Fission of Silicon–Arsenic and Tin–Arsenic Bonds by Covalent Halides and Protic Reagents

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The effect of halides and protic reagents upon the silicon–arsenic and tin–arsenic bonds in $Me_3SiAsMe_2$ and $Me_3SnAsMe_2$ respectively has been investigated. Halogens and covalent halides have invariably caused fission of both the silicon–arsenic and the tin–arsenic bonds.

Protic reagents were, however, somewhat more selective, in that whilst hydrogen sulphide and thiols caused fission of both silicon–arsenic and tin–arsenic bonds, water and alcohols only attacked the silicon–arsenic bond. Ammonia, diethylamine, diphenylphosphine, cyclopentadiene, and phenylacetylene failed to react with silicon or tin arsines.

THE synthesis of organotin arsines in an aqueous medium suggests that the tin–arsenic bond(s) in these materials are stable to hydrolysis.[1] This is confirmed by prolonged treatment of trimethylstannyldimethylarsine by water; and further, we find that alcohols have no reaction with tin–arsenic compounds. In contrast, the silicon–arsenic bond is rapidly attacked by water [2] to form a disiloxane, or alternatively by alcohols to produce alkoxysilanes.

$$2Me_3Si{\cdot}AsMe_2 + H_2O \longrightarrow Me_3Si{\cdot}O{\cdot}SiMe_3 + 2Me_2AsH \quad (1)$$

$$Me_3Si{\cdot}AsMe_2 + RSH \longrightarrow Me_3Si{\cdot}SR + Me_2AsH \quad (2)$$

Such selectivity of action is lost with hydrogen sulphide and thiols, which attack both the organosilicon- and the organotin-arsines.

$$Me_3M{\cdot}AsMe_2 + H_2S \longrightarrow Me_3M{\cdot}SMMe_3 + 2Me_2AsH \quad (3)$$

$$Me_3M{\cdot}AsMe_2 + RSH \longrightarrow Me_3M{\cdot}SR + Me_2AsH \quad (4)$$

$$M = Si \text{ and } Sn.$$

The organotin amines $R_3Sn{\cdot}NR^1_2$, in which the tin–nitrogen bond has been shown to be very reactive, undergoes a wide range of reactions with protic reagents AH, to release the organic amine R^1_2NH and form the organotin derivative R_3SnA.[3] Thus acidic hydrocarbons, phosphines, arsines, thiols, *etc.*, have all displaced amine to produce respectively organotin-acetylides, -phosphines, -arsines, -mercaptides *etc.* Such a high reactivity for a bond between a heavy Group IV element (Sn) and a light Group V element (N) could conceivably be present in the silicon–arsines where the reversed roles of a light Group IV element (Si) and heavy Group V element (As) are bonded.

We find, however, that the very high reactivity to protic reagents of the tin–nitrogen bond is not repeated for the silicon–arsenic bond, despite the encouraging reactions with alcohols and thiols reported above. Thus, although reactions might be reasonably expected, we found, nevertheless, that trimethylsilyldimethylarsine was completely unattacked by ammonia, diethylamine, diphenylphosphine, cyclopentadiene and phenylacetylene.

Halogens, iodine monochloride, and hydrogen bromide caused fission of the silicon– and tin–arsenic bonds to yield the halides, the products from ICl and HBr being in accord with the polarity of the Si–As bond.

$$Me_3M{\cdot}AsMe_2 + X_2 \longrightarrow Me_3MX + Me_2AsX$$

$$(X = Br \text{ and } I;\ M = Si;\ Sn)$$

$$Me_3Si{\cdot}AsMe_2 + ICl \longrightarrow Me_3SiCl + Me_2AsI \quad (6)$$

$$Me_3Si{\cdot}AsMe_2 + HBr \longrightarrow Me_3SiBr + Me_2AsH \quad (7)$$

We find that organotin and organolead chlorides displace trimethylchlorosilane from trimethylsilyldimethylarsine to produce the corresponding organotin and organolead arsines as shown in equations (8) and (9). Such displacements of one Group IVB element by another are not uncommon, and the direction of reaction is dependent upon what reactive group is bound to each Group IVB element. There are, however, a number of examples in the organometallic phosphines, arsines and stibines, where the heavier Group IVB element does displace the lighter Group IVB element.[4,5]

