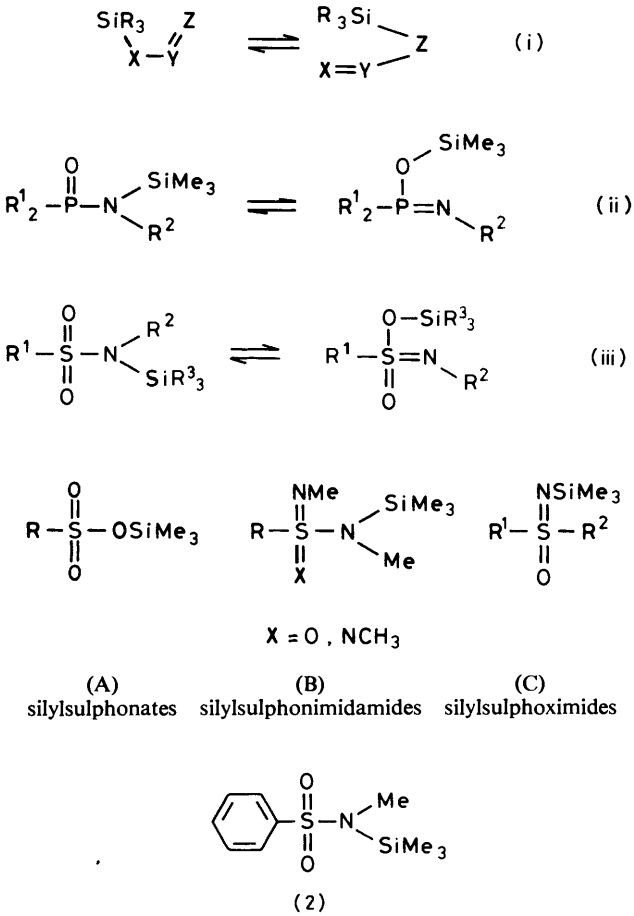
The structures of eighteen silylsulphonamides have been determined by ^{29}Si n.m.r. The chemical shifts of the compounds were compared with those of model compounds. The *N*-silyl tautomer was the only isomer observed, except in cases where strongly electron-withdrawing groups (*e.g.* Cl, NMe_2) were attached to nitrogen; in such cases the *O*-silyl tautomer dominates. The results have been rationalised in terms of the effect of substituents on the S–N π-bond order. An estimate of the hitherto unmeasured S=N molar bond enthalpy as 325 kJ mol^{-1} was obtained.

Silatropism is common in systems containing an allyl-like framework [1] [equation (i)]. The silylamide–silylimidate equilibrium (X = NR, Y = C, Z = O) has been studied extensively and characterised.[2] The imidate tautomer $R^1(Me_3SiO)C{=}NR^2$ is favoured by substituents (R^1 and R^2) that decrease the C–N π-electron density in the amides.[2] Steric effects at silicon [3] show that increasing the steric bulk of the silyl groups tends to increase the proportion of imidate isomer in the equilibrium mixture, no doubt because unfavourable steric interactions are removed in the imidate.

Tautomerism has also been established for the related silylphosphylamidate–silylphosphylimidate system[4,5] [equation (ii)]. Here, too, it seems that electron donation to phosphorus (increasing the P–N π-character) increases the proportion of amidate tautomer.[4,5] Bulky groups at silicon do not significantly increase the proportion of imidate.[4]

This study is concerned with the analogous silylsulphonamide–sulphonimidate system [equation (iii)]. Although sulphonamides are chemically and biologically important, and silylated sulphonamides are useful silylating agents, there have been no definitive structural studies on silylsulphonamides. Previous studies of these compounds have relied on ^1H n.m.r. and i.r. spectroscopic analyses.[6,7] The evidence from these studies is not strong but suggests that the silylsulphonamide is the exclusive form,[6] although in one case a sulphonamide–sulphonimidate equilibrium was proposed.[7] Bis(silyl)-sulphonamides were tentatively suggested, on i.r. evidence, to exist as a tautomeric mixture. In the work presented here ^{29}Si n.m.r. was used to elucidate the structure of eighteen silylated sulphonamides and related compounds. ^{29}Si N.m.r. has been used previously to study the structure of $SO_2[N(SiMe_3)_2]_2$.[8] Three signals were observed and assigned to the three silicon atoms of $SO(OSiMe_3)(NSiMe_3)N(SiMe_3)_2$. Our evidence indicates that the silylsulphonamide is the predominant form except when strongly electron-withdrawing substituents are attached to the nitrogen atom.



