

## NOTE

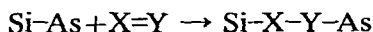
### SOME INSERTION REACTIONS OF SILICON-ARSENIC BONDS

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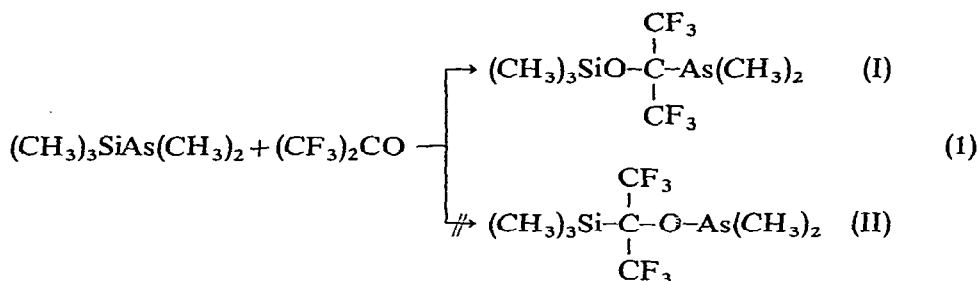
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The chemical properties of the few known organosilylarsines have been little investigated. To date we have reported the fission reactions of the silylarsines with halides and protic species<sup>1</sup>, and those reactions with metal carbonyls where the silylarsines remain intact as ligands<sup>2</sup>. We now report some reactions in which the organo-arsenic and organosilicon moieties of the silylarsine undergo separation by an insertion<sup>3</sup> type of reaction.



This type of reaction for the silicon-arsenic bond has been only reported to date for the insertion of carbon disulphide<sup>4,5</sup>. We have extended these insertion reactions to certain perhaloketones and dimethyl acetylenedicarboxylate.

The carbonyl group of hexafluoroacetone is known to insert under mild conditions into a variety of organosilicon amines<sup>6</sup>, ethers<sup>7</sup>, sulphides<sup>8,9</sup> and phosphines<sup>10</sup>. Similarly, we find (trimethylsilyl)dimethylarsine and hexafluoroacetone react rapidly at room temperature.



In most previous cases studied, the hexafluoroacetone has inserted into organosilicon compounds with resultant formation of a siloxane<sup>7,8</sup> analogous to product (I) in eqn. (1) above. In the case of the hexafluoroacetone insertion into a silicon-phosphorus bond, however, a mixture of the two possible products was formed<sup>10</sup>. The <sup>1</sup>H and <sup>19</sup>F nuclear magnetic resonance spectrum of the product from reaction (1) indicates only one isomer is present. The shielding of the methylsilicon protons is virtually identical to the  $\tau$  value of 9.77 reported for the methylsilicon protons in the closely analogous environment in  $\text{HC(CF}_3\text{)}_2\text{OSi(CH}_3\text{)}_3$ <sup>11</sup>. Similarly



1 mol.) were sealed in a glass tube at  $-80^{\circ}$ , and then allowed to stand at  $20^{\circ}$  for 12 h. Subsequent distillation gave [2-(dimethylarsino)hexafluoro-2-propoxy]trimethylsilane (7.5 g, 88%), b.p.  $58^{\circ}/18$  mm. (Found: C, 28.1; H, 4.5; F, 33.4.  $C_8H_{15}AsF_6OSi$  calcd. C, 27.9; H, 4.4; F, 33.2%.)  $^1H$  NMR peaks at  $\tau$  9.77 (septet  $J=0.5$  Hz), 8.88 (septet  $J=1$  Hz);  $^{19}F$  NMR peak at 69.8 ppm from  $CFCl_3$  (broad). Infrared maxima at 2970 (2), 2920 ( $1\frac{1}{2}$ ), 1420 ( $1\frac{1}{2}$ ), 1290 (8), 1260 (9), 1215 (9), 1195 (10), 1170 (7), 1160sh (6), 1130 ( $4\frac{1}{2}$ ), 955 (5), 905sh ( $2\frac{1}{2}$ ), 890 (5), 870 (7), 850 ( $7\frac{1}{2}$ ), 760 (2), 735 (2), 710 (5)  $cm^{-1}$ .

*Interaction of dimethylsilylenebis(dimethylarsine) and hexafluoroacetone*

Hexafluoroacetone (4.1 g, 2 mols.) and dimethylsilylene bis(dimethylarsine) (3.35 g, 1 mol.) were sealed in a glass tube at  $-80^{\circ}$ , and allowed to stand at  $20^{\circ}$  for 12 h. Subsequent distillation gave bis[2-(dimethylarsino)hexafluoro-2-propoxy]dimethylsilane (7.0 g, 94%), b.p.  $74^{\circ}/0.02$  mm. (Found: C, 24.1; H, 3.1.  $C_{12}H_{18}As_2F_{12}O_2Si$  calcd.: C, 24.0; H, 3.0%.)  $^1H$  NMR peaks at  $\tau$  9.60 (broad), 8.79 (broad);  $^{19}F$  NMR peak at 69.7 ppm from  $CFCl_3$ . Infrared maxima at 3000 (1), 2930 (2), 1430 (2), 1290 (9), 1265 ( $9\frac{1}{2}$ ), 1220 (10), 1200 (10), 1150 (9), 1135sh (8), 950 (7), 910sh (4), 890 (7), 880 (8), 850 (4), 760 (6), 740 ( $4\frac{1}{2}$ ), 710 (8), 680 (2)  $cm^{-1}$ .