$$Me_3SnCl + Me_3Si{\cdot}AsMe_2 \longrightarrow Me_3Sn{\cdot}AsMe_2 + Me_3SiCl \quad (8)$$

$$\begin{aligned} Me_3PbCl + Me_3Si{\cdot}AsMe_2 &\longrightarrow Me_3SiCl + [Me_3Pb{\cdot}AsMe_2] \quad (9) \\ Me_4Pb + Pb + (Me_2As)_2 + Me_3As &\longleftarrow \end{aligned}$$

The product of reaction (8) is stable, but the lead–arsine believed to be formed initially, undergoes rapid decomposition to a variety of products as shown in equation (9), although the corresponding phenyl derivative $Ph_3Pb{\cdot}AsPh_2$ has been synthesized.[6] The stability of the tin–arsenic bases suggested the possibility that the corresponding arsonium salts containing a tin–arsenic bond might be synthesised. We find, however, that iodomethane causes fission of the tin–arsenic bond,

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[1] E. W. Abel, R. Honigschmidt-Grossich, and S. M. Illingworth, *J. Chem. Soc.* (*A*), 1968, 2623.

[2] C. Russ and A. MacDiarmid, *Angew. Chem. Internat. Edn.*, 1966, **5**, 418.

[3] K. Jones and M. F. Lappert, *Proc. Chem. Soc.*, 1964, 22; *J. Organometallic Chem.*, 1965, **3**, 295.

[4] S. Craddock, E. Ebsworth, A. Davidson, and L. Woodward, *J. Chem. Soc.* (*A*), 1967, 1229.

[5] S. Vyazankin, G. Razuvaev, O. Kruglaya, and G. Semichikova, *J. Organometallic Chem.*, 1966, **6**, 474.

[6] H. Schumann and M. Schmidt, *Inorg. Nuclear Chem. Letters*, 1965, **1**, 1.

and the resulting arsonium salt contains no tin–arsenic bond.

$$\mathrm{Me_3Sn\cdot AsMe_2 + 2MeI \longrightarrow Me_4AsI + Me_3SnI} \quad (10)$$

Acetyl and benzoyl chlorides bring about the quantitative removal of trimethylchlorosilane from trimethylsilyldimethylarsine, thus providing a very convenient route to the acetyl[7] and benzoyl dimethylarsines.

$$\mathrm{Me_3Si\cdot AsMe_2 + RCOCl \longrightarrow Me_2As\cdot COR + Me_3SiCl} \quad (11)$$
$$\mathrm{R = Me\ and\ Ph}$$

Similar quantitative evolution of trimethylchlorosilane takes place when trimethylsilyldimethylarsine is attacked by arsenic trichloride, phosphorus trichloride, chlorodiphenylphosphine, and chlorodimethylarsine.

Only in the last mentioned of these reactions, however, was the primary product isolated (equation 12).

$$\mathrm{Me_3Si\cdot AsMe_2 + Me_2AsCl \longrightarrow Me_2As\cdot AsMe_2 + Me_3SiCl} \quad (12)$$

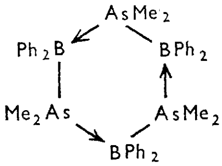
With arsenic and phosphorus trichlorides, although the tris(dimethylarsino)arsine and -phosphine were possibly formed in an initial reaction, they subsequently disproportionate (equation 13).

$$\begin{array}{c}\mathrm{3Me_3Si\cdot AsMe_2 + MCl_3 \longrightarrow [(Me_2As)_3M] + 3Me_3SiCl} \quad (13)\\ \downarrow \\ \mathrm{Me_2As\cdot AsMe_2 + M} \\ \mathrm{(M = P\ and\ As).}\end{array}$$

