

Silylated and Germylated Polyarsines

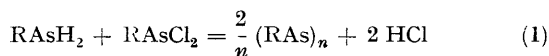
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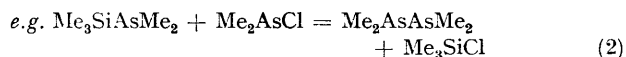
Summary The reaction of trisilyl- or trigermyl-arsine with chloro(dimethyl)arsine leads to the formation of penta-silylcyclopenta-arsine, $(\text{SiH}_3\text{As})_5$, or pentagermylcyclo-

penta-arsine, $(\text{GeH}_3\text{As})_5$, respectively; these are the first examples of metalloid-substituted polyarsines.

TRIALKYLARSINES form adducts with trihalogeno-, dihalogeno(organo)- and halogeno(diorgano)-arsines¹ whereas arsine reacts with arsenic trichloride to give hydrogen chloride and arsenic. Primary arsines and dihalogenoarsines undergo the Michaelis-Kohler reaction² leading to cyclic arsines, reaction (1).

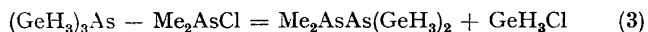


Silicon³ and tin⁴ arsines react in a similar manner to arsenic hydrides, reaction (2).

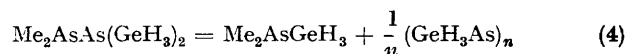


Our investigations of the reactions of trisilyl- and trigermyl-arsines with chloro(dimethyl)arsine lead to the identification of silylated and germylated cyclic arsines which are the first examples of metalloid-substituted polyarsines.

In a typical experiment under vacuum-line conditions, chloro(dimethyl)arsine and an equimolar amount of trigermylarsine were allowed to warm slowly from -196 to -78° . Chlorogermene was evolved in an amount consistent with reaction (3). On warming to room temperature,



dimethyl(germyl)arsine was evolved in an amount consistent with reaction (4). A yellow solid remained in the



reaction vessel. Although there was some indication of its decomposition at room temperature by the evolution of small quantities of arsine and a darkening of its colour, *ca.* 30% of the involatile product could be dissolved in benzene. The solution showed no signs of decomposition after 1 h.

Molecular weight determinations gave the value of n as 5. I.r. spectra in benzene and KBr discs showed broad bands at 2060 cm^{-1} and in the $750\text{--}800 \text{ cm}^{-1}$ region attributable to GeH_3 stretches and deformations respectively. The Raman spectra of the solution and the extracted solid showed a broad band at $250\text{--}265 \text{ cm}^{-1}$ as expected for Ge-As and As-As stretching modes. However, decomposition was rapid even in a weak (30 mW) laser beam as shown by the darkening colour and an increasing number of bands. The ^1H n.m.r. spectrum showed a broad feature at δ *ca.* 4.46 p.p.m. which in one sample was resolved into three peaks at 4.44, 4.47, and 4.49 p.p.m. with relative intensities of 1.0:1.9:1.7. A 1:2:2 ratio was noted for pentamethylcyclopenta-arsine^{5,6} in which the ring is puckered and not planar.

$(\text{GeH}_3\text{As})_5$ reacted with anhydrous hydrogen chloride to cleave quantitatively the Ge-As bond giving the expected amount of chlorogermene as well as arsine and arsenic subhydrides.⁷ Its thermal instability prevented a mass spectroscopic confirmation of molecular weight.

Identical reactions occurred between trisilylarsine and chloro(dimethyl)arsine to give eventually pentasilylcyclopenta-arsine, $(\text{SiH}_3\text{As})_5$, whose vibrational spectra showed bands at 2140 (SiH_3 stretches), 890–840 (SiH_3 deformations), 350–340 (Si-As stretches), and *ca.* 270 cm^{-1} (As-As stretches) and whose ^1H n.m.r. spectrum showed a broad peak at 4.50 p.p.m.

We have no direct evidence for the proposed intermediates 1,1-digermyl-2,2-dimethyldiarsine and its silyl analogue, but a mode of decomposition as in reaction (4) has been observed for the more stable Group IV substituted diphosphines.⁸ Finally tris-trimethylsilyl-, -trimethylgermyl- and -trimethylstannyl-arsines appear to behave similarly and work is in progress to characterise the products and determine the ring sizes.

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