

Mass Spectra of Organoarsenic Compounds. IV. Electron Impact-induced Fragmentation of 1,3,2-Dioxarsolanes, 1,3,2-Dithiarsolanes and 1,3,2-Oxathiarsolanes

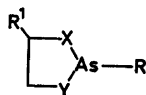
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The electron impact-induced fragmentations of a series of 2-substituted 1,3,2-dioxarsolanes, 1,3,2-oxathiarsolanes, and 1,3,2-dithiarsolanes have been studied. The five-membered cyclic arsenium ion formed by loss of the 2-substituent from the dioxarsolanes appears to be less stable than the corresponding six-membered cyclic arsenium ion formed in the fragmentation of 1,3,2-dioxarsenanes. The stability of the five-membered ring system increases when one or two sulfur atoms are introduced in the ring. The formation of the $[C_7H_7]^+$ ion is discussed.

As a part of our investigation of organic arsenic compounds¹⁻³ we now report the mass spectra (Figs. 1 to 4) of the following 1,3,2-dioxarsolanes, 1,3,2-dithiarsolanes, and 1,3,2-oxathiarsolanes.

In a brief communication⁴ the electron impact-induced fragmentation of IV, VI, and VIII has been reported to give rise to the formation



	R	X	Y	R ¹
I	CH ₃	O	S	H
II	CH ₃	O	S	CH ₃
III	CH ₃	S	S	H
IV	C ₆ H ₅	O	O	H
V	C ₆ H ₅	O	O	CH ₃
VI	C ₆ H ₅	O	S	H
VII	C ₆ H ₅	O	S	CH ₃
VIII	C ₆ H ₅	S	S	H
IX	C ₆ H ₅	S	S	CH ₃

of very stable five-membered cyclic arsenium ions by the ready loss of the 2-substituent. Furthermore a rearrangement leading to the formation of the tropylium ion was observed.

In accordance with these results the $[M-R]^+$ ion gives rise to the base peak in the mass spectra of I, II, and III (Fig. 1) where R=CH₃. However, when R is phenyl (IV to IX) the As-R bond scission is less likely, probably due to $p\pi-p\pi$ interaction of the lone pair electrons on arsenic with the benzene nucleus and consistent with our previous findings.³ In the mass spectrum (Fig. 2) of 2-phenyl-1,3,2-dioxarsolane (IV) the $[C_6H_5As]^+$ ion thus gives rise to the base peak whereas the five-membered cyclic $[M-C_6H_5]^+$ ion has an abundance of only 12%. The corresponding six-membered arsenium ion forms in the fragmentation of 2-phenyl-1,3,2-dioxarsenane the base peak. In this case the $[C_6H_5As]^+$ ion amounts to 42%. For both types of compounds introduction of a methyl group in the heterocyclic ring tends to decrease the abundance of the $[M-C_6H_5]^+$ ion.

Introduction of one or two sulfur atoms in the five-membered ring causes a considerable increase in the stability of the molecular ions and of the $[M-C_6H_5]^+$ ions (Figs. 3 and 4). The difference between the As-O and As-S bond is clearly reflected in the fragmentation of the $[M-C_6H_5]^+$ ion. Thus the oxathiarsolanes (VI and VII) are forming the abundant $[AsS]^+$ ion (m/e 107) by elimination of $R^1C_2H_3O$ ($R^1=H, CH_3$). The corresponding loss of $R^1C_2H_3S$ (to yield the $[AsO]^+$ ion at m/e 91) is here almost

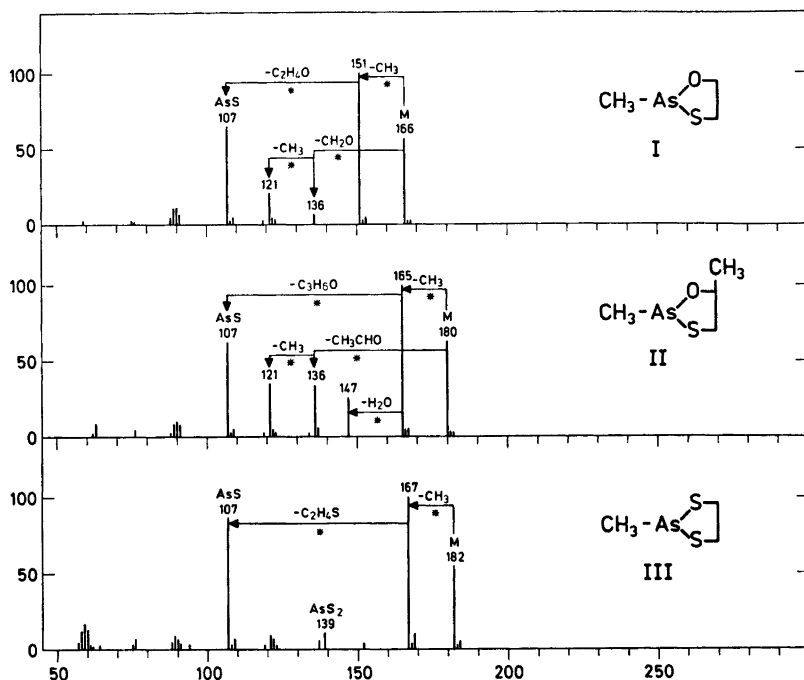


Fig. 1. Mass spectra of I, II, and III.