Here again the methyl derivatives of type $\mathrm{(Me_2As)_3M}$ are considerably less stable than the corresponding phenyl compounds which may be isolated.[8] This point is further brought out by the action of chlorodiphenylphosphine upon the silylarsine (equation 14), where diphenylphosphinodimethylarsine, if formed, undergoes disproportionation to the diarsine and diphosphine.

$$\begin{array}{c}\mathrm{Ph_2PCl + Me_3Si\cdot AsMe_2 \longrightarrow [Ph_2P\cdot AsMe_2] + Me_3SiCl} \quad (14)\\ \downarrow \\ \mathrm{Ph_2P\cdot PPh_2 + Me_2As\cdot AsMe_2}\end{array}$$

Chlorodiphenylboron and trimethylsilyldimethylarsine evolve trimethylchlorosilane to form diphenylborondimethylarsine. The white crystalline product appears to be quite stable in the air, and molecular weight measurements indicate a trimeric formulation $\mathrm{(Ph_2B\cdot AsMe_2)_3}$, which may be satisfactorily accommodated by the ring structure shown.



EXPERIMENTAL

All reactions were carried out under dry nitrogen. Trimethylsilyl and trimethyltin dimethylarsines were prepared as previously described.[1] ^{1}H N.m.r. spectra were recorded as neat liquids with tetramethylsilane as internal standard. I.r. spectra were recorded on a Perkin-Elmer 257 instrument, and the bracketed figures after each absorption refer to the relative peak heights, on a scale of ten for the most intense absorption.

Interaction of Trimethylsilyldimethylarsine and Water.—Water (0·09 g., 0·5 mol.) was added slowly with stirring to trimethylsilyldimethylarsine (1·8 g., 1 mol.) and the resultant liquid was fractionally distilled to give dimethylarsine (0·9 g., 85%), b.p. 36—38° (identified by i.r. spectroscopy), and hexamethyldisiloxane (0·60 g., 89%), b.p. 78—80° (identified by i.r. and ^{1}H n.m.r. spectroscopy).

Interaction of Trimethylsilyldimethylarsine and n-Butanol.—n-Butanol (0·74 g., 1 mol.) was added slowly, with stirring, to trimethylsilyldimethylarsine (1·8 g., 1 mol.). The resultant liquid was fractionally distilled to give dimethylarsine (0·65 g., 61%), b.p. 36—38° (identified by i.r. spectroscopy) and n-butoxytrimethylsilane (1·0 g., 66%), b.p. 114—116° (identified by ^{1}H n.m.r. spectroscopy).

Interaction of Trimethylsilyldimethylarsine and Hydrogen Sulphide.—Trimethylsilyldimethylarsine (1·8 g., 2 mol.) and hydrogen sulphide (0·17 g., 1 mol.) were allowed to react overnight in a sealed vessel. Subsequent distillation gave dimethylarsine (0·20 g., 28%), b.p. 30—32° (identified by i.r. spectroscopy) and hexamethyldisilthiane (0·6 g., 81%), b.p. 48/30 mm. (identified by ^{1}H n.m.r. and i.r. spectroscopy).

Interaction of Trimethylsilyldimethylarsine and Methanethiol.—Trimethylsilyldimethylarsine (1·8 g., 1 mol.) and methanethiol (0·48 g., 1 mol.) were allowed to react overnight in a sealed vessel. Subsequent distillation gave dimethylarsine (0·4 g., 38%), b.p. 34—36° (identified by i.r. spectroscopy) and methylthiotrimethylsilane (0·8 g., 64%) b.p. 108—110° (identified by ^{1}H n.m.r. and i.r. spectroscopy).

Interaction of Trimethylstannyldimethylarsine and Methanethiol.—Trimethylstannyldimethylarsine (2·6 g., 1 mol.) and methanethiol (0·48 g., 1 mol.) were set aside for 12 hr. in a sealed vessel. Subsequent distillation gave dimethylarsine (0·3 g., 28%), b.p. 36° (identified by i.r. spectroscopy) and trimethylmethylthiotin (1·40 g., 66%), (identified by i.r. and ^{1}H n.m.r. spectroscopy).

