Silylated and Germylated Polyarsines

By J. W. Anderson and J. E. Drake*

(*Department of Chemistry, University of Windsor, Windsor, Ontario, Canada*)

Summary The reaction of trisilyl- or trigermyl-arsine with chloro(dimethyl)arsine leads to the formation of pentasilylcyclopenta-arsine, $(SiH_3As)_5$, or pentagermylcyclopenta-arsine, $(GeH_3As)_5$, respectively; these are the first examples of metalloid-substituted polyarsines.

TRIALKYLARSINES form adducts with trihalogeno-, dihalogeno(organo)- and halogeno(diorgano)-arsines[1] whereas arsine reacts with arsenic trichloride to give hydrogen chloride and arsenic. Primary arsines and dihalogenoarsines undergo the Michaelis–Kohler reaction[2] leading to cyclic arsines, reaction (1).

$$RAsH_2 + RAsCl_2 = \frac{2}{n}(RAs)_n + 2\,HCl \qquad (1)$$

Silicon[3] and tin[4] arsines react in a similar manner to arsenic hydrides, reaction (2).

$$\textit{e.g.}\ Me_3SiAsMe_2 + Me_2AsCl = Me_2AsAsMe_2 + Me_3SiCl \qquad (2)$$

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°. Chlorogermane was evolved in an amount consistent with reaction (3). On warming to room temperature,

$$(GeH_3)_3As + Me_2AsCl = Me_2AsAs(GeH_3)_2 + GeH_3Cl \qquad (3)$$

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

$$Me_2AsAs(GeH_3)_2 = Me_2AsGeH_3 + \frac{1}{n}(GeH_3As)_n \qquad (4)$$

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—800 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—265 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.

$(GeH_3As)_5$ reacted with anhydrous hydrogen chloride to cleave quantitatively the Ge–As bond giving the expected amount of chlorogermane 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, $(SiH_3As)_5$, 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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