Volatile Compounds of the Hydrides of Silicon and Germanium with Elements of Groups V and VI

By John E. Drake and Chris Riddle
UNIVERSITY OF WINDSOR, ONTARIO, CANADA

1 Introduction

Discussion is centred around volatile, ternary hydrides represented by the general formula $M_xM'_yH_z$ (M = Si or Ge; M′ = an element of Group V or VI). Hydrides with organic groups attached to M or M′ will also be referred to when relevant to any discussion.

The development by Stock[1] of vacuum line techniques for handling air-sensitive compounds provided the initial impetus to study of the parent binary silanes and germanes. Subsequent progress has been covered by several texts, including those of MacDiarmid,[2] Stone,[3] Ebsworth,[4] Mackay,[5] Aylett,[6] and Glockling,[7] which have influenced our treatment of the ternary hydrides. Of outstanding interest in these hydrides is the possible participation of the vacant *d*-orbitals on silicon or germanium in additional bonding. In several molecules, filled orbitals on a Group V or VI atom are apparently of the correct symmetry and energy to allow π-interactions. Qualitatively, changes in bond-lengths, bond-angles and donor properties have been related to the degree of *p*-character in bonds and in turn to the extent of π-bonding. A comprehensive summary of the evidence on π-bonding has been presented by Ebsworth,[8] and his co-workers have recently reported some pertinent structural work.[9]

Dynamically too, as in the stabilisation of reaction intermediates, there appear to be good reasons for invoking *d*-orbital participation. The formation of additional σ-bonds to silicon increases its co-ordination number beyond four and possibly reduces the activation energy of an overall reaction process. Such mechanistic routes would not be available for carbon. A further feature that reflects differences in the chemistry of species containing Si—H and Ge—H rather than C—H is the change not only in the degree of polarity of the M—H

---

[1] A. Stock, 'Hydrides of Boron and Silicon', Cornell University Press, 1933.

[2] A. G. MacDiarmid, *Adv. Inorg. Chem. Radiochem.*, 1961, **3**, 207.

[3] F. G. A. Stone, 'Hydrogen Compounds of the Group IV Elements', Prentice Hall, 1962.

[4] E. A. V. Ebsworth, 'Volatile Silicon Compounds', Pergamon Press, 1963.

[5] K. M. Mackay, 'Hydrogen Compounds of the Metallic Elements', Spon, 1966.

[6] B. J. Aylett, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 249.

[7] F. Glockling, 'The Chemistry of Germanium', Academic Press, 1969.

[8] E. A. V. Ebsworth in 'Organometallic Compounds of the Group IV Elements', Dekker, 1968.

[9] (*a*) B. Beagley, A. G. Robiette, and G. M. Sheldrick, *Chem. Comm.*, 1967, 601; (*b*) D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, B. Beagley, and T. G. Hewitt, *J. Inorg. Nuclear Chem.*, 1969, **31**, 2351; (*c*) C. Glidewell, D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, S. Cradock, E. A. V. Ebsworth, and B. Beagley, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 417.

bond, but also in its direction. Thus, nucleophilic attack at silicon and germanium is expected to take place much more readily.

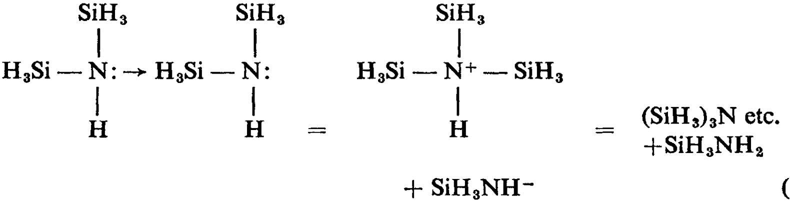
2 Hydrides Containing a Group V Element Bound to Silicon or Germanium

A. Silicon-Nitrogen Compounds.—Several such compounds are now known. Comparison of these with the analagous carbon compounds provides good evidence for additional bonding between Si and N.

Trisilylamine, $(SiH_3)_3N$, a volatile liquid that spontaneously ignites in air, was first prepared by Stock and Somieski from reaction of SiH_3Cl and NH_3.[1] They proposed the reaction was step-wise (1—3) although they were unable to isolate mono- and di-silylamine. Varying conditions give quantities of a polymeric solid and silane[10] proposedly by reaction (4).

$$\begin{aligned} 6SiH_3Cl + 12NH_3 &= 6SiH_3NH_2 + 6NH_4Cl && (1)\\ 6SiH_3NH_2 &= 3(SiH_3)_2NH + 3NH_3 && (2)\\ 3(SiH_3)_2NH &= 2(SiH_3)_3N + NH_3 && (3)\\ n(SiH_3)_2NH &= nSiH_4 + [SiH_2(NH)]_n && (4) \end{aligned}$$

Subsequently, it was suggested that the formation of $(SiH_3)_3N$ is indicative of the donor properties of disilylamine (5) and also that the instability of the intermediates results from ammonia-catalysed decomposition similar to the base-catalysed SiH redistribution observed with $(SiH_3)_2O$.[11] Substantial verification of the mechanism has followed the recent isolation of $(SiH_3)_2NH$ (Table 1).[12] This, although stable as a gas up to 150°, disproportionates (3) at 0° to trisilylamine and also yields the latter on reaction with SiH_3I. Its donor property is confirmed by the formation of a complex with Me_3B, and in the presence of NH_3 at 130° it indeed polymerises with evolution of SiH_4 (4).



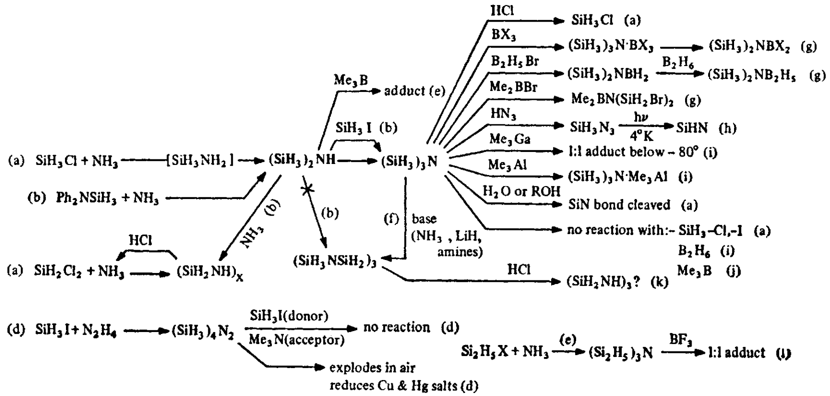
$$H_3Si-\overset{SiH_3}{\underset{H}{N:}} \rightarrow H_3Si-\overset{SiH_3}{\underset{H}{N:}} = H_3Si-\overset{SiH_3}{\underset{H}{N^+}}-SiH_3 + SiH_3NH^- = \begin{matrix}(SiH_3)_3N \text{ etc.}\\ +SiH_3NH_2\end{matrix} \qquad (5)$$

The structure of $(SiH_3)_3N$ is unique amongst the trisilyls and trigermyls (Table 2) in that the Si_3N skeleton is planar.[13] The simplest bonding 'picture' suggests sp^2-hybridisation of the nitrogen orbitals for σ-bonding to silicon. The remaining *p*-orbital interacts with the appropriate vacant *d*-orbitals on the silicon atoms to give $(p \rightarrow d)\pi$-bonding for which the planar structure allows optimum overlap (Figure). The 'short' Si—N bond and the 'high' force constant required to describe the skeletal vibrations provide physical support.[14] The

---

[10] A. B. Burg and E. S. Kulijan, *J. Amer. Chem. Soc.*, 1950, **72**, 3103.
[11] See Ref. 4; p. 110
[12] B. J. Aylett and M. J. Hakim, *J. Chem. Soc.* (*A*), 1969, 639.
[13] K. Hedburg, *J. Amer. Chem. Soc.*, 1955, **77**, 6491.
[14] See Ref. 4, p. 161; Ref. 8, p. 86.