Interaction of Trimethylsilyldimethylarsine and Hydrogen Bromide.—Trimethylsilyldimethylarsine (1·8 g., 1 mol.) and hydrogen bromide (0·81 g., 1 mol.) were allowed to react overnight in a sealed vessel. Subsequent distillation gave dimethylarsine (0·30 g., 28%) (identified by i.r. spectrum spectroscopy) and bromotrimethylsilane (1·3 g., 85%), b.p. 78—80° (identified by ^{1}H n.m.r. spectroscopy).

Interaction of Trimethylsilyldimethylarsine and Bromine.—

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[7] H. Albers, W. Kunzel, and W. Schuler, *Chem. Ber.*, 1952, **85**, 239.

[8] T. A. George and M. F. Lappert, *Chem. Comm.*, 1966, 463.

Bromine (2·93 g., 1 mol.) was added slowly to trimethyl silyldimethylarsine (1·78 g., 1 mol.) at −78°, an exothermic reaction took place and a brown liquid resulted. Fractional distillation gave bromotrimethylsilane (0·75 g., 49%), b.p. 78—80° (characterised by ^{1}H n.m.r. spectroscopy, τ 9·45) and bromodimethylarsine (0·70 g., 38%), b.p. 126—128°, ^{1}H n.m.r. spectrum, τ 8·18.

Interaction of Trimethylsilyldimethylarsine and Iodine Monochloride.—Iodine monochloride (1·62 g., 1 mol.) was added slowly to trimethylsilyldimethylarsine (1·78 g., 1 mol.) at −78°. An exothermic reaction took place and subsequent fractional distillation gave chlorotrimethylsilane (0·55 g., 50%), b.p. 54—56° characterised by ^{1}H n.m.r. spectroscopy, and iododimethylarsine (1·1 g., 47%), b.p. 156°; ^{1}H n.m.r. spectrum: τ 7·96).

Interaction of Trimethylstannyldimethylarsine and Iodine.—Iodine (1·46 g., 1 mol.) in diethyl ether (10 ml.) was added slowly to trimethylstannyldimethylarsine (1·54 g., 1 mol.). An exothermic reaction took place and the diethyl ether was removed under reduced pressure from the mixture of products. All volatiles were sublimed and i.r. spectroscopy showed the presence of a mixture (1·13 g., 69%) of iodotrimethyltin (b.p. 170°) and iododimethylarsine (b.p. 155°).

Interaction of Trimethylsilyldimethylarsine and Chlorotrimethyltin.—Trimethylsilyldimethylarsine (1·8 g., 1 mol.) was added slowly to chlorotrimethyltin (2·0 g., 1 mol.) at −196°, and was then allowed to warm to room temperature. The resultant colourless liquid was fractionally distilled to give chlorotrimethylsilane (0·5 g., 46%), b.p. 52—54° (characterised by its refractive index and ^{1}H n.m.r. spectroscopy), and trimethylstannyldimethylarsine (2·0 g., 75%), b.p. 52°—54/10 mm., n_D^{20} 1·5423, found C, 22·1; H, 5·34; $C_5H_{15}AsSn$ requires C, 22·34; H, 5·6%; the i.r. and ^{1}H n.m.r. spectra were identical with an authentic sample.

Interaction of Trimethylsilyldimethylarsine and Chlorotrimethyl-lead.—Trimethylsilyldimethylarsine (1·5 g., 1 mol.) was added slowly to chlorotrimethyl-lead at −196° and then allowed to warm up to room temperature. The clear liquid rapidly darkened and a black solid was precipitated. Fractional distillation gave chlorotrimethylsilane, b.p. 55—56°, characterised by its refractive index and ^{1}H n.m.r. spectroscopy. The small amount of colourless liquid left had a ^{1}H n.m.r. spectrum with main peaks τ 9·28, $J(^{207}Pb–C–H)$ 61 c./sec. and 8·94, (Me_4Pb protons at τ 9·27, $J(^{207}Pb–C–H)$ 61·5 c./sec. Me_4As_2, Me_2As protons at τ 8·96).