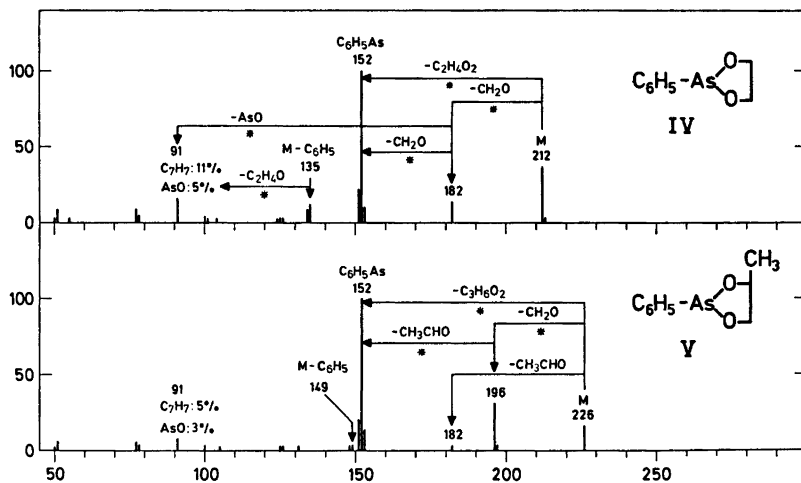


Fig. 2. Mass spectra of IV and V.

negligible. However, in the spectra of the diarsolanes elimination of this fragment leads to the formation of the prominent $[\text{AsS}]^+$ ion.

Formation of $[\text{C}_7\text{H}_7]^+$. Although $[\text{C}_7\text{H}_7]^+$ (most probably the tropylium ion) is formed in

all cases when $\text{R} = \text{C}_6\text{H}_5$ it gives rise to prominent peaks in the spectra of VI and VII only. In these cases it was found to be formed both directly from the molecular ion and indirectly *via* the $[\text{M}-\text{R}^1\text{CHO}]^{+\cdot}$ ion. This suggests that

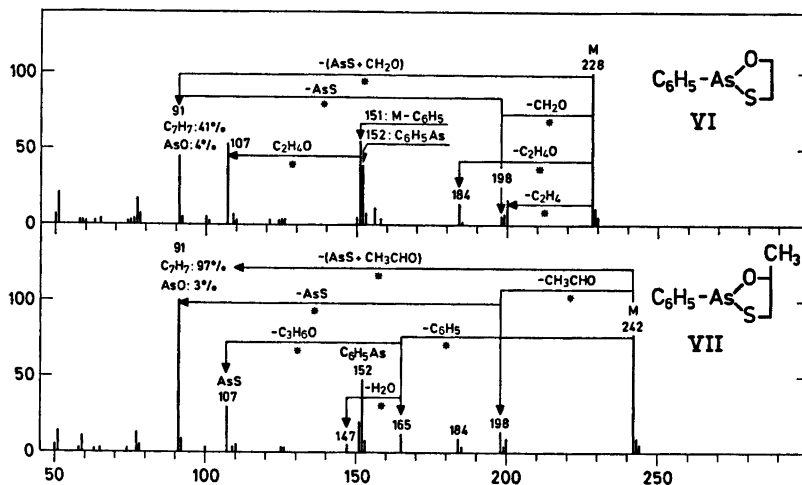


Fig. 3. Mass spectra of VI and VII.