(2)

Results and Discussion

The method used was similar to that employed for silylamides.[2] It depends on the sensitivity of ^{29}Si n.m.r. chemical shifts to changes in molecular environment, and a condition of success is that the different environments produce ^{29}Si chemical shifts in non-overlapping regions. There are three different possible silicon environments in silylsulphonamides and sulphonimidates: $R_3SiN<$ in the amide form; R_3SiO^- in the imidate form; and $R_3SiN{=}S$ in the imidate form of bis(silyl)sulphonimidates. For trimethylsilyl derivatives, a series of model compounds was prepared, in which the silyl group was unambiguously in one of the three environments. Their ^{29}Si n.m.r. chemical shifts are given in Table 1. Silyl sulphonates (A) were used to model $-OSiMe_3$; silylated sulphonimidamides (B) [9] to model $Me_3Si-N<$; and silylsulphoximides (C) for $Me_3Si-N{=}S$.

The three trimethylsilyl environments in the model compounds fall into three, non-overlapping, chemical shift regions; Me_3SiO δ *ca.* 30—45; Me_3SiN δ *ca.* 0—10; $Me_3SiN{=}S$ δ *ca.* −3 to −5. It is to be expected that $R^1SO_2NR^2SiMe_3$ should appear to the high frequency end of the range (δ *ca.* >10) as the model compounds contain the $RS(O)(NMe)-N{=}$ or $RS(NMe)_2-N{=}$ fragments. As previously experienced for other compounds,[2] and shown by the examples in Table 1, oxygen is more deshielding than nitrogen.[10] Similarly the $RS(O)(NR)OSiMe_3$ resonances are expected to fall in the lower frequency range (δ *ca.* 30) of the $-OSiMe_3$ model. The $Y{=}N-SiMe_3$ signals appear remarkably independent of Y [*cf.* equation (i)].[2]

Table 1. ^{29}Si Chemical shifts of model compounds in [$^2H_6$]benzene

	δ [a]
Environments with $Me_3SiN<$	
$C_8H_{17}S(O)(NMe)NMeSiMe_3$	9.66
$C_2H_5S(NMe)_2NMeSiMe_3$	0.88
$C_4H_9S(NMe)_2NMeSiMe_3$	0.38
Environments with $Me_3SiN{=}S$	
$Me_2S(O)NSiMe_3$	−4.99
$MePhS(O)NSiMe_3$	−3.04
Environments with $Me_3SiO{-}S$	
$PhSO_2OSiMe_3$	31.31
4-$MeC_6H_4SO_2OSiMe_3$	30.83
$MeSO_2OSiMe_3$	30.47
$CF_3SO_2OSiMe_3$	43.48
Environments with $R_3SiO{-}S$	
4-$MeC_6H_4SO_2OSiBu^tMe_2$	32.28
4-$MeC_6H_4SO_2OSiBu^tPh_2$	13.50

[a] Referenced to internal Me_4Si.

Table 2. ^{29}Si Chemical shifts of silylated sulphonamides, $R^1SO_2NR^2SiX_3$, in [$^2H_6$]benzene

Compd.	R^1	R^2	SiX_3	δ [a]
(1)	Ph	H	$SiMe_3$	9.82
(2)	Ph	Me	$SiMe_3$	14.18
(3)	Ph	Ph	$SiMe_3$	14.22
(4)	Ph	Cl	$SiMe_3$	9.74, 27.51
(5)	Ph	NMe_2	$SiMe_3$	13.33, 26.96
(6)	Ph	$SiMe_3$	$SiMe_3$	10.26 and 25.89, −3.24
(7)	4-MeC_6H_4	H	$SiMe_3$	9.43
(8)	4-MeC_6H_4	Me	$SiMe_3$	13.82
(9)	4-MeC_6H_4	Ph	$SiMe_3$	13.99
(10)	4-MeC_6H_4	Bu^t	$SiMe_3$	9.57
(11)	4-MeC_6H_4	Cl	$SiMe_3$	9.38, 27.13
(12)	4-MeC_6H_4	Ph	$SiBu^tMe_2$	18.10
(13)	4-MeC_6H_4	Ph	$SiBu^tPh_2$	−2.55
(14)	Me	H	$SiMe_3$	9.34
(15)	CF_3	Ph	$SiMe_3$	25.42
(16)	Me_2N	Me	$SiMe_3$	13.99
(17)	Me_2N	Ph	$SiMe_3$	13.36
(18)	Me_3SiO	H	$SiMe_3$	10.20, 28.03

[a] Referenced to internal Me_4Si.