Interaction of Trimethylstanyldimethylarsine and Methyl Iodide.—Methyl iodide (0·64 g., 2 mol.) was added to trimethylstannyldimethylarsine (0·62 g., 1 mol.). Immediately a white precipitate was formed. The solid was washed with diethyl ether and dried to give tetramethylarsonium iodide (0·62 g., 80%) (Found: C, 18·1; H, 4·55; $C_4H_{12}AsI$ requires C, 18·3; H, 4·6%) (identified by i.r. and ^{1}H n.m.r. spectroscopy [9]).

Interaction of Trimethylsilyldimethylarsine and Acetyl Chloride.—Acetyl chloride (0·78 g., 1 mol.) was added slowly to trimethylsilyldimethylarsine (1·8 g., 1 mol.). The resultant colourless liquid was fractionally distilled to give chlorotrimethylsilane (0·6 g., 54%) (characterised by its b.p., refractive index, and ^{1}H n.m.r. spectrum), and acetyldimethylarsine (1·0 g., 75%), b.p. 60/60 mm. (lit.[7] 40°/14 mm.) (Found: C, 32·13; H, 6·08; C_4H_9AsO requires C, 32·4; H, 6·08%), ^{1}H n.m.r. τ 8·91 and 7·7 (1·9 : 1), i.r. peaks: 3350 (1·5), 3000 (8), 2970sh (6), 2925 (10), 2820 (3·5), 1740 (3), 1680—1695 (8), 1470 (2·5), 1420 (6), 1345 (6), 1260 (4·5), 1110 (8·5), 1030 (4·5), 980 (5), 945 (6), 900 (6), 850 (6), and 800sh (2·5).

Interaction of Trimethylsilyldimethylarsine and Benzoyl Chloride.—Benzoyl chloride (1·40 g., 1 mol.) was added slowly to trimethylsilyldimethylarsine (1·8 g., 1 mol.). The resultant liquid was fractionally distilled to give chlorotrimethylsilane (0·4 g., 36%), identified by boiling point and ^{1}H n.m.r., and benzoyldimethylarsine (1·45 g., 70%), b.p. 66—68/0·005 mm., a yellow liquid (Found: C, 52·1; H, 5·1; $C_9H_{11}AsO$ requires C, 51·4; H, 5·25%), ^{1}H n.m.r. spectrum: τ 8·95, 2·7 (m), and 2·16 (m) (6 : 3 : 2·3), i.r. peaks at 3180 (1), 3080 (1·5), 3060 (2), 3020 (1·5), 2990 (2·5), 2915 (4), 2810 (0·5), 1775 (2), 1720 (2·5), 1690 (2), 1650 (10), 1595 (5), 1580 (6), 1445 (7), 1415 (3), 1310 (3), 1300 (2), 1275 (2), 1255 (3), 1200 (10), 1170 (7), 1100 (1), 1070 (2·5), 1020 (2), 1000 (2·5), 925 (2), 885 (9·5), 850 (4), 830sh (2·5), 795 (1), 760 (7·5), 710 (2·5), 685 (8), and 670 (7).

Interaction of Trimethylsilyldimethylarsine and Phosphorus Trichloride.—Phosphorus trichloride (0·45 g., 1 mol.) was added slowly to trimethylsilyldimethylarsine (1·8 g., 3 mol.) at −78°. An exothermic reaction took place resulting in an orange liquid which deposited orange solid as it warmed up to room temperature. Fractional distillation gave chlorotrimethylsilane (0·7 g., 64%), characterised by b.p. and ^{1}H n.m.r., and tetramethyldiarsine (1·6 g., 76%), b.p. 35—40/10 mm. ^{1}H n.m.r. spectrum: τ 8·92.

