NOTE

SOME INSERTION REACTIONS OF SILICON-ARSENIC BONDS

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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 species¹, and those reactions with metal carbonyls where the silylarsines remain intact as ligands². We now report some reactions in which the organoarsenic and organosilicon moieties of the silylarsine undergo separation by an insertion³ type of reaction.

 $Si-As+X=Y \rightarrow Si-X-Y-As$

This type of reaction for the silicon-arsenic bond has been only reported to date for the insertion of carbon disulphide^{4,5}. 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 amines⁶, ethers⁷, sulphides^{8,9} and phosphines¹⁰. Similarly, we find (trimethylsilyl)dimethylarsine and hexafluoroacetone react rapidly at room temperature.

$$(CH_{3})_{3}SiAs(CH_{3})_{2} + (CF_{3})_{2}CO - \begin{pmatrix} CF_{3} \\ 1 \\ CH_{3} \end{pmatrix}_{3}SiO - C - As(CH_{3})_{2} & (I) \\ CF_{3} \\ (CH_{3})_{3}Si - C - O - As(CH_{3})_{2} & (II) \\ CF_{3} \\ \end{pmatrix}$$

$$(1)$$

In most previous cases studied, the hexafluoroacetone has inserted into organosilicon compounds with resultant formation of a siloxane^{7.8} 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 formed¹⁰. The ¹H and ¹⁹F 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 τ value of 9.77 reported for the methylsilicon protons in the closely analogous environment in HC(CF₃)₂OSi(CH₃)₃¹¹. Similarly

TABLE 1

PROTON AND FLUORINE CHEMICAL SHIFTS FOR THE SILOXANES	s (CH ₃) _n Si[OC(CF ₃) ₂ As(CH ₃) ₂] _{4-n}
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Compound	τ(Si-CH ₃) ⁴	τ(As-CH ₃) ^a	¹⁹ F shift ^b (ppm from CFCl ₃)
(CH ₃) ₃ SiOC(CF ₃) ₂ As(CH ₃) ₂	9.77	8.88	69.8
$(CH_3)_2Si[OC(CF_3)_2As(CH_3)_2]_2$	9.60	8.79	69.7
$CH_3Si[OC(CF_3)_2As(CH_3)_2]_3$	9.25	8.72	69.6

^a As neat liquid, internal tetramethylsilane reference. ^b As neat liquid, internal CFCl₁ reference.

the methylarsenic protons have a τ value close to 8.84, that of the methylarsenic protons in HOC(CF₃)₂As(CH₃)₂¹². In this light we believe the product of reaction (1) to be exclusively (I), with no (II) isomer formed.

As indicated in eqns. (2) and (3), the diarsine dimethylsilylenebis(dimethylarsine) and the triarsine methylsilylidynetris(dimethylarsine) insert respectively two and three hexafluoroacetone molecules. Table 1 shows the steadily decreasing shielding of both the silicon and arsenic-methyl protons with the increasing fluorine content of the resulting siloxanes.

$$(CH_3)_2Si[As(CH_3)_2]_2 + 2 (CF_3)_2CO \rightarrow (CH_3)_2Si[OC(CF_3)_2As(CH_3)_2]_2 (2)$$

$$CH_3Si[As(CH_3)_2]_3 + 3 (CF_3)_2CO \rightarrow CH_3Si[OC(CF_3)_2As(CH_3)_2]_3 (3)$$

The two perhaloketones chloropentafluoroacetone and 1,3-dichloro-1,1,3,3tetrafluoroacetone also have sufficiently activated ketone groups to insert into the silicon-arsenic bond, as illustrated in eqns. (4) and (5).

$$(CH_3)_3SiAs(CH_3)_2 + CF_3COCF_2Cl \rightarrow (CH_3)_3SiOC(CF_3)(CF_2Cl)As(CH_3)_2$$
(4)

$$(CH_3)_3 SiAs(CH_3)_2 + (CF_2Cl)_2 CO \rightarrow (CH_3)_3 SiOC(CF_2Cl)_2 As(CH_3)_2$$
(5)

The siloxane $(CH_3)_3SiOC(CF_3)(CF_2Cl)As(CH_3)_2$ produced in reaction (4) has a particular interest in that the insertion generates an asymmetric carbon atom, and the prochirality renders the two fluorine atoms of the CF₂Cl group non-equivalent. The resultant ABX₃ pattern of the ¹⁹F nuclear magnetic resonance spectrum, together with those of other base insertion products of this ketone, are discussed in detail elsewhere¹³.

