

NOTE

THE SYNTHESIS AND PROPERTIES OF SOME ORGANOSILICON SECONDARY ARSINES AND A CYCLIC ORGANOSILICON ARSINE

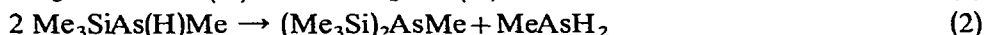
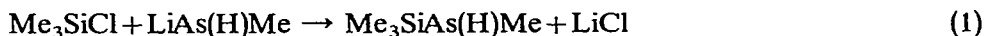
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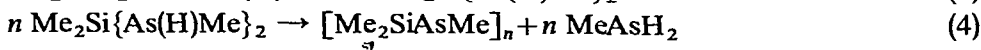
Tertiary arsines containing one or more organosilicon-arsenic bonds are now well known¹, and have been extensively studied^{1,2}. We have now attempted to prepare organosilicon secondary arsines.

Trimethylchlorosilane and lithium methylarsenide at -80° yield about 10% of trimethylsilylmethylarsine according to eqn. (1).



The major product from this reaction, however, was bis(trimethylsilyl)methylarsine, which could have been formed directly from the trimethylchlorosilane and lithium methylarsenide, or more likely, by the disproportionation of the (trimethylsilyl)methylarsine according to eqn. (2). This disproportionation of the secondary arsine $\text{Me}_3\text{SiAs(H)Me}$ is so facile, that it has not proved possible to obtain analytically pure samples of $\text{Me}_3\text{SiAs(H)Me}$, due to the easy loss of methylarsine. (Trimethylsilyl)methylarsine is completely decomposed to bis(trimethylsilyl)methylarsine and methylarsine [eqn. (2)], upon heating, and the reaction is catalysed by addition of ammonium sulphate in a manner analogous to the corresponding secondary amines³.

The reaction between dimethyldichlorosilane and two molar proportions of lithium methylarsenide follow a similar course to the ones reported above. The dimethylsilylenebis(methylarsine) formed, [eqn. (3)], was a minority yield, and not isolable in an analytically pure state due to very easy disproportionation [eqn. (4)], to methylarsine and (dimethylsilylene)methylarsine polymer.



The volatile fraction of the polymeric (dimethylsilylene)methylarsine appears to be tetrameric from molecular weight measurements. Dimethylsilylenebis(methylarsine) was easily converted into the cyclic tetrameric (dimethylsilylene)methylarsine [eqn. (4), $n = 4$] by heat, and in the presence of ammonium sulphate as catalyst.

The proton magnetic resonance spectra of the four compounds reported above are detailed in Table 1. In the two compounds where the H-As-CH_3 moiety occurs, the AB_3 second order spectrum is clearly discernible.

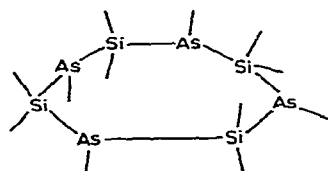


Fig. 1. Diagrammatic representation of the $[\text{Me}_2\text{SiAsMe}]_4$ ring system.

Of particular interest is the spectrum of the eight membered ring $[\text{Me}_2\text{SiAsMe}]_4$. At 40° there are four well resolved methylsilyl resonances in the intensity ratio 2/3/3/2. At 90° these four peaks have collapsed to a doublet, and at 140° the methylsilyl proton resonance is a sharp single line. The changes are reversible on cooling, returning to the original quartet. Fig. 1 is a diagrammatic representation of the eight membered ring. This shows how the different environments of the methylsilyl groups can arise due to the different conformations of the methylarsenic groups around the ring.