An interesting aside is that for the sulphonimidamides (Table 1) only one methyl group environment was observed in the ^1H n.m.r. spectra, indicating a rapid intra- or intermolecular exchange of the trimethylsilyl group between one nitrogen and the other(s).

The chemical shifts of silylated sulphonamides and some related compounds are given in Table 2. Comparison of the shifts of $R^1SO_2NR^2SiMe_3$ (Table 2) with those of the model compounds (Table 1) leads to a number of conclusions. First, when R^1 and R^2 were alkyl or aryl, the only detectable structures (*i.e.* in most cases >98%) were the silylsulphonamides. For example, the silylated *N*-methyl benzenesulphonamide (2) gave one sharp signal at δ 14.18, which is unambiguously from the *N*-silyl tautomer. The ^{29}Si chemical shift of (2) is *ca.* 5 p.p.m. to high frequency of that of the closest model compound, as expected from the replacement of S=N by S=O. The other silylated sulphonamides with R^1,R^2 = Ph, 4-MeC_6H_4, H, Me, and Bu^t [(2), (3), (7)—(10), (14)] also show single resonances in the region δ 9—14, appropriate to the silylsulphonamide structure. Even the presence of the Bu^t group on nitrogen (10) does not produce a detectable quantity of sulphonimidate. The silylated *N*-phenyltrifluoromethanesulphonamide (15) gives a single resonance at δ 25.4. Although this is outside the normal silylsulphonamide region it is, again, compatible only with the *N*-silyl tautomer. The resonance for trimethylsilyl trifluoromethanesulphonate appears at δ 43.48, and consistently in this work we have found (Tables 1 and 2) that the *N*-silylsulphonamido resonances are *ca.* 20 p.p.m. to high frequency of those of the corresponding sulphonates.

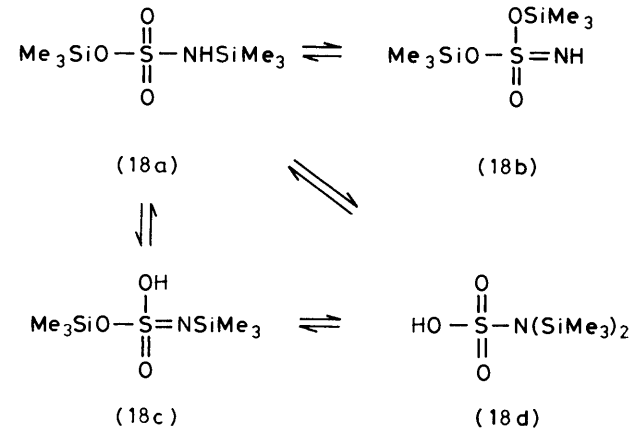
Heteroatoms attached to sulphur have no tendency to favour the sulphonimidate. Compounds (16) and (17) have spectra consistent with the silylsulphonamide structure giving single peaks in the $Me_3SiN<$ region (δ 13.99 and 13.36, respectively). Compound (17), $Me_2N{-}S(O)_2NPhSiMe_3$, has previously been reported on the basis of ^1H n.m.r. as a 5 : 1 mixture of sulphonamide and sulphonimidate, respectively, in CD_2Cl_2.[7] We found only one Me_3Si and one NMe_2 signal in the ^1H n.m.r. spectrum of (17) in CD_2Cl_2, $CDCl_3$, CCl_4, and C_6D_6, and only one ^{29}Si n.m.r. signal; we cannot therefore support the previous finding. Compound (18) has two resonances for the Me_3Si groups, of equal intensity in both ^1H and ^{29}Si n.m.r. spectra; four tautomeric forms can be envisaged for this compound (Scheme). The structure (18a) appears to be the exclusive form. The resonances for (18) are at δ 10.20 and 28.03, appropriate to one Me_3SiO and one Me_3SiN environment. The alternatives are therefore (18a) as the sole contributor, or an equimolar mixture of (18b) and (18d), as ^1H n.m.r. gives equal integrations for the two Me_3Si resonances. The i.r. spectrum confirms the presence of NH and the absence of OH (ν 3 365 cm^{-1}) thus ruling out (18d) and, of necessity, (18b). Furthermore, the i.r. absorptions at 1 350 and 1 175 cm^{-1} are characteristic of O=S=O and not O=S=N.

