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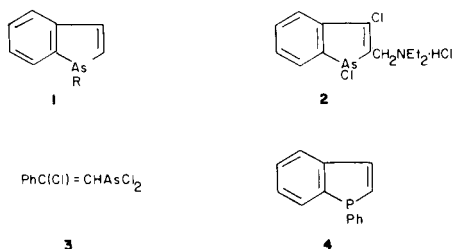
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Received February 25, 1980

The ultraviolet and mass spectra of the title compound have been recorded and compared with those of 2-chloro-2-phenylvinylidichloroarsine (and other chloroarsines). The spectra of the arsindole resemble those of related indoles, phosphindoles and other aromatic heterocyclic systems, and are markedly different from those of the above acyclic chloroarsine, indicating the probable involvement of arsenic in a cyclic π -delocalised system.

J. Heterocyclic Chem., 17, 1341 (1980).

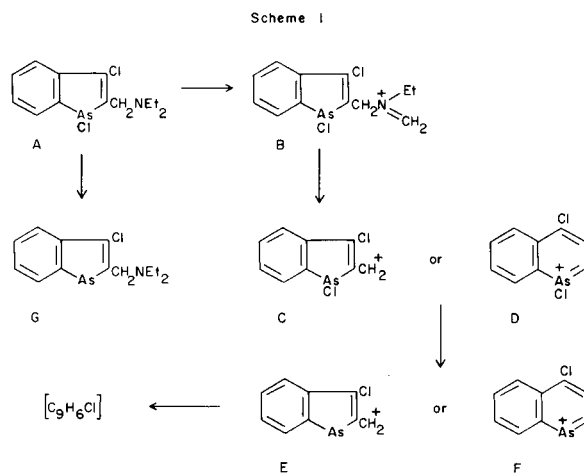
A number of examples of the arsindole (benzo[*b*]arsole) ring system **1** have been known since 1935, yet such compounds have been little studied (1-4). In view of current interest in potentially "aromatic" heterocyclic systems involving the heavier group V elements, we have reinvestigated the arsindole **2**, originally prepared by Mannich in 1935 (1), and report here a study of its ultraviolet spectrum and its behaviour under electron-impact, together with a comparison with the acyclic dichloroarsine **3**, and other heterocyclic chloroarsines investigated previously.



Mannich (1) described the preparation of the arsindole **2** from the reaction of the hydrochloride of 1-diethylaminomethyl(2-phenyl)acetylene with arsenic trichloride, and considerable support for the arsindole structure was obtained by degradative studies. We have repeated Mannich's synthesis to give the arsindole **2**, as the hydrochloride, m.p. 199°. The ^1H nmr spectrum of **2** in trifluoroacetic acid solution is in accord with the arsindole structure. The ultraviolet spectrum of **2** is reproduced in Figure 1 and shows considerable differences in the position of absorption bands compared to the acyclic dichloroarsine **3**, in that in the spectrum of the former there is a shift of the bands to longer wavelength, indicating a greater degree of π -electron delocalisation in the arsindole **2**. The position of the long-wavelength band in the spectrum of the arsindole is similar to the bands in this region observed in the spectrum of the phosphindole **4**, and also in that of the related indole (5) again indicating a delocalised cyclic π -electron system. Evidence for cyclic (4p-2p) π delocalisation in arsindoles has also been obtained from

nmr studies of pyramidal inversion at arsenic (4).

The mass spectrum of the arsindole **2** is presented in Figure 2, and reveals several features of interest, demonstrating the similarity in the behaviour of the arsindole and other five-membered ring aromatic heterocycles. On introduction of the arsindole (as the hydrochloride) into the mass spectrometer, a molecular ion at m/e 331, corresponding to the free arsindole, is observed, providing further support for the suggested structure. The molecule fragments as shown in Scheme 1.