Dimethyl acetylenedicarboxylate, in common with its reactions with many other organometallic bases³, inserts readily into (trimethylsilyl)dimethylarsine (eqn. 6).

$$(CH_3)_3SiAs(CH_3)_2 + CH_3OOCC \equiv CCOOCH_3 \rightarrow (CH_3)_3Si - C = C - As(CH_3)_2 (6)$$

The proton magnetic resonance spectrum of the product shows only one product, but we are unable to differentiate between the structure represented in eqn. (6), and the alternative isomer with methoxycarbonyl groups mutually *trans*.

EXPERIMENTAL

Interaction of (trimethylsilyl)dimethylarsine and hexafluoroacetone

Hexafluoroacetone (4.1 g, 1 mol.) and (trimethylsilyl)dimethylarsine (4.4 g,

1 mol.) were sealed in a glass tube at -80° , and then allowed to stand at 20° for 12 h. Subsequent distillation gave [2-(dimethylarsino)hexafluoro-2-propoxy]trimethylsilane (7.5 g, 88%), b.p. 58°/18 mm. (Found : C, 28.1; H, 4.5; F, 33.4. C₈H₁₅AsF₆OSi calcd. C, 27.9; H, 4.4; F, 33.2%.) ¹H NMR peaks at τ 9.77 (septet J = 0.5 Hz), 8.88 (septet J = 1 Hz): ¹⁹F NMR peak at 69.8 ppm from CFCl₃ (broad). Infrared maxima at 2970 $(2), 2920(1\frac{1}{2}), 1420(1\frac{1}{2}), 1290(8), 1260(9), 1215(9), 1195(10), 1170(7), 1160sh(6), (6), (10), ($ 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° , and allowed to stand at 20° for 12 h. Subsequent distillation gave bis [2-(dimethylarsino)hexafluoro-2-propoxy]dimethylsilane (7.0 g, 94%), b.p. 74°/0.02 mm. (Found : C, 24.1; H, 3.1. C₁₂H₁₈As₂F₁₂-O₂Si calcd.: C, 24.0; H, 3.0%.) ¹H NMR peaks at τ 9.60 (broad), 8.79 (broad); ¹⁹F NMR peak at 69.7 ppm from CFCl₃. 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° , and then allowed to stand at 20° for 12 h. Subsequent distillation gave tris[2-(dimethylarsino)hexafluoro-2-propoxy]methylsilane (7.5 g, 87%), b.p. 120°/0.02 mm (Found: C, 22.7; H, 2.65. C₁₆H₂₁As₃- $F_{18}O_3Si \text{ calcd.}: C, 22.4; H, 2.45\%)$ ¹H NMR peaks at τ 9.25 (broad), 8.72 (broad); ¹⁹F NMR peak at 69.6 ppm from CFCl₃. 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. C₈H₁-AsClF₅OSi calcd.: C, 26.7; H, 4.16; F, 26.4%.) ¹H NMR peaks at 7 9.73 (broad), 8.86 (multiplet); ¹⁹F NMR peaks at 67.7 ppm from CFCl₃ (triplet J = 10.5 Hz) and 55.3 ppm from CFCl₃ (overlapping quartets J = 10.5 Hz). Infrared maxima at 2960 (3), 2920 (2), 1420 (2), 1275 (7), 1260 (8¹/₂), 1190 $(10), 1175 \text{sh} (9), 1140 (4\frac{1}{2}), 1100 (3\frac{1}{2}), 1065 (5), 1025 \text{sh} (2), 1000 (6\frac{1}{2}), 915 (5), 865 \text{sh} (8),$ 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. C₈H₁₅-AsCl₂F₄OAs calcd.: C, 25.5; H, 3.97; F, 20.2%.) ¹H NMR peaks at τ 9.75 and 8.86 (broad); ¹⁹F NMR peak at 52.7 ppm from CFCl₃ (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-

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methylsilyl)dimethylarsine (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. C₁₁H₂₁AsO₄Si calcd.: C, 41.2; H, 6.56%). ¹H NMR peaks at τ 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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