Only one bis(silyl)sulphonamide was prepared, $PhSO_2N(SiMe_3)_2$ (6), and this gives three ^{29}Si n.m.r. signals. The major resonance (*ca.* 98%) is at δ 10.26, corresponding to the bis(silyl)sulphonamide (7a). However, two minor, equally intense, resonances (*ca.* 1% each) appear at δ −3.24 and 25.89, in the region for the sulphonimidate tautomer (7b). The sulphonimidate tautomer was a significant component only for those compounds with Cl or N bound to the sulphonamide nitrogen atom, *i.e.* compounds (4), (5), and (11). For these compounds there are two ^{29}Si n.m.r. signals: one at δ 9—13 and the other at δ *ca.* 27. The relative proportions of sulphonamide and sulphonimidate as determined by ^1H n.m.r. are 1 : 2.5 for (4), 1 : 1.75 for (5), and 1 : 1.3 for (11). Comparison of (4) with (11) shows that electron donation to sulphur through the benzene ring decreases the amount of imidate tautomer (11b).

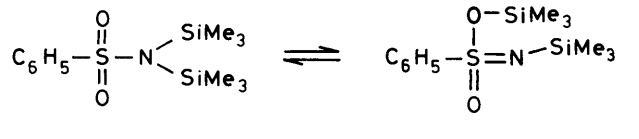
Increasing the steric bulk at silicon by itself does not favour sulphonimidate formation. Compounds (12) and (13) have single resonances *ca.* 15 p.p.m. to low frequency of those due to the analogous silylsulphonates; this is appropriate only to the silylsulphonamide structures.

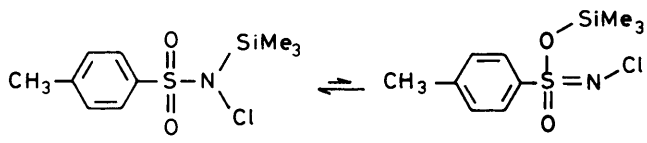
Before attempting to rationalise the above results it is appropriate to compare sulphonamides with amides. It is apparent that the silylamide–imidate equilibrium is more susceptible to substituent effects than the silylsulphonamide–sulphonimidate equilibrium.[2] A dominant factor in the amide case is postulated to be the C–N π-bond character, from (*p*–*p*) π overlap. The S–N π-bond overlap in sulphonamides is dependent on (*p*–*d*)π overlap,[11] and could be expected to be relatively small. In addition the S=O/S=N bond energy difference is expected to be much greater than the C=O/C=N difference. We have made an approximate estimate of the S=N bond enthalpy (see later) that confirms this expectation.

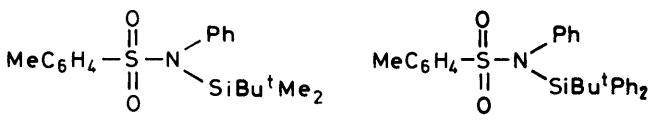
The enthalpy difference between the silylsulphonamide and



Scheme.







silylsulphonimidate [equation (iii)] is given by equation (iv).* All the molar bond enthalpies, except $B(S^{VI}-N)$, are known.†

$$\Delta H_{298} = B(Si-O) + B(S^{VI}-O) + B(S^{VI}=N) - B(Si-N) - B(S^{VI}-N) - B(S^{VI}=O) \quad (iv)$$

However, an estimate of 160 kJ mol^{-1} for $B(S^{VI}-N)$ can be obtained using Pauling's geometric mean equation.[12] Thus an approximate value for ΔH_{298} is [$B(S^{VI}=N)$ − 315] kJ mol^{-1}. Using the equilibrium constant for the bis(silyl)-sulphonamide, $K = 0.02$, as lying between those compounds that favour the sulphonamide structure and those that favour the sulphonimidate, we obtain $\Delta H_{298} \simeq \Delta G_{298} = 10$ kJ mol^{-1}. Consequently $B(S^{VI}=N)$ is *ca.* 325 kJ mol^{-1}. This is *ca.* 190 kJ mol^{-1} less stable than $S^{VI}=O$. The corresponding enthalpy difference between C=O and C=N is 135 kJ mol^{-1}.