*Interaction of methylsilylidynetris(dimethylarsine) and hexafluoroacetone*

Hexafluoroacetone (5.0 g, 3 mols.) and methylsilylidynetris(dimethylarsine) (3.6 g, 1 mol.) were sealed in a glass tube at  $-80^{\circ}$ , and then allowed to stand at  $20^{\circ}$  for 12 h. Subsequent distillation gave tris[2-(dimethylarsino)hexafluoro-2-propoxy]-methylsilane (7.5 g, 87%), b.p.  $120^{\circ}/0.02$  mm (Found: C, 22.7; H, 2.65.  $C_{16}H_{21}As_3F_{18}O_3Si$  calcd.: C, 22.4; H, 2.45%.)  $^1H$  NMR peaks at  $\tau$  9.25 (broad), 8.72 (broad);  $^{19}F$  NMR peak at 69.6 ppm from  $CFCl_3$ . Infrared maxima at 3020 ( $\frac{1}{2}$ ), 3000 ( $\frac{1}{2}$ ), 2930 ( $1\frac{1}{2}$ ), 1430 (2), 1290 (9), 1270 ( $9\frac{1}{2}$ ), 1225 (10), 1200 (10), 1145 (9), 950 (7), 895 (7), 850 (3), 830 (2), 800 ( $3\frac{1}{2}$ ), 790sh (3), 755 (4), 740 (3), 725 ( $2\frac{1}{2}$ ), 710 (8)  $cm^{-1}$ .

*Interaction of (trimethylsilyl)dimethylarsine with chloropentafluoroacetone and 1,3-dichloro-1,1,3,3-tetrafluoroacetone*

The two ketones were separately sealed with an equimolar quantity of the arsine and allowed to stand for 12 h. Subsequent distillations of the two products yielded [2-(dimethylarsino)-1-chloropentafluoro-2-propoxy]trimethylsilane (76%). (Found: C, 26.9; H, 4.39; F, 26.7.  $C_8H_{15}AsClF_5OSi$  calcd.: C, 26.7; H, 4.16; F, 26.4%.)  $^1H$  NMR peaks at  $\tau$  9.73 (broad), 8.86 (multiplet);  $^{19}F$  NMR peaks at 67.7 ppm from  $CFCl_3$  (triplet  $J=10.5$  Hz) and 55.3 ppm from  $CFCl_3$  (overlapping quartets  $J=10.5$  Hz). Infrared maxima at 2960 (3), 2920 (2), 1420 (2), 1275 (7), 1260 ( $8\frac{1}{2}$ ), 1190 (10), 1175sh (9), 1140 ( $4\frac{1}{2}$ ), 1100 ( $3\frac{1}{2}$ ), 1065 (5), 1025sh (2), 1000 ( $6\frac{1}{2}$ ), 915 (5), 865sh (8), 840 ( $9\frac{1}{2}$ ), 760 (4), 725 ( $3\frac{1}{2}$ ), 700 (4)  $cm^{-1}$ ; and [2-(dimethylarsino)-1,3-dichlorotetrafluoro-2-propoxy]trimethylsilane (84%). (Found: C, 25.3; H, 3.96; F, 20.3.  $C_8H_{15}AsCl_2F_4OAs$  calcd.: C, 25.5; H, 3.97; F, 20.2%.)  $^1H$  NMR peaks at  $\tau$  9.75 and 8.86 (broad);  $^{19}F$  NMR peak at 52.7 ppm from  $CFCl_3$  (broad). Infrared maxima at 2960 (3), 2920 ( $2\frac{1}{2}$ ), 1660 ( $1\frac{1}{2}$ ), 1410 ( $2\frac{1}{2}$ ), 1270 ( $5\frac{1}{2}$ ), 1255 (8), 1210 (7), 1150 (9), 1085 ( $4\frac{1}{2}$ ), 1045 (5), 1015sh (6), 1005 (7), 960 (6), 890sh ( $6\frac{1}{2}$ ), 850 (10), 760 (5), 740 (5)  $cm^{-1}$ .

*Interaction of (trimethylsilyl)dimethylarsine and dimethyl acetylenedicarboxylate*

Dimethyl acetylenedicarboxylate (1.42 g, 1 mol.) was added slowly to (tri-

methyldimethylarsine (1.8 g, 1 mol.) resulting in an exothermic reaction. Distillation of the resulting dark red liquid gave 1,2-bis(methoxycarbonyl)-1-(trimethylsilyl)-2-(dimethylarsino)ethylene (2.3 g, 72%) as a colourless oil, b.p. 87°/0.003 mm. (Found: C, 40.9; H, 6.51.  $C_{11}H_{21}AsO_4Si$  calcd.: C, 41.2; H, 6.56%)  $^1H$  NMR peaks at  $\tau$  9.67, 8.83, 6.32 (two peaks separated by 2 Hz). Integrations 3/2/2 respectively. Infrared maxima at 2990 ( $2\frac{1}{2}$ ), 2960 ( $4\frac{1}{2}$ ), 2920 (3), 2910sh (2), 2840 (1), 1725 (10), 1565 ( $2\frac{1}{2}$ ), 1460sh (2), 1435 ( $5\frac{1}{2}$ ), 1230 (10), 1055 (6), 1010 ( $2\frac{1}{2}$ ), 935 (1), 890 (6), 850 ( $8\frac{1}{2}$ ), 785 ( $1\frac{1}{2}$ ), 765 ( $2\frac{1}{2}$ ), 695 (2)  $cm^{-1}$ .

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