Table 1 *Preparative and Reaction Routes for Silicon-Nitrogen Hydrides*



[a] A. Stock and C. Somieski, *Chem. Ber.*, 1921, **54**, 740. [b] Ref. 12. [c] B. J. Aylett and H. J. Hakim, *Inorg. Chem.*, 1966, **5**, 167. [d] Ref. 19. [e] Refs. 10, 17. [f] Ref. 16. [g] Refs. 10, 15*a*,*c*. [h] Ref. 21; J. F. Ogilvie and S. Cradock, *Chem Comm.*, 1966, 364. [i] Ref. 15*d*. [j] Ref. 15*b*. [k] Ref. 3, p. 29. [l] M. Abedini and A. G. MacDiarmid, *Inorg. Chem.*, 1963, **2**, 608.

Table 2 *Structural Data for Trisilyl- and Trigermyl-Hydrides*

Compound	r_{M-H}(Å)	$r_{M-M'}$(Å)	$M\widehat{M'}M$°	*Predicted* $r_{M-M'}$(Å)	*Ref.*
$(SiH_3)_3N$	1·54 ±0·05	1·738±0·02	119·6 ±1	1·77	a
$(SiH_3)_3P$	1·50 ±0·02	2·247±0·005	95 ±2	2·25	b
$(SiH_3)_3As$	1·48 ±0·02	2·352±0·005	91·5 ±2	2·36	b
$(SiH_3)_3Sb$	1·394±0·027	2·557±0·004	88·6 ±0·2	2·57	c
$(GeH_3)_3P$	1·510±0·008	2·308±0·003	95·39±0·05	2·31	c

$(GeH_3)_3N$, $(GeH_3)_3As$, and $(GeH_3)_3Sb$ all believed to have non-planar M_3M' skeletons from vibrational spectra.

(a) Ref. 13. (b) Ref. 9*a*. (c) Ref. 9*b*.

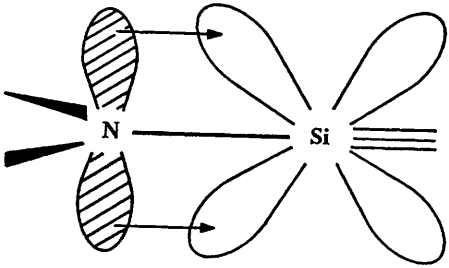


Figure *The* (p→d)π*-bond in* $(SiH_3)N$. *Shading indicates filled nitrogen* p*-orbital.*

effective donation of electrons from N to Si required by the π-bonding would be expected to decrease the 'availability' of the lone-pair on N and hence reduce its donor properties. Its reactions towards boron Lewis acids are less extensive than those of Me_3N so that no adduct is formed by $(SiH_3)_3N$ with B_2H_6 or Me_3B and only weak adducts with BF_3 and BCl_3.[10,15]

A re-investigation[16] of the $SiH_3Cl + NH_3$ reaction identified, among the expected products, NN′N″ trisilylcyclotrisilazane, $(SiH_3NSiH_2)_3$, which may also be formed in the liquid-phase reaction between $(SiH_3)_3N$ and NH_3. Deuterium labelling established that there is no protonic exchange between ammonia and trisilylamine and that the reaction is probably intermolecular. The kinetics indicate the formation of a weak complex with an ammonia attached to each silyl group, $N[(SiH_3) . NH_3]_3$, so that $(SiH_3)_3N$ can also act as a Lewis acid. This mechanism requires 5-co-ordinate silicon, possibly through *d*-orbital participation, and hence is not found in the methylamines.

The reaction of ammonia with disilanyl halides gives condensation to tris-(disilanyl)amine, $(Si_2H_5)_3N$,[17] while with SiH_2Cl_2, $SiHCl_3$, and $SiCl_4$ polymeric species are formed.[1] A recent review of silicon-nitrogen polymers[18] includes work on systems such as $(SiN_2H_2)_n$. Hydrazine reacts with SiH_3I to give $(SiH_3)_4N_2$ [19] which apparently does not show typical acid or base properties. An interpretation of its vibrational spectrum[20] supports possible N—Si $(p \rightarrow d)\pi$-bonding. Whereas the non-linear skeleton claimed for silyl azide, SiH_3N_3,[21] suggests that any π-bonding is not strongly stereochemically significant. By contrast, SiH_3NCO [22] and SiH_3NCS [23] are linear but it seems likely that complete methyl-substitution at silicon (*i.e.*, Me_3SiNCO and Me_3SiNCS) leads to a bending of the Si—N—C angle[24] as is found with Me_3SiN_3.[25] These results suggest that the differences in energy between linear and bent heavy-atom skeletons are small, so that comparatively minor electronic changes may have significant effects on bond-angles.

B. Germanium-Nitrogen Compounds.—These are less extensive than those of silicon so that the very unstable trigermylamine $(GeH_3)_3N$, has only recently been prepared by a carefully controlled reaction between GeH_3Cl and NH_3.[26] In contrast to $(SiH_3)_3N$, the preliminary i.r. spectrum suggests that $(p \rightarrow d)\pi$-

---

[15] (*a*) J. M. Gamboa, *Anales de Quim.*, 1950, **72**, 3103; (*b*) S. Sujishi and S. Witz, *J. Amer. Chem. Soc.*, 1954, **76**, 4631; (*c*) S. Sujishi and S. Witz, *J. Amer. Chem. Soc.*, 1957, **79**, 2447; (*d*) H. M. Manasevit, *U.S. Dept. Com.*, Office Tech. Serv., P.B. Report 143, 572, 1959, 1.

[16] R. Schaeffer and R. L. Wells, *J. Amer. Chem. Soc.*, 1966, **88**, 37.

[17] L. G. L. Ward and A. G. MacDiarmid, *J. Inorg. Nuclear Chem.*, 1961, **21**, 287.

[18] B. J. Aylett, *Organometallic Chem. Rev.*, 1968, **3**, 151.

[19] B. J. Aylett, *J. Inorg. Nuclear Chem.*, 1956, **2**, 325.

[20] B. J. Aylett, J. R. Hall, D. C. McKean, R. Taylor, and L. A. Woodward, *Spectrochim. Acta*, 1960, **16**, 747.