Thus substituent effects in silylated sulphonamides can be expected to be attenuated relative to those in silylamides. However, we believe that our data show that the same general effects operate in the two systems.

The factors affecting silylsulphonamide–sulphonimidate equilibria can be rationalised and summarised as follows.

(*a*) The electronic effect of substituents at nitrogen dominates. Strongly electron-withdrawing groups (Cl, NMe_2) decrease the S–N π-bond energy in the sulphonamide form, thereby enabling a significant contribution from the sulphonimidate tautomer to be observed. The Me_3Si group also appears to reduce the S–N π-bond character in bis(silyl)sulphonamides.

(*b*) In the absence of electron-withdrawing groups on nitrogen the sulphonamide is the sole contributor; steric effects at silicon, nitrogen, and sulphur are not important in these cases.

(*c*) The electronic effect at sulphur is not as important as that at nitrogen, *e.g.* the CF_3 and Me_2N groups attached at sulphur do not produce a detectable amount of the sulphonimidate. In the presence of electron-withdrawing groups at nitrogen, the electronic effect at sulphur becomes important in determining the equilibrium proportions of the silyl sulphonamide and sulphonimidate tautomers; it appears that electron donation to sulphur increases the sulphonamide tautomer as the S–N π-electron density increases.

Experimental

N.m.r. spectra (^1H and ^{29}Si) were recorded for solutions in [$^2H_6$]benzene using a JEOL FX90Q spectrometer and are referenced to external Me_4Si. ^{29}Si N.m.r. spectra were recorded using one of three sets of conditions: (i) gated [^1H] decoupling during acquisition only; (ii) complete [^1H] decoupling in the presence of $Cr(acac)_3$ (30° pulse width, 2 s delay) to estimate the proportions of isomers (in favourable cases this gave results comparable with those from the ^1H spectra); (iii) ^{29}Si with INEPT pulse sequence; [13] this was not used to estimate isomer ratios, but was used in an attempt to observe very small amounts of minor isomers. I.r. spectra were recorded using a Unicam SP1050 spectrometer and melting temperatures were determined using a Buchi 510 apparatus. Elemental analyses were performed by either Butterworth's Laboratories or the Open University Microanalytical Service. Silylated sulphonamides are referred to by their entry number in Table 2.

Silyl Sulphonates.—Trimethylsilyl trifluoromethanesulphonate, trimethylsilyl methanesulphonate, and trimethylsilyl benzenesulphonate were purchased from Fluka. Trimethylsilyl toluene-4-sulphonate was synthesised by refluxing toluene-4-sulphonic acid and *N*,*N*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) in acetonitrile for 1 h, and had $\nu_{max.}$ 855, 943, 1 180, 1 260, and 1 350 cm^{-1}; δ (^1H) 0.24 (9 H, s), 2.01 (3 H, s), 6.86—6.95 (2 H, d, *J* 8 Hz), and 7.79—7.88 (2 H, d, *J* 8 Hz). t-Butyldimethylsilyl toluene-4-sulphonate and t-butyldiphenylsilyl toluene-4-sulphonate were synthesised by stirring equimolar amounts of silver toluene-4-sulphonate and the corresponding chlorosilane in acetonitrile at room temperature. *t-Butyldimethylsilyl toluene-4-sulphonate* had δ (^1H) 0.26 (6H, s) 0.83 (9 H, s), 1.94 (3 H, s), 6.78—6.87 (2 H, d, *J* 8 Hz), and 7.76—7.84 (2 H, d, *J* 8 Hz) (Found: C, 54.3; H, 7.8. $C_{13}H_{22}O_3SSi$ requires C, 54.5; H, 7.7%). *t-Butyldiphenylsilyl toluene-4-sulphonate* had δ (^1H) 1.15 (9 H, s), 1.88 (3 H, s), and 7.16—7.19 and 7.21—7.84 (14 H, m) (Found: C, 67.3; H, 6.5. $C_{23}H_{26}O_3SSi$ requires C, 67.3; H, 6.4%).