TABLE I

PROTON MAGNETIC RESONANCE SPECTRA OF SILYLARSINES

Compound	τ (ppm)			J (Hz)
	CH_3Si	CH_3As	HAs	H-As- CH_3
$\text{Me}_3\text{SiAs(H)Me}$	9.72	9.07	8.80	7.0
$\text{Me}_2\text{Si}\{\text{As(H)Me}\}_2$	9.51	9.05	8.67	7.0
$(\text{Me}_3\text{Si})_2\text{AsMe}$	9.75	9.13		
$[\text{Me}_2\text{SiAsMe}]_4$	9.55	9.02		
	9.52	8.76		
	9.48			
	9.45			

In the right environment, it has been shown by NMR measurements and optical resolutions, that the inversion time of arsenic can be very long by an NMR time scale at ordinary temperatures⁴⁻⁶. Thus different isomers of the ring system with finite stabilities will be present at room temperature. As the rate of inversion of arsenic increases with temperature rise, the life times of isomers shorten, until at 140° all of the methylsilyl protons appear equivalent on an NMR time scale. The inversion about two sulphur atoms in a ring has been similarly shown to have a temperature variation effect on the environment of two methyl groups⁷.

EXPERIMENTAL

All reactions were carried out in an atmosphere of dry nitrogen, solvents were dried and deoxygenated. Infrared spectra were obtained on a Perkin-Elmer 257 Spectrometer, proton magnetic resonance spectra were obtained on a Varian A60 instrument with TMS as internal reference.

Interaction of lithium methylarsenide and trimethylchlorosilane

2 N n-Butyl-lithium (127 ml, 1 mol.) in hexane was added slowly with stirring to methylarsine (23.4 g, 1 mol.) in diethyl ether (250 ml) at -80° , and the resulting fine yellow suspension stirred into trimethylchlorosilane (28 g, 1 mol.) in diethyl ether (50 ml) at -80° . A white precipitate was formed, and the solution became dark brown, after which the mixture was allowed to warm to room temperature. The solution layer was decanted from the precipitate and distilled to yield (trimethylsilyl)methylarsine (5 g, 12%), b.p. $118-120^{\circ}$, and bis(trimethylsilyl)methylarsine (10 g, 33%), b.p. $58^{\circ}/15$ mm. (Found: C, 36.1; H, 8.8. $C_7H_{21}AsSi_2$ calcd.: C, 35.6; H, 8.9%.)

Interaction of lithium methylarsenide and dimethyldichlorosilane

Lithium dimethylarsenide (36 g, 2 mols.) prepared as described above, was added to dimethyldichlorosilane (23 g, 1 mol.) in diethyl ether (50 ml) at -80° with stirring. Subsequent decantation and distillation yielded dimethylsilylenebis(methylarsine) (5 g, 12%) b.p. $60^{\circ}/20$ mm, and cyclic tetrameric (dimethylsilylene)methylarsine (10 g, 30%) b.p. $90^{\circ}/0.05$ mm. (Found: C, 24.3; H, 6.0; mol.wt., 567. $C_{12}H_{36}As_4Si_4$ calcd.: C, 24.3; H, 6.1%; mol.wt., 592.)

Infrared spectra of the silylarsines

Spectra were recorded as thin films, and the bracketed figure after each absorption maximum refers to the relative peak height, on a scale of 10 for the most intense absorption. The arsenic-hydrogen stretching frequencies at 2088 (7) and 2087 (8) are prominent features in the spectra of $Me_3SiAs(H)Me$ and $Me_2Si\{As(H)Me\}_2$ respectively.

$Me_3SiAsHMe$. 2968 (7), 2938 (5), 2908 (4), 2088 (7), 1400 (3), 1245 (8), 1036 (2), 912 (4), 893 (4), 834 (10), 744 (4), 690 (4).

$(Me_3Si)_2AsMe$. 2970 (6), 2930 (4), 2910 (4), 1425 (2), 1395 (2), 1305 (1), 1242 (8), 830 (10), 818 (10), 743 (4), 683 (4).

$Me_2Si(AsHMe)_2$. 2985 (3), 2965 (6), 2935 (7), 2868 (3), 2087 (8), 1415 (3), 1240 (5), 1086 (5), 1037 (4), 981 (1), 912 (6), 833 (8), 798 (10), 760 (5), 690 (3), 655 (5).

$[Me_2SiAsMe]_4$. 2967 (6), 2935 (6), 1419 (3), 1397 (3), 1247 (7), 1080 (5), 890 (5), 863 (5), 826 (10), 804 (10), 754 (6), 687 (4), 650 (7).

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