[21] E. A. V. Ebsworth and M. J. Mays, *J. Chem. Soc.*, 1964, 3450.

[22] M. C. L. Jerry, J. C. Thompson, and T. M. Sugden, *Nature*, 1966, **211**, 846.

[23] D. R. Jenkins, R. Kewley, and T. M. Sugden, *Trans. Faraday Soc.*, 1962, **58**, 1284.

[24] K. Kimura, S. Katada, and S. H. Bauer, *J. Amer. Chem. Soc.*, 1966, **88**, 416.

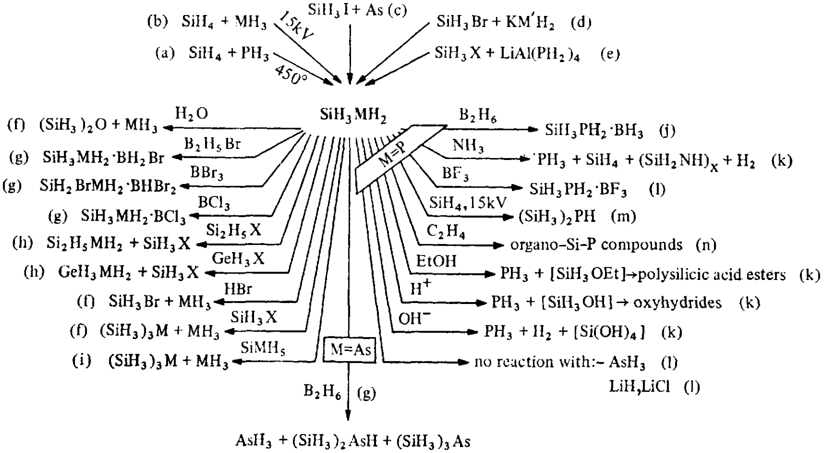
[25] J. S. Thayer and R. West, *Inorg. Chem.*, 1964, **3**, 889.

[26] D. W. H. Rankin, *Chem. Comm.*, 1969, 194; *J. Chem. Soc.* (*A*), 1969, 1926.

bonding, if present, does not stabilise a planar structure although clarification should come with electron diffraction data. The vibrational spectrum of the azide, prepared from $GeH_3F + Me_3SiN_3$, indicates a non-linear GeH_3N_3 skeleton[27] as does that of GeH_3NCO.[28] The only other volatile Ge—N hydrides reported are GeH_3NH_2 and $GeH_2(NH_2)_2$ which were mass spectroscopically detected among the products from the hydrolysis of CaGeN alloys,[29] and $Ge(NH_2)_4$ which has been proposed as an unstable intermediate that polymerises to $Ge(NH)_2$.[30]

C. Phosphorus, Arsenic, and Antimony Compounds.—The first primary species, SiH_3PH_2, was synthesised in 1953 by the pyrolysis of SiH_4 and PH_3.[31] Further interest was stimulated by the introduction in 1961 of electrical discharge techniques as a synthetic route in this area.[32] Of the preparative routes now available (Tables 3—7) for the phosphines and arsines, 'exchange reactions' (6) have been used for the preparation of specifically deuteriated species.[33]

Table 3 *Preparative and Reaction Routes for Monosilyl-phosphine and -arsine*



[a] Ref. 31. [b] Ref. 32. [c] B. J. Aylett, Ph.D. Thesis, Cambridge University, 1954. [d] C. Glidewell and G. M. Sheldrick, *J. Chem. Soc.* (*A*), 1969, 350. [e] A. D. Norman, *Chem. Comm.*, 1968, 812. [f] Ref. 51. [g] Ref. 52*a,b*. [h] J. E. Drake, N. Goddard, and J. Simpson, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 361. [i] Ref. 50. [j] Refs. 52*a*, 54; G. E. Bagley, *Dissertation Abstr.*, 1959, **20**, 66. [k] G. Fritz, *Angew. Chem.*, 1966, **78**, 80. [l] Ref. 52*c*. [m] S. D. Gokhale and W. L. Jolly, *Inorg. Chem.*, 1965, **4**, 596. [n] G. Fritz, *Z. Anorg. Chem.*, 1955, **280**, 332.

---

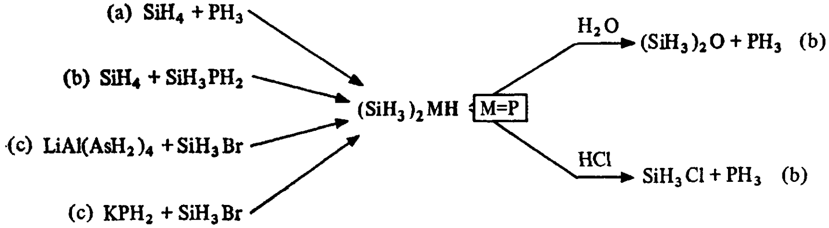
[27] S. Cradock and E. A. V. Ebsworth, *J. Chem. Soc.* (*A*), 1968, 1420.
[28] J. E. Griffiths and A. L. Beach, *Chem. Comm.*, 1965, 437.
[29] P. Royen and C. Rocktaschel, *Z. anorg. Chem.*, 1966, **346**, 290.
[30] D. Rustad and W. L. Jolly, *Inorg. Chem.*, 1967, **6**, 1986.
[31] G. Fritz, *Z. Naturforsch.*, 1953, **8B**, 776.
[32] J. E. Drake and W. L. Jolly, *Chem. and Ind.*, 1961, 1470.
[33] (*a*) J. E. Drake and C. Riddle, *J. Chem. Soc.* (*A*), 1968, 1675; (*b*) J. E. Drake and C. Riddle, *J. Chem. Soc.* (*A*), 1968, 2452.

$$SiH_3PH_2 + GeD_3Cl = GeD_3PH_2 + SiH_3Cl \qquad (6)$$

Three antimony compounds are known: SiH_3SbH_2, formed in the reaction of SiH_3Br with $KSbH_2$[34] which, unlike the corresponding reactions with KPH_2 and $KAsH_2$ will not give the trisilyl derivative; $(SiH_3)_3Sb$, formed when silyl halides react with Sb [35] or Li_3Sb;[34] and $(GeH_3)_3Sb$, formed by exchange between GeH_3Br and $(SiH_3)_3Sb$.[36]

Detailed vibrational spectra studies have been reported for the primary hydrides $MH_3M'H_2$ (M = Si or Ge; M′ = P or As)[37,38] which conform to C_s symmetry, like $MeNH_2$ and $MePH_2$. In early work on the spectra of $(SiH_3)_3P$ and $(SiH_3)_3As$ it was suggested,[39] from the activity and relative intensities of the skeletal modes, that the heavy-atom skeleton was planar. Subsequently, electron diffraction work showed that it was in fact pyramidal.[9] It has been pointed out that structural conclusions based on the relative intensities of bands also proved incorrect for $(SiH_3)_2O$.[40]

Table 4 *Preparative and Reaction Routes for Disilyl-phosphine and -arsine*



[a] S. D. Gokhale and W. L. Jolly, *Inorg. Chem.*, 1964, **3**, 1141. [b] S. D. Gokhale and W. L. Jolly, *Inorg. Chem.*, 1965, **4**, 596. [c] C. Glidewell and G. M. Sheldrick, *J. Chem. Soc. (A)*, 1969, 350.