Silylsulphoximides.—*N*-Trimethylsilyl-*S*,*S*-dimethylsulphoximide and *N*-trimethylsilyl-*S*-methyl-*S*-phenylsulph-

* We follow Johnson's usage of $B(X-Y)$ as the molar bond enthalpy and $D(X-Y)$ as the molar bond dissociation energy of the bond X–Y.[12]

† $B(Si-O)$ = 445 kJ mol^{-1} and $B(Si-N)$ = 335 kJ mol^{-1}, see ref. 4; $B(S^{VI}-O)$ = 249 kJ mol^{-1} and $B(S^{VI}=O)$ = 514 kJ mol^{-1}, see ref. 12.

oximide were synthesised by refluxing a solution of the corresponding sulphoximide [14,15] and BSTFA in acetonitrile for 1 h. *N-Trimethylsilyl-S,S-dimethylsulphoximide* had b.p. 32 °C at 0.005 mmHg, $\nu_{max.}$ 732, 753, 853, 932, 1 160, 1 304, and 2 960 cm^{-1}, δ (^1H) 0.13 (9 H, s) and 2.97 (6 H, s) (Found: C, 36.3; H, 9.0; N, 8.6; S, 19.6. $C_5H_{15}NOSSi$ requires C, 36.3; H, 9.1; N, 8.5; S, 19.4%). *N-Trimethylsilyl-S-methyl-S-phenylsulphoximide* had b.p. 80—82 °C at 0.009 mmHg, $\nu_{max.}$ 730, 839, 852, 910, 1 088, 1 154, 1 250, 1 293, 1 320, 1 447, 2 900, 2 960, and 3 070 cm^{-1}, δ (^1H) 0.11 (9 H, s), 2.98 (3 H, s), 7.46—7.70 (3 H, m), and 7.90—8.13 (2 H, m) (Found: C, 52.9; H, 7.5; N, 6.2. $C_{10}H_{17}NOSSi$ requires C, 52.8; H, 7.5; N, 6.2%).

