

Gaseous Bivalent Arsenic Cations

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Summary A mass spectrometric study of a series of heterocyclic arsenic compounds shows that the five-membered cyclic arsenium ions are very stable.

ALTHOUGH there has been considerable interest in the mass spectra of organometallic compounds those containing arsenic appear to have been ignored. We now report our findings on a series of heterocyclic arsenic compounds:

$Y-CH_2CH_2-X-AsR$ where $R=Ph, Et, Me_2N, Et_2N$; $X=O, S$; $Y=O, S$; and $R=Et, Me_2N$; $X=O$; $Y=NMe$.

The most interesting features are:—

(a) In all compounds the group R is readily lost resulting in the bivalent arsenium ion, which, in most cases, is one of the most intense peaks in the mass spectrum (Scheme).

(b) Where $R = \text{phenyl}$ a rearrangement is observed, similar to that found for the analogous boron heterocycles,¹ which leads to the formation of the tropylium ion.

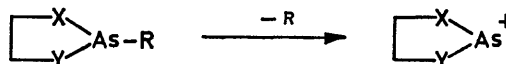
It is interesting that the lone pair on arsenic has the ability to stabilise the five-membered cyclic arsenium ions in contrast to the analogous boron systems where, as yet, little evidence has been found for the formation of five-membered boronium ions.²

Some indication of the stability of the arsenium ions is given in the Table.

¹ R. H. Cragg and J. F. J. Todd, *Chem. Comm.*, 1970, 386.

² J. C. Kotz, R. J. V. Zanden, and R. G. Cooks, *Chem. Comm.*, 1970, 923.

R	Compound			Relative intensity (%)	
	X	Y	Parent	Arsenium ion	
Ph	S		100	32	
Ph	O		4	2	
Ph	O	S	100	50	
Me ₂ N	S		8	32	
Me ₂ N	O	S	29	62	
Me ₂ N	O		43	100	
Et ₂ N	S		3	17	
Et ₂ N	O	S	16	100	
Et ₂ N	O		13	100	
Et	S		43	100	
Et	O	S	37	100	
Et	O		49	100	
Et	NMe	O	16	100	
Me ₂ N	NMe	O	8	100	



SCHEME

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