The reactions of $(SiH_3)_3P$ (Table 5) suggest it is a weaker nucleophile than Me_3P which may be indicative of some delocalisation of the phosphorus lone-pair into silicon *d*-orbitals. The low Si—P—Si angle of 96·5° has led to speculation that this additional bonding is not through $(p \rightarrow d)\pi$-bonds, but through $(s \rightarrow d)\sigma$-bonds in which the essentially *s*-character lone-pair of P interacts with d_{z^2}-orbitals of Si (where the z axis is along the P—Si bond).[41] Reference to additional bonding in discussing the bond-angles, bond-strengths,

---

[34] E. Amberger, H. D. Boeters, and M. R. Kula, *Angew. Chem.*, 1964, **76**, 573.

[35] B. J. Aylett, H. J. Emeléus, and A. G. Maddock, *Research*, 1953, **6**, 30 S.

[36] E. A. V. Ebsworth, D. W. H. Rankin, and G. M. Sheldrick, *J. Chem. Soc. (A)*, 1968, 2828.

[37] J. E. Drake and C. Riddle, *Spectrochim. Acta*, in press.

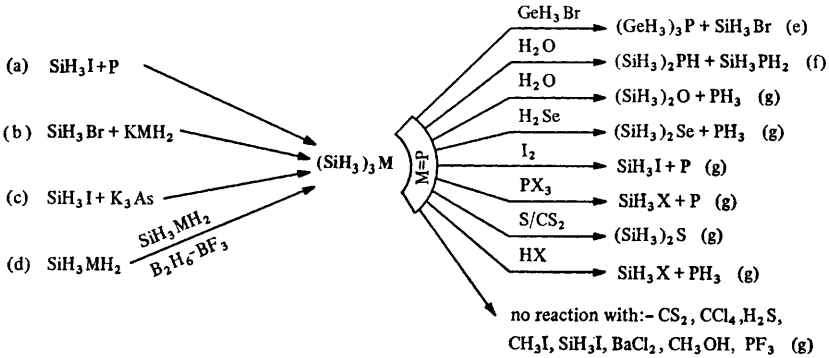
[38] K. M. Mackay, K. J. Sutton, S. R. Stobart, J. E. Drake, and C. Riddle, *Spectrochim. Acta*, 1969, **25A**, 925; 1969, **25A**, 941.

[39] G. Davidson, L. A. Woodward, E. A. V. Ebsworth, and G. M. Sheldrick, *Spectrochim. Acta*, 1966, **22**, 67; 1967, **23A**, 2609.

[40] D. C. McKean, *Spectrochim. Acta*, 1968, **24A**, 1253.

[41] E. A. V. Ebsworth, C. Glidewell, and G. M. Sheldrick, *J. Chem. Soc. (A)*, 1969, 352.

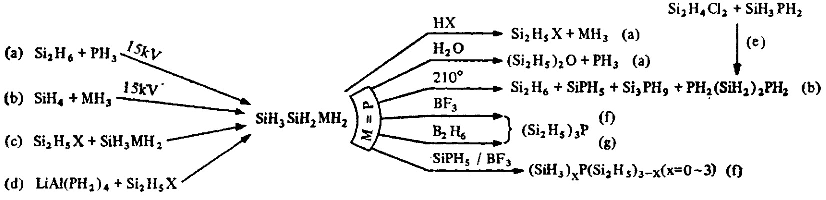
Table 5 *Preparative and Reaction Routes for Trisilyl-phosphine and -arsine*



[a] Ref. 35. [b] E. Amberger and H. D. Boeters, *Angew. Chem.*, 1962, **74**, 32 and 293. [c] Ref. 2, p. 247. [d] Refs. 50, 52. [e] S. Cradock, G. Davidson, E. A. V. Ebsworth, and L. A. Woodward, *Chem. Comm.*, 1965, 515. [f] W. L. Jolly and A. D. Norman, *Preparative Inorganic Reactions*, 1968, **4**, 35. [g] Ref. 41.

and reactions of these mixed hydrides may be misleading. The minimum H—H distances for hydrogen atoms not attached to the same atom, in $(SiH_3)_3P$ and $(SiH_3)_3As$ are both essentially the same, being *ca.* twice the van der Waal's radius of hydrogen. This may be an important controlling factor on the Si—M—Si angles, so that it is unnecessary to search for extraordinary features in the bonding unless deviations from this distance are unusually large. This is the case for $(SiH_3)_3N$ in which the minimum H—H distance is much larger suggesting that here additional bonding is important, particularly since the corresponding distances are smaller in Me_3N and Me_3P. Also, as is shown (Table 2), it is only for $(SiH_3)_3N$ that the M—M′ bond is significantly shorter than the predicted length, a further indication that additional bonding is not important in the related species.

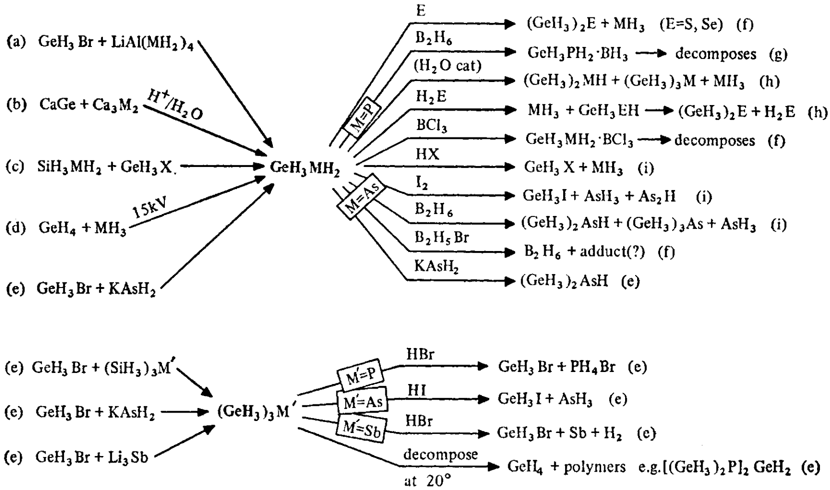
Table 6 *Preparative and Reaction Routes for Disilanyl-phosphine and -arsine*



[a] S. D. Gokhale and W. L. Jolly, *Inorg. Chem.*, 1965, **4**, 596. [b] Ref. 32; S. D. Gokhale and W. L. Jolly, *Inorg. Chem.*, 1964, **3**, 1141. [c] J. E. Drake, N. Goddard, and J. Simpson, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 361. [d] A. D. Norman, *Chem. Comm.*, 1968, 812. [e] Ref. 46. [f] W. L. Jolly and A. D. Norman, *Preparative Inorganic Reactions*, 1968, **4**, 32. [g] Ref. 45.