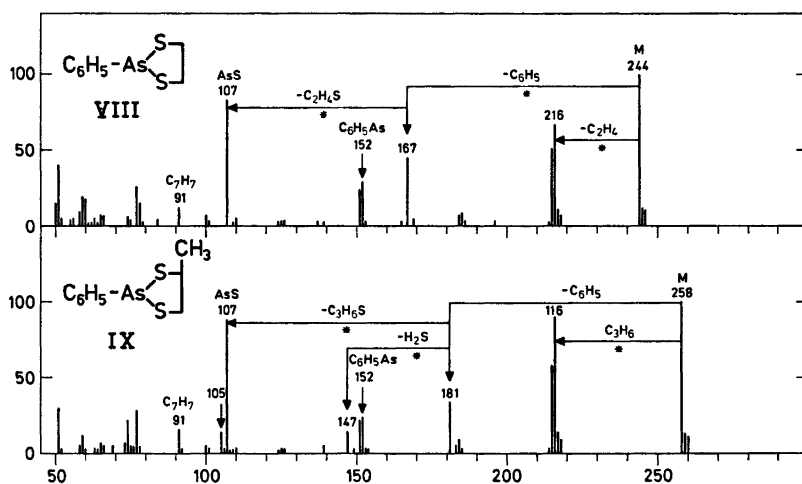
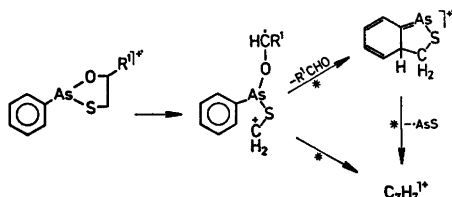


Fig. 4. Mass spectra of VIII and IX.

the primary bond scission occurs at the C—C bond in the heterocyclic ring (Scheme 1). Accordingly, the high abundance (100 %) of the



Scheme 1.

$[C_7H_7]^+$ ion in the fragmentation of VII may be due to preferred fragmentation at the branching point.

The mass spectra of the dioxarsolanes also exhibit ions corresponding to the elimination of $RCHO$ from the molecular ions. The further loss of $\cdot AsO$ yields the $[C_7H_7]^+$ ion. However, in case of V the ion corresponding to the loss of CH_2O is much more pronounced than that corresponding to the elimination of CH_3CHO , and a direct formation of the $[C_7H_7]^+$ ion from the molecular ions of IV and V was not ob-

served. This may suggest that in these cases the primary scission takes place at one of the As—O bonds.

It is notable that ions corresponding to the initial loss of CH_2S are absent in the spectra of the oxathiarsolanes. This was found also to be the case in the spectra of the dithiarsolanes (nor was there observed any loss of CH_2CHS in IX). The spectrum of IX exhibit in addition to the $[\text{C}_7\text{H}_7]^+$ ion a possible methyltropylium ion (m/e 105).

The different ability of the three types of 2-phenyl substituted arsolananes to form the $[\text{C}_7\text{H}_7]^+$ ion may be explained in terms of differences in the As—O and As—S bond energies. (No thermochemical data are available for As—S bonds, but the present mass spectral results strongly suggest that the As—S bond energy is greater than that of the As—O bond).

The higher stability of CH_2O and CH_2CHO as compared to CH_2S^* is probably also reflected in the activation energies for the various fragmentation pathways.

It is interesting that the corresponding 2-phenylborolananes⁷ give rise to the formation of $[\text{C}_7\text{H}_7]^+$ in analogous processes. However, in these cases CH_2S is lost preferentially to CH_2O . As pointed out by the authors,⁷ this behaviour may be attributed to the very large difference in the B—O and B—S bond energies.

Primary ejection of aldehyde was found also to be a characteristic feature upon ionisation of the corresponding phenyl substituted six-membered heterocyclic dioxarsenanes.³ Subsequent ejection of $\cdot\text{AsO}$ leads in these cases to the formation of an $[\text{C}_6\text{H}_5]^+$ ion. The methyltropylium structure has been suggested for this fragment.

An alternative to the loss of thioaldehyde is the elimination of alkene from the molecular ions of VI to IX. In the spectra of VIII and IX this process leads to the important $[\text{C}_6\text{H}_5\text{AsS}_2]^+$ ions. The corresponding $[\text{C}_6\text{H}_5\text{AsOS}]^+$ ion is formed in less abundance in the spectra of VI and VII, whereas the $[\text{C}_6\text{H}_5\text{AsO}_2]^+$ ion could not be detected (Fig. 2).

* The heat of formation of CH_2S and CH_2O are 24^5 and -27^6 kcal/mol, respectively.

The $[\text{C}_6\text{H}_5\text{AsS}_2]^+$ ion (m/e 215, Fig. 4) is formed directly from the molecular ion as well as from m/e 216. It is a precursor for the $[\text{AsS}]^+$ ion (m/e 107).

EXPERIMENTAL

The mass spectra were all recorded with an AEI MS-902 mass spectrometer operating at 70 eV. Samples were introduced through the heated glass inlet system, and the source and sample temperatures were kept as low as possible. The exact mass measurements were made relative to heptacosafuorotributylamine. The metastable defocusing technique has been applied to establish evidence for some of the important transitions not accompanied by metastable ions in the spectra.

The purity of the compounds under investigation was established by elemental analysis. The various arsolananes were prepared according to well known methods,⁸ and were purified by fractional distillation.

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