Silylsulphonamides.—The silylated sulphonamides (1),[6] (3),[5] (4),[16] (6),[6] (7),[6] (11),[16] (14),[17] (16),[7] (17),[7] and (18)[18] were prepared by standard literature procedures. Silylsulphonamides (2), (5), (8), (9), and (15) were prepared by refluxing the corresponding sulphonamide with an excess of BSTFA in acetonitrile for 3 h. The silylsulphonamide (10) was prepared by treating the sulphonamide with butyl-lithium in hexane followed by an excess of chloromethylsilane and refluxing for 2 h. Compound (10) was isolated by decanting the supernatant liquid from lithium chloride followed by removal of the solvent. Recrystallisation from hexane afforded pure (10). Compounds (12) and (13) were prepared by stirring equimolar amounts of silver *N*-phenyltoluene-4-sulphonamide with the corresponding chlorosilane in acetonitrile at room temperature overnight. Physical data for the compounds are as follows: *compound* (2), b.p. 97—100 °C at 0.04 mmHg, $\nu_{max.}$ 683, 719, 755, 850, 889, 1 097, 1 158, 1 255, 1 328, 1 447, and 2 963 cm^{-1}, δ (^1H) 0.25 (9 H, s), 2.44 (3 H, s), 7.00—7.30 (3 H, m), and 7.70—8.05 (2 H, m) (Found: C, 49.1; H, 7.0; N, 5.8; S, 13.2. $C_{10}H_{17}NO_2SSi$ requires C, 49.4; H, 7.1, N, 5.7; S, 13.3%); *compound* (5), b.p. 108—112 °C at 1 mmHg, $\nu_{max.}$ 687, 755, 852, 1 141, 1 260, 1 335, 1 448, and 2 965 cm^{-1}, δ (^1H) 0.13 and 0.17 (9 H, s), 2.08 and 2.60 (3 H, s), 6.85—7.10 (3 H, m), and 7.52—7.70 (2 H, m) (Found: C, 48.9; H, 7.3; N, 10.5. $C_{11}H_{20}N_2O_2SSi$ requires C, 48.5; H, 7.4; N, 10.3%); *compound* (8), b.p. 103 °C at 0.07 mmHg, $\nu_{max.}$ 640, 671, 703, 760, 810, 850, 885, 1 095, 1 158, 1 185, 1 254, 1 328, 1 598, and 2 960 cm^{-1}, δ (^1H) 0.24 (9 H, s), 2.00 (3 H, s), 2.41 (3 H, s), 6.79—7.05 (2 H, d, *J* 7.5 Hz), and 7.60—7.85 (2 H, d, *J* 7.5 Hz) (Found: C, 51.1; H, 7.4; N, 5.6; S, 12.4. $C_{11}H_{19}NO_2SSi$ requires C, 51.3; H, 7.4; N, 5.4; S, 12.5%); *compound* (9), b.p. 135 °C at 0.025 mmHg, $\nu_{max.}$ 620, 652, 691, 762, 810, 849, 894, 918, 964, 1 091, 1 163, 1 215, 1 255, 1 338, 1 487, 1 598, and 2 970 cm^{-1}, δ (^1H) 0.28 (9 H, s), 1.85 (3 H, s), 6.56—6.82 (2 H, d, *J* 8.5 Hz), 6.93 (5 H, s), and 7.48—7.73 (2 H, d, *J* 8.5 Hz) (Found: C, 60.0; H, 6.3; N, 4.6. $C_{16}H_{21}NO_2SSi$ requires C, 60.1; H, 6.6; N, 4.4%); *compound* (10) had m.p. 102—104 °C, $\nu_{max.}$ 670, 812, 853, 900, 977, 1 090, 1 148, 1 255, 1 310, and 1 470 cm^{-1}, δ (^1H) 0.60 (9 H, s), 1.27 (9 H, s), 1.95 (3 H, s), 6.76—6.85 (2 H, d, *J* 8 Hz), and 7.67—7.86 (2 H, d, *J* 8 Hz) (Found: C, 55.9; H, 8.6; N, 4.9. $C_{14}H_{25}NO_2SSi$ requires C, 56.1; H, 8.4; N, 4.7%); *compound* (12) had $\nu_{max.}$ 662, 692, 820, 900, 965, 1 093, 1 165, 1 338, 1 493, and 1 602 cm^{-1}, δ (^1H) 0.19 (6 H, s), 1.19 (9 H, s), 1.92 (3 H, s), 6.69—6.78 (2 H, d, *J* 8 Hz), 6.96 (5 H, s), and 7.47—7.56 (2 H, d, *J* 8 Hz) (Found: C, 63.0; H, 7.2; N, 4.1. $C_{19}H_{27}NO_2SSi$ requires C, 63.1; H, 7.5; N, 3.9%); *compound* (13) had m.p. 157—158 °C, $\nu_{max.}$ 655, 690, 702, 816, 890, 908, 956, 1 095, 1 110, 1 165, 1 337, and 1 470 cm^{-1}, δ (^1H) 1.23 (9 H, s), 1.88 (3 H, s), 6.57—6.66 (2 H, d, *J* 8 Hz), 6.95—7.22 (13 H, m), and 7.76—7.80 (4 H, m) (Found: C, 72.1; H, 6.5; N, 2.9. $C_{29}H_{31}NO_2SSi$ requires C, 71.7; H, 6.4; N, 2.9%); *compound* (15) had b.p. 62 °C at 0.1 mmHg, ν_{max} 688, 835, 970, 1 140, 1 205, and 1 378 cm^{-1}, δ (^1H) 0.12 (9 H, s) and 6.99 (5 H, s) (Found: C, 39.7; H, 4.3. $C_{10}H_{14}F_3NO_2SSi$ requires C, 40.4; H, 4.7%).