Steps **A** \rightarrow **B** and **B** \rightarrow **C** are supported by the appearance in the spectrum of the appropriate metastable peaks at m/e 302 (Th. 301.7) and 213 (Th. 212.8), respectively. The base peak in the spectrum occurs at m/e 259, corresponding to loss of the diethylamino group from the parent ion. In view of the readiness with which arsenic-chlorine bonds cleave in the mass spectra of the heterocyclic chloroarsines **5** and **6** (6-8), and also in that of the acyclic chloroarsine **3** (Fig. 3), (thereby resulting in very low intensities for ions containing such bonds), the occurrence of the ion at m/e 259 as the base peak in the spectrum of the arsindole is perhaps significant, indicating this ion to be relatively stable.



Thus the ring-expanded structure **D** (Scheme 1), *i.e.* an arsenic analogue of a quinolinium ion, is proposed. It is noteworthy that the mass spectra of the 2-methyl derivatives of indole, furan, thiophen and benzoselenophene all show prominent M-1 peaks for which similar ring-expanded structures have been proposed (9-11). Loss of chlorine then occurs to give an ion of m/e 224 for which a similar ring-expanded structure **F** is likely. This ion then loses arsenic to give an ion of m/e 149.

As indicated above, the mass spectrum of the dichloroarsine **3** is significantly different from that of the arsindole **2**. The molecule fragments readily (Scheme 2) with progressive cleavage of As-Cl and C-As bonds, resulting in very low intensities for ions containing these bonds. The base peak occurs at m/e 102 (phenylacetylene?), corresponding to complete loss of the elements of $AsCl_3$ from the parent ion.

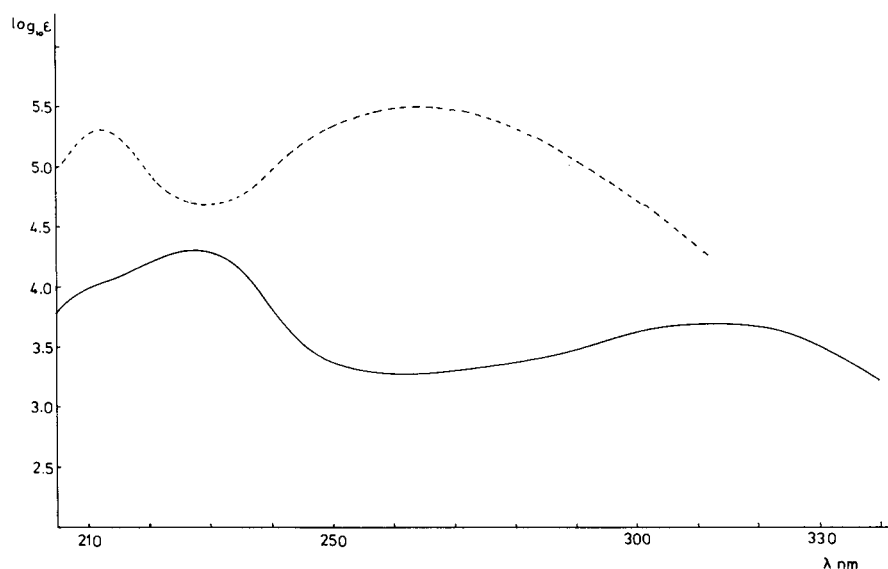
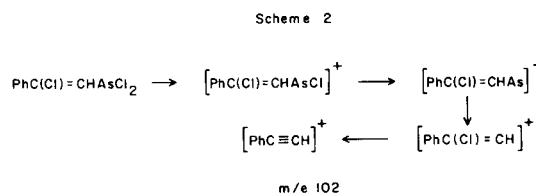


Figure 1. Ultraviolet absorption spectra of the arsindole **2** (——) and 2-chloro-2-phenylvinyl dichloroarsine (**3**) (-----).