The ^1H n.m.r. spectra of the ternary hydrides, unlike those of most binary hydrides, are often first order. In addition, the variations in chemical shift are fairly predictable, so that species may be readily characterised. Reactions can be followed over a wide temperature range under non-destructive conditions that require only small samples. The values of the coupling constants for directly bonded nuclei (*e.g.*, $J_{^{29}SiH}$ and $J_{^{31}PH}$)[42,43] have been related, as with $J_{^{13}CH}$[44] to the degree of *s*-character in the bonding orbitals and in turn to the shape of the molecule. The spectra of several silyl- and germyl-phosphines show that the value of the direct coupling constant J_{PH}, varies only slightly from that in PH_3. Thus, no marked changes in '*s*' character and hence in the shapes of the basic skeletons are suggested for SiH_3—,[45] GeH_3—,[33] GeH_2Cl—,[46] or Si_2H_5—[45] substitution in PH_3, a further indication that additional bonding need not be involved for these molecules. In a given series, the chemical shift

Table 7 *Preparative and Reaction Routes for Germyl-phosphines, -arsines, and -stibines*



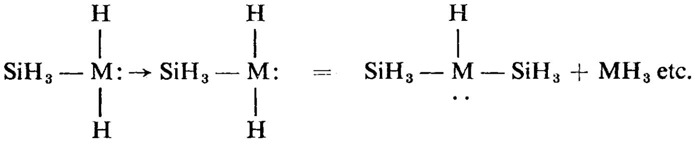
M = P, As, M′ = P, As, Sb.
[a] D. C. Wingleth and A. D. Norman, *Chem. Comm.*, 1967, 1218; Ref. 49. [b] P. Royen, C. Rocktaschel, and W. Mosch, *Angew. Chem.*, 1964, **76**, 860. [c] J. E. Drake, N. Goddard, and J. Simpson, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 361. [d] Ref. 32. [e] Refs. 36; S. Cradock, E. A. V. Ebsworth, G. Davidson, and L. A. Woodward, *J. Chem. Soc.* (*A*), 1967, 1229. [f] Ref. 74. [g] Ref. 33*a*. [h] Refs. 49, 73. [i] Ref. 33*b*.

---

[42] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy', Pergamon Press, 1966, 1052.
[43] G. Mavel, *Progr. N.M.R. Spectroscopy*, 1966, **1**, 251.
[44] See Ref. 42; p. 191.
[45] J. E. Drake and N. Goddard, *J. Chem. Soc.* (*A*), 1969, 662.
[46] J. E. Drake, N. Goddard, and C. Riddle, *J. Chem. Soc.* (*A*), 1969, 2074.

of a MH_3—M′ group (M = Si or Ge; M′ = Group V element) is progressively to higher field as the electronegativity of the M′ element is decreased. Thus, for the series $(SiH_3)_3$—N,[47] —P, —As, —Sb [48] the chemical shifts are 5·56, 6·08, 6·20, and 6·37 τ respectively and for $(GeH_3)_3$—N,[26] —P, —As,[49] —Sb [36] are 5·09, 5·96, 6·02, and 6·39 τ. The same effect is found, where the chemical shifts are known, for $(MH_3)_2M'H$ and $MH_3M'H_2$ species.[49]

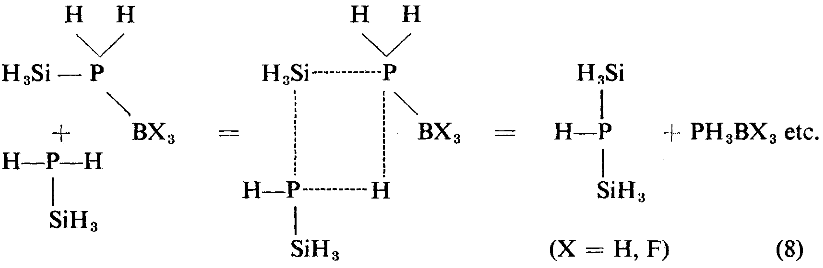
The tendency of the primary species to condense to the tertiary decreases below the first row element. Whereas SiH_3NH_2 is unknown, SiH_3PH_2, SiH_3AsH_2, and SiH_3SbH_2 disproportionate very slowly.[34,50] MacDiarmid has suggested that this is associated with a decrease in the positive charge induced at silicon so that formation of the internuclear bond (7) is more difficult.[2]



$$SiH_3-\underset{H}{\overset{H}{M}}{:}\rightarrow SiH_3-\underset{H}{\overset{H}{M}}{:} \;=\; SiH_3-\underset{\cdot\cdot}{\overset{H}{M}}-SiH_3 + MH_3 \text{ etc.} \qquad (7)$$

Equally well, the ‘availability’ of the lone-pair of P or As could be less than that of N. The trend exists for the germyl analogues but is less marked. GeH_3PH_2 condenses readily and the rates of disproportionation of both it and GeH_3AsH_2 are markedly increased by the introduction of water.[49] The silyl analogues react with water immediately giving $(SiH_3)_2O$ and MH_3.[51]

Condensation of the silyl species, as well as the germyl, is facilitated by the introduction of diborane or boron trifluoride in the liquid phase.[33,52] Deuteriation studies of the SiH_3PH_2/BF_3 reaction indicate that entire SiH_3 groups are transferred. A four-centre mechanism (8) is possible in which



(X = H, F) (8)

the activation energy of disproportionation is lowered by adduct formation.[53]

---

[47] G. Rocktaschel, E. A. V. Ebsworth, D. W. H. Rankin, and J. C. Thompson, *Z. Naturforsch.*, 1968, **23B**, 598.

[48] E. A. V. Ebsworth and G. M. Sheldrick, *Trans. Faraday Soc.*, 1966, **62**, 3282.

[49] J. E. Drake and C. Riddle, *J. Chem. Soc.* (*A*), 1968, 2709.

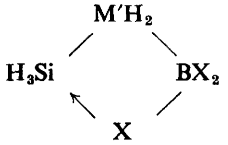
[50] C. Riddle and J. Simpson, unpublished observations.

[51] J. Simpson, Ph.D. Thesis, Southampton Univ., 1967.

[52] (*a*) J. E. Drake and J. Simpson, *Inorg. Chem.*, 1967, **6**, 1984; (*b*) J. E. Drake and J. Simpson, *J. Chem. Soc.* (*A*), 1968, 1039; (*c*) C. R. Russ, Ph.D. Thesis, University of Pennsylvania, 1965; (*d*) C. R. Russ and A. G. MacDiarmid, *Angew. Chem.*, 1966, **78**, 391.

[53] A. D. Norman and W. L. Jolly, private communication, 1969.