Silylsulphonimidamides.—These compounds were prepared by refluxing the corresponding sulphonimidamides [9] with BSTFA in acetonitrile for 3 h. *N-Methyl-N-trimethylsilyl-octanesulphono-(N-methylimid)amide* had b.p. 119 °C at 0.6 mmHg, $\nu_{max.}$ 855, 1 105, 1 162, 1 257, 1 468, 2 810, 2 875, and 2 935 cm^{-1}, δ (^1H) 0.29 (9 H, s) 0.89 (3 H, t, *J* 5 Hz), 1.16 (12 H, m), 2.62 (6 H, s), and 2.83 (2 H, q, *J* 5 Hz) (Found: C, 53.1; H, 11.1; N, 9.6. $C_{13}H_{32}N_2OSSi$ requires C, 53.4; H, 11.0; N, 9.6%). *N-Methyl-N-trimethylsilylethanesulphono(bis-N-methylimid)amide* had b.p. 41—44 °C at 0.05 mmHg, $\nu_{max.}$ 765, 850, 918, 1 055, 1 104, 1 192, 1 232, 1 460, 2 795, 2 875, and 2 955 cm^{-1}, δ (^1H) 0.32 (9 H, s), 0.90 (3 H, t, *J* 7.5 Hz), 2.57 (9 H, s), and 2.71 (2 H, q, *J* 7.5 Hz) (Found: C, 43.6; H, 10.1; N, 19.1. $C_8H_{23}N_3SSi$ requires C, 43.4; H, 10.5; N, 19.0%). *N-Methyl-N-trimethylsilylbutanesulphono(bis-N-methylimid)amide* had b.p. 83 °C at 0.5 mmHg, $\nu_{max.}$ 850, 925, 1 104, 1 188, 1 224, 2 795, 2 880, and 2 970 cm^{-1}, δ (^1H) 0.38 (9 H, s) 0.85 (3 H, t, *J* 8 Hz), 1.09—1.60 (4 H, m), 2.65 (9 H, s), and 2.85 (2 H, q, *J* 8 Hz) (Found: C, 48.0; H, 10.9; N, 16.8. $C_{10}H_{27}N_3SSi$ requires C, 48.1; H, 10.9; N, 16.8%).

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References

1 A. R. Bassindale and A. G. Brook in 'Rearrangements in Ground and Excited States,' vol. 2, ed. P. de Mayo, Academic Press, New York, 1980, ch. 9.
2 A. R. Bassindale and T. B. Posner, *J. Organomet. Chem.*, 1976, **117**, 273, and references therein.
3 C. L. Hausman and C. H. Yoder, *J. Organomet. Chem.*, 1978, **161**, 313.
4 C. Glidewell, *J. Organomet. Chem.*, 1976, **108**, 335.
5 P. K. G. Hodgson, R. Katz, and G. Zon, *J. Organomet. Chem.*, 1976, **117**, C63.
6 L. Golebiowsky and Z. Lasocki, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1976, **24**, 439.
7 W. Maringgele and A. Meller, *Z. Naturforsch., Teil B*, 1979, **34**, 969.
8 A. Blaschette, D. Rinne, and H. C. Marsmann, *Z. Anorg. Allg. Chem.*, 1976, **420**, 55.
9 R. G. Laughlin, *J. Am. Chem. Soc.*, 1968, **90**, 2651.
10 J. Schraml and J. M. Bellama in 'Studies of Organic Compounds by Physical Methods,' ed. F. C. Nachod and J. J. Zuckerman, Academic Press, New York, 1976, ch. 4.
11 T. Jordan, H. W. Smith, L. L. Lohr, and W. N. Lipscomb, *J. Am. Chem. Soc.*, 1963, **85**, 846; T. S. Cameron, K. Prout, B. Denton, R. Spagna, and E. White, *J. Chem. Soc., Perkin Trans. 2*, 1975, 176; W. B. Jennings and R. Spratt, *Chem. Commun.*, 1970, 1418.
12 D. A. Johnson, 'Some Thermodynamic Aspects of Inorganic Chemistry,' 2nd edn., Cambridge University Press, Cambridge, 1982, ch. 7.
13 G. A. Morris and R. Freeman, *J. Am. Chem. Soc.*, 1979, **101**, 760.
14 C. R. Johnson and P. E. Rogers, *J. Org. Chem.*, 1973, **38**, 1793.
15 C. R. Johnson, M. Haake, and C. W. Schroek, *J. Am. Chem. Soc.*, 1970, **92**, 6594.
16 A. M. Pinchuk, L. P. Filanenko, and M. G. Suleimanova, *Zh. Obshch. Khim.*, 1972, **42**, 2116.
17 K. Barlos, G. Hubler, H. Noth, B. Wanninger, N. Wiberg, and P. Wrackmeyer, *J. Magn. Reson.*, 1978, **31**, 363.
18 B. E. Cooper and S. Westall, *J. Organomet. Chem.*, 1976, **118**, 135.

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