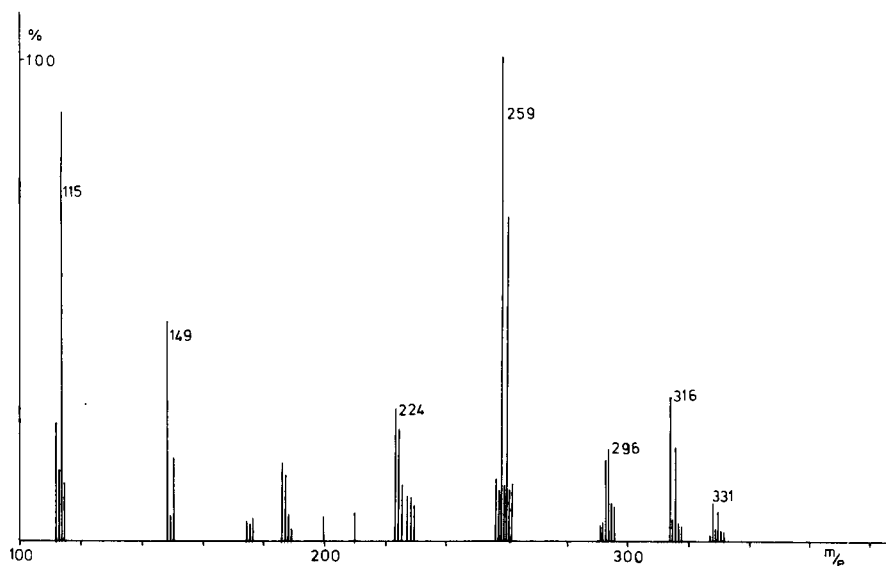


Figure 2. Mass spectrum of the arsindole **2**.

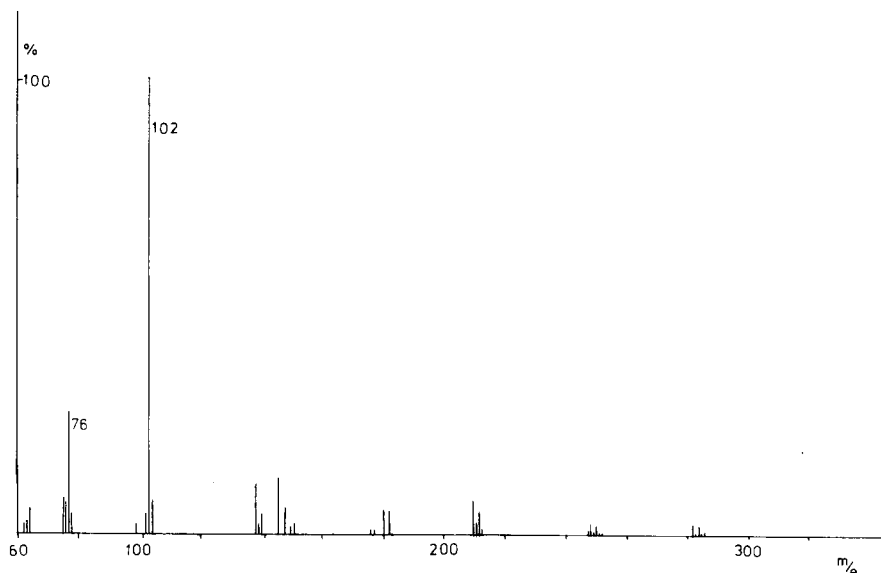


Figure 3. Mass spectrum of the 2-chloro-2-phenylvinylidichloroarsine (**3**).

EXPERIMENTAL

^1H Nmr spectra were recorded at 60 MHz using a JEOL spectrometer. Mass spectra were recorded on an AEI MS 30 instrument at an ionising voltage of 70 eV.

Preparation of Compounds.

The arsindole **2** was prepared as described by Mannich (1), to give crystals (from ethanol) m.p. 199° (lit. (1), m.p. 199°); nmr (trifluoroacetic acid): ppm 8.0-7.5, (m, 4H); 4.65 (d, $^3\text{J}_{\text{HNCH}}$ 6 Hz, 2H); 3.58 (m, 4H) and 1.58 (t, 6H). The ultraviolet spectrum was recorded in ethanol as solvent and is reproduced in Figure 1. The mass spectrum is presented in Figure 2.

2-Chloro-2-phenylvinylidichloroarsine (**3**).

This compound was prepared by the addition of arsenic trichloride to phenylacetylene, as described by Ipatiew *et al* (12), to give crystals m.p. $38-41^\circ$ (lit. (12) m.p. $40-42^\circ$). The ultraviolet spectrum was recorded in ethanol as solvent and is reproduced in Figure 1. The mass spectrum is presented in Figure 3.

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