With the arsines there is no direct evidence for adduct formation but the condensations are indeed step-wise and disilyl- and digermyl-arsines can be isolated, so (8) is probably appropriate here.[52b,33b] B_2H_6 reacts with the stoicheiometric amounts of phosphines to give the triple mixed hydrides, $MH_3PH_2BH_3$ ($M = Si$ or Ge) as is confirmed by their ^1H n.m.r. spectra.[33a,54] With excess SiH_3PH_2, disproportionation occurs to $(SiH_3)_3P$ as expected (8) but neat $SiH_3PH_2BH_3$ when sealed under pressure decomposes after about 12 hr. to give silane and an intractable polymer. The adducts formed by SiH_3PH_2 and SiH_3AsH_2 with boron halides also decompose to give a volatile silane and polymer possibly through the formation of an intramolecular transition state (9).[52,53] There is an interesting gradation in that, under similar



$$= SiH_3X + 1/n(M'H_2BX_2)_n \qquad (9)$$

$$(M = P \text{ or } As;\ X = H, F, Cl, \text{ or } Br)$$

conditions, BF_3 also encourages the condensation process (8); BCl_3 gives SiH_3Cl quantitatively; and BBr_3 gives more SiH_2Br_2 than SiH_3Br possibly through the intermediate formation of $SiH_2BrPH_2BH_3$. Recently it has been shown that species MH_2XPH_2 can be formed during exchange processes so that SiH_3PH_2 reacts with GeH_2X_2 to form GeH_2XPH_2 ($X = Cl$, Br).[46] Thus there is experimental evidence in support of the intermediates.

That over half the compounds in this section were first reported as recently as 1968 means that much is still to be learnt of their physical and chemical properties. With new preparative routes being developed, the opportunities to examine them in greater depth should emerge.

3 Hydrides Containing a Group VI Element Bound to Silicon or Germanium

A. Silicon Compounds.—The extensive chemistry of silicon bound to oxygen is dominated by the tendency to form linkages involving alternate Si and O atoms. The simple volatile 'parents' of these polymeric species were discovered by Stock, who coined the name *siloxanes*.[1] He isolated $(SiH_3)_2O$ and $(Si_2H_5)_2O$ while subsequently the condensation reactions of the former have led to the preparation of $(SiH_3O)_2SiH_2$ and $(SiH_3O)_3SiH$.[16]

Despite extensive work on organo derivatives, no silanol with hydrogen bound to the silicon atom has yet been characterised. SiH_3OH, $SiH_2(OH)_2$, and $SiH(OH)_3$ have never been isolated and though hydrolysis of SiH_2X_2 ($X = Cl$ or Br) may proceed *via* $SiH_2(OH)_2$ this then forms polymeric $(H_2SiO)_n$.[1] Similarly, $Si_2H_4X_2$ hydrolyses to high molecular weight polymers although Si_2H_5X gives $(Si_2H_5)_2O$ possibly *via* Si_2H_5OH.[1] The hydrolysis of most SiH_3-containing species usually results in the formation of $(SiH_3)_2O$

---

[54] J. E. Drake and J. Simpson, *Chem. Comm.*, 1967, 249.

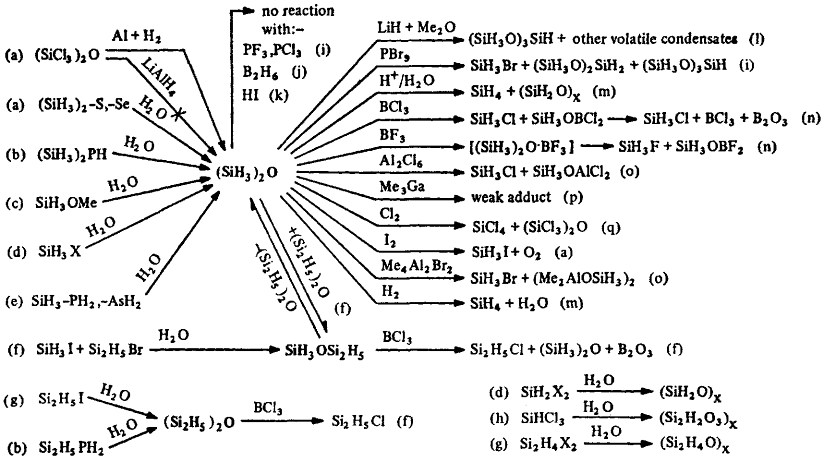
possibly *via* SiH_3OH. With SiH_3X the yield is only *ca.* 40% suggesting that hydrogen halides may catalyse an alternative decomposition route of SiH_3OH (11) reducing the amount of disiloxane formed (10).[55] The mode of condensation proposed for the silylamines (7) is equally applicable to this disproportionation (10).

$$SiH_3X \xrightarrow{H_2O} [SiH_3OH] \longrightarrow (SiH_3)_2O + H_2O \qquad (10)$$

$$\qquad\qquad\qquad \llcorner\!\!\longrightarrow SiH_4 + (SiH_2O)_n \qquad (11)$$

Disiloxane is quite thermally stable and, in contrast to most SiH_3-containing species, is stable in air unless ignited.[1] $(Si_2H_5)_2O$ more typically is spontaneously inflammable.[56] In general, Lewis acids cleave the Si—O bond (*e.g.* Al_2Cl_6,[57] Table 8) while Lewis bases (*e.g.* NH_3 [58]) encourage condensation.

Table 8 *Preparative and Reaction Routes for Silicon-Oxygen Hydrides*



[(a)] Ref. 71. [(b)] S. D. Gokhale and W. L. Jolly, *Inorg. Chem.*, 1965, **4**, 596. [(c)] B. Sternbach and A. G. MacDiarmid, *J. Amer. Chem. Soc.*, 1961, **83**, 3384. [(d)] A. Stock and C. Somieski, *Chem. Ber.*, 1917, **50**, 1739. [(e)] Ref. 51. [(f)] C. H. Van Dyke and A. G. MacDiarmid, *Inorg. Chem.*, 1964, **3**, 747. [(g)] A. Stock and C. Somieski, *Chem. Ber.*, 1920, **53**, 759. [(h)] A. Stock and F. Zeidler, *Chem. Ber.*, 1923, **56B**, 986. [(i)] Ref. 59. [(j)] Ref. 60*a*. [(k)] H. J. Emeléus and M. Onyszchuk, *J. Chem. Soc.*, 1958, 604. [(l)] Ref. 58. [(m)] A. Stock and C. Somieski, *Chem. Ber.*, 1923, **56B**, 132. [(n)] M. Onyszchuk, *Canad. J. Chem.*, 1961, **39**, 808. [(o)] Ref. 57. [(p)] Ref. 15*c*. [(q)] A. Stock, C. Somieski, and R. Wintgen, *Chem. Ber.*, 1917, **50**, 1754.

---

[55] See Ref. 4, p. 127.

[56] L. G. L. Ward and A. G. MacDiarmid, *J. Amer. Chem. Soc.*, 1960, **82**, 2151.

[57] W. A. Kriner, A. G. MacDiarmid, and E. C. Evers, *J. Amer. Chem. Soc.*, 1958, **80**, 1546.

[58] T. Yoshioka and A. G. MacDiarmid, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 69.