Interaction of Trimethylsilyldimethylarsine and Arsenic Trichloride.—Arsenic trichloride (0·9 g., 1 mol.) in diethyl ether (5 ml.) was added slowly to trimethylsilyldimethylarsine (2·67 g., 3 mol.) in diethyl ether (20 ml.) at −78°. An exothermic reaction took place resulting in a yellow solution which turned red-black and deposited black solid upon being warmed to room temperature. Fractional distillation gave chlorotrimethylsilane (1·0 g., 61%), characterised by its b.p. and ^{1}H n.m.r., and tetramethyldiarsine (1·30 g., 82%), b.p. 35—40/10 mm., ^{1}H n.m.r. spectrum: τ 8·93.

Interaction of Trimethylsilyldimethylarsine and Chlorodiphenylphosphine.—Chlorodiphenylphosphine (2·9 g., 1 mol.) was added slowly to trimethylsilyldimethylarsine (1·8 g. 1 mol.) and the clear liquid chlorotrimethylsilane (0·6 g. 54%), identified by its b.p. and ^{1}H n.m.r. spectrum), was distilled off from the white solid, tetraphenyldiphosphine, the latter compound was dried *in vacuo* and had m.p. 138—140° (Found: C, 77·2; H, 5·4; $C_{24}H_{20}P_2$ requires C, 77·8; H, 5·4%), ^{1}H n.m.r. spectrum: τ 2·75 (m).

Interaction of Trimethylsilyldimethylarsine and Chlorodimethylarsine.—Chlorodimethylarsine (1·4 g., 1 mol.) was added slowly to trimethylsilyldimethylarsine (1·8 g., 1 mol.), at −78° and then allowed to warm up to room temperature. The resultant colourless liquid was fractionally distilled to give chlorotrimethylsilane (0·7 g., 63%), b.p. 54—56° (characterised by its refractive index and ^{1}H n.m.r. spectrum and tetramethyldiarsine (1·7 g., 80%) b.p. 39—40/10 mm. (lit.,[10] 170°), ^{1}H n.m.r. spectrum: τ 8·92 (lit.,[11] τ 8·89) (Found: C, 24·15; H, 5·85. $C_4H_{12}As_2$ requires C, 22·85; H, 5·7%).

Interaction of Trimethylsilyldimethylarsine and Chlorodiphenylboron.—Chlorodiphenylboron (2 g., 1 mol.) was added slowly to trimethylsilyldimethylarsine (1·8 g., 1 mol.) at −80° and the mixture was then warmed to 50°. The clear liquid chlorotrimethylsilane (0·45 g., 40%) (character-

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[9] W. Cullen, G. Deacon, and J. Green, *Canad. J. Chem.*, 1965, **43**, 3193.

[10] J. Phillips and J. Vis, *Canad. J. Chem.*, 1967, **45**, 675.

[11] R. Harris and R. Hayter, *Canad. J. Chem.*, 1964, **42**, 2282.

ised by its b.p. refractive index, and ^1H n.m.r. spectrum), was fractionally distilled from the white solid, diphenylborondimethylarsine (2·3 g., 85%), ^1H n.m.r. spectrum: τ 2·85 (s) and 9·25, (1 : 1·8) (Found: C, 61·75; H, 5·75; $C_{14}H_{16}AsB$ requires C, 62·2; H, 5·9%), m.p. 164—169° (decomp.); *M* (Found) 731, 777; *M* [Calc. for $(Ph_2BAsMe_2)_3$] 810.

Some experiments involving trimethylsilyldimethylarsine and trimethyltindimethylarsine respectively, reresulted in the recovery of the starting materials. $Me_3SiAsMe_2$ failed to undergo reaction with the following reagents (conditions in parentheses) diethylamine (reflux/24 hr.), ammonia (sealed tube, 20°/12 hr.), phenylacetylene (reflux/1 hr.), cyclopentadiene (reflux/1 hr.), and diphenylphosphine (reflux/1 hr.); and, similarly $Me_3SnAsMe_2$: water (20°/12 hr.) and n-butanol (reflux/1 hr.).

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