Van Dyke has shown[59] that the amphoteric phosphorus(III) halides cleave SiH_3OMe at low temperature but not $(SiH_3)_2O$, indicating a reduction in Lewis basicity with additional silyl substitution as is also found for the series Me_3N through to $(SiH_3)_3N$.[15b] With B_2H_6 [60] and Me_3Ga [15d] as reference acids it is clear that $(SiH_3)_2O$ is a weaker nucleophile than Me_2O but stronger than $(SiH_3)_3N$. This is expected since the result of several investigations indicate that the skeletal Si—O—Si angle is *ca.* 144°,[61] (Table 9). A marked degree of $(p \rightarrow d)\pi$-bonding is implied by such a wide angle although it would need to be 180° to make the lone-pairs as 'unavailable' as in trisilylamine.

Table 9 *Molecular Parameters for* $(MH_3)_2M'$ ($M{=}Si, Ge$; $M'{=}O, S, Se$)

Molecule	$r_{M-M'}$(Å)	r_{M-H} (Å)	$\widehat{MM'M}$ °	*Predicted* $r_{M-M'}$(Å)	*Ref.*
$(SiH_3)_2O$	1·634	1·486	144·1	1·75	a
$(SiH_3)_2S$	2·136	1·494	97·4	2·14	b
$(SiH_3)_2Se$	2·273	1·516	96·6	2·28	c
$(GeH_3)_2O$	1·774	1·53	125·6	1·83	d
$(GeH_3)_2S$	2·205	1·53	99·1	2·21	d

(a) Ref. 61. (b) Ref. 62. (c) Ref. 63. (d) Ref. 9*c*.

By contrast, the skeletal angles in $(SiH_3)_2S$ [62] and $(SiH_3)_2Se$ [63] are close to 90°, and as with $(SiH_3)_3P$ and $(SiH_3)_3As$,[9a] the H—H distance for hydrogen atoms on adjacent silicons is *ca.* 2 Å. Despite surface tension measurements which were interpreted as indicating a large amount of π-bond character in the Si—S linkages,[64] the Si—S bond-length is as expected for a single bond.[62] Long-range H—H coupling is observed in the ^1H n.m.r. spectrum of $(SiH_3)_2S$.[65] Since such coupling is not observed with $(SiH_3)_2O$, it has been suggested that it may be associated with *d*-orbitals on sulphur rather than with $(p \rightarrow d)\pi$-bonding. Support comes from a recent survey on the absolute values of J_{HH} coupling which increases along the series of C—S—M (M, C→ Si→ Ge) linkages (Table 10).[66] The trend in chemical shifts, as with the group V ternary hydrides, is for the MH_3 resonance to shift progressively to higher field when the electronegativity of the M′ atom is decreased. Thus for the series

---

[59] C. H. Van Dyke, *J. Inorg. Nuclear Chem.*, 1968, **30**, 81.

[60] (*a*) S. Sujishi, E. L. Gasner, and A. D. Payton, *133rd Meeting Amer. Chem. Soc.*, 1958, Communication 52Q.; (*b*) S. Sujishi, E. L. Gasner, and A. D. Payton, Office of Ordnance Research, Project No. TB2-0001 (817).

[61] A. Almenningen, O. Bastiansen, V. Ewing, K. Hedberg, and M. Traetteberg, *Acta Chem. Scand.*, 1963, **17**, 2455.

[62] A. Almenningen, K. Hedberg, and R. Seip, *Acta. Chem. Scand.*, 1963, **17**, 2264.

[63] A. Almenningen, L. Fernholt, and H. M. Seip, *Acta Chem. Scand.*, 1963, **22**, 51.

[64] A. G. MacDiarmid, *J. Inorg. Nuclear Chem.*, 1956, **2**, 323.

[65] E. A. V. Ebsworth and J. J. Turner, *J. Chem. Phys.*, 1962, **36**, 2628.

[66] J. T. Wang and C. H. Van Dyke, *Chem. Comm.*, 1967, 612.

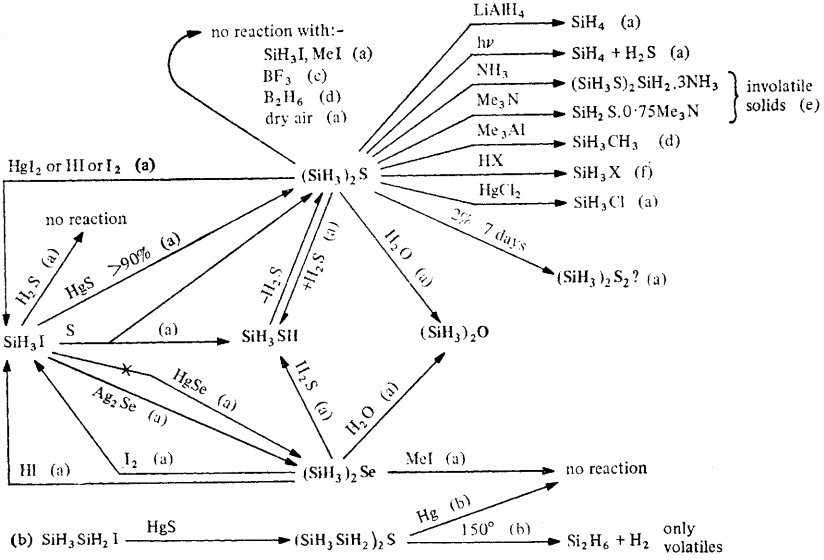
$(SiH_3)_2$—O,[67] —S, —Se, and —Te[68] the chemical shifts are 5·39, 5·65, 5·91, and 6·33 τ respectively. The same trend is found for $(GeH_3)_2M'$, $SiH_3M'H$ and $GeH_3M'H$.[68]

Table 10 *Long-Range Coupling in some Sulphide Systems*[66]

J_{HH} (Hz)	0·30	0·45	0·70	0·60	not observed
Compound	Me_2S	SiH_3Me	$(SiH_3)_2S$	GeH_3SMe	$(GeH_3)_2S$

Studies on the Si—S, —Se, and —Te systems have centred around the nature of the heavy-atom bonding. The syntheses (Table 11) are mainly from earlier preliminary work although, like the Group V mixed hydrides, there is a current revival of interest. Recently, $(SiH_3)_2Te$ was prepared from SiH_3I and Li_2Te[69] while $(SiH_3)_2S$ and $(SiH_3)_2Se$ were prepared from the cleavage of the Si—P bond in $(SiH_3)_3P$ by S and H_2Se respectively (Table 5).[41] There is apparently no direct action of silyl halides with H_2S although Stock reported a volatile product, possibly SiH_3SH, when SiH_3Cl reacted with H_2S at 150° for several

Table 11 *Preparative and Reaction Routes for Silicon-Sulphur and Silicon-Selenium Hydrides*



[(a)] Refs. 35, 71. [(b)] Ref. 17. [(c)] M. Onyszchuk, *Canad. J. Chem.*, 1961, **39**, 808. [(d)] Ref. 60*a*. [(e)] A. G. MacDiarmid, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1534. [(f)] Ref. 4.

---

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

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

[69] H. Burger and U. Goetze, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 549.

days in the presence of Al_2Cl_6.[70] A conversion series[2] which indicates which silyl compound can be converted specifically into another by means of a silver or heavy-metal salt is partially shown (12). The hydrolysis of $(SiH_3)_2S$ gives $(SiH_3)_2O$ in over 90% yield[71] which is twice as good as the yield from the

$$SiH_3I \rightarrow (SiH_3)_2Se \rightarrow (SiH_3)_2S \rightarrow SiH_3Br \rightarrow SiH_3Cl \rightarrow (SiH_3)_2O \qquad (12)$$

hydrolysis of the halides discussed previously. This suggests either that the former reaction is a simple exchange process not involving the intermediate formation of silanol (10), or that H_2S is not acting as a catalyst for the polymer formation (11).[55] Several reactions of $(SiH_3)_2S$ indicate that it is a weak electron donor, weaker even than $(SiH_3)_2O$ with BF_3 as reference acid.[72] It is concluded however that the Si—S bond is an essentially single bond of mainly *p*-character.

B. Germanium Compounds.—The introduction of two preparative routes making use of (i) reactions with H_2S, S, H_2Se, and Se [49,73,74] and (ii) exchange reactions[75] has enlivened interest in the germanium-Group VI mixed hydrides. The former reagents react with either germyl-phosphine or -arsine to give $(GeH_3)_2S$ and $(GeH_3)_2Se$ *via* GeH_3SH and GeH_3SeH as is proved by ^1H n.m.r. spectroscopy. The exchange reactions of $(SiH_3)_2Se$ and $(SiH_3)_2Te$ with germyl-bromide give $(GeH_3)_2Se$ and $(GeH_3)_2Te$ (Table 12).

The hydrolysis of organo-germanes, R_3GeX, gives $(R_3Ge)_2O$ except in a few cases *e.g.*, for R = Ph, $PhCH_2$, and Pr^i [7] when R_3GeOH is formed. However, GeH_3OH has not been detected and although $GeH_3M'H$ (M′ = S,[49] Se,[73] Te [68]) disproportionate to $(GeH_3)_2M'$ and $M'H_2$ very readily, there is less tendency towards disproportionation below the first row elements as was noted with the Group V species. The attempt by Dennis and Work in 1933 to prepare $(GeH_3)_2O$ by hydrolysis of GeH_3Cl [76] failed to yield a volatile product presumably because even if $(GeH_3)_2O$ forms it is unstable and its condensation to polymeric species is probably water catalysed.[77] Condensation is evident to a small extent in $(GeH_3)_2Se$ leading to $(GeH_3Se)_2GeH_2$ and probably $(GeH_3Se)_3GeH$ and $(GeH_3Se)_4Ge$.[73]

The observed PR separations in the i.r. spectra of $(GeH_3)_2O$ and $(GeH_3)_2S$ have been used to calculate the skeletal angles as $111^{+26}_{-18}{}^\circ$ and $116^{+21}_{-13}{}^\circ$ respectively, which was interpreted as indicating a lack of π-bond character in both species.[77] Recently, a more detailed i.r. study using a Valence Force Field approach estimated the apex angles as 139° and 100° respectively,[78] whilst

---

[70] A. Stock and C. Somieski, *Chem. Ber.*, 1923, **56B**, 247.

[71] H. J. Emeléus, A. G. MacDiarmid, and A. G. Maddock, *J. Inorg. Nuclear Chem.*, 1955, **1**, 194.

[72] M. Onyszchuk, *Canad. J. Chem.*, 1961, **39**, 808.

[73] J. E. Drake and C. Riddle, *J. Chem. Soc.* (*A*), 1969, 1573.

[74] C. Riddle, Ph.D. Thesis, Southampton Univ., 1969.

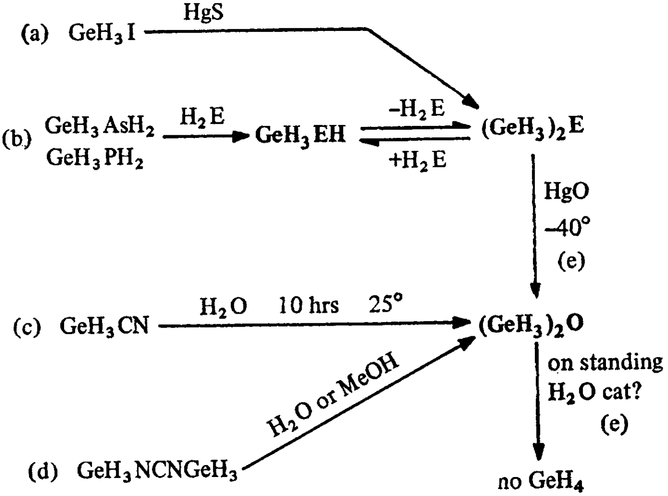
[75] S. Cradock, E. A. V. Ebsworth, and D. W. H. Rankin, *J. Chem. Soc.* (*A*), 1969, 1628.

[76] L. M. Dennis and R. W. Work, *J. Amer. Chem. Soc.*, 1933, **55**, 4486.

[77] T. D. Goldfarb and S. Sujishi, *J. Amer. Chem. Soc.*, 1964, **86**, 1679.

[78] S. Cradock, *J. Chem. Soc.* (*A*), 1968, 1426.

Table 12 *Preparative and Reaction Routes for Germanium-Group VI Hydrides*
E = S,Se



(a) S. Sujishi and W. Ando, U.S. Dept. Com., Office Tech. Serv., PB Rept. 143, 572, 1959, 93; S. Sujishi, *Abstracts of XVIIth Intern. Congr. of Pure and Appl. Chem.*, 1959, 53. (b) Refs. 52, 73. (c) T. D. Goldfarb and S. Sujishi, *140th Meeting Amer. Chem. Soc.*, 1961, Communication N92. (d) S. Cradock and E. A. V. Ebsworth, *J. Chem. Soc.* (*A*), 1968, 1422. (e) T. D. Goldfarb and S. Sujishi, *J. Amer. Chem. Soc.*, 1964, **86**, 1679.

electron diffraction measurements now place the angles at 126° and 99° respectively.[9c] That the bond length in the oxide is shorter than the predicted covalent bond-length, as in disiloxane, coupled with the higher angle is indicative that some multiple bond character is present. The H—H minimum distance in the sulphide is about twice that of the van der Waal's radius of hydrogen (*ca.* 2·2 Å) whereas in the oxide it is *ca.* 2·7 Å. Thus, as was seen in Group V, the simple stereochemical consideration is adequate for elements below the first short period, but for nitrogen and oxygen it is reasonable to consider some degree of π-bonding.

4 Conclusion

The literature reflects a rapid growth of interest in ternary hydrides. Although extensive chemical properties are largely unknown, it is some compensation that fairly detailed ^1H n.m.r. and vibrational spectroscopic studies, for which these hydrides are particularly suited, have been made. However, caution is essential in interpreting this data to give physical parameters. Bonding theories have provoked discussion but at the moment it is prudent to merely indicate trends and allow speculation to stimulate further studies. Hopefully, as more researchers accept the vacuum techniques that are standard for the study of these volatile hydrides, more synthetic routes will be discovered and their chemical and even fairly simple physical properties examined in greater depth.