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

PAUL FRØYEN a and JØRGEN MØLLER b

a Department of Chemistry, University of Bergen, N-5000 Bergen, Norway and b Department of Chemistry, University of Odense, Niels Bohrs Alle, DK-5000 Odense, Denmark

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-dioxasenanes. The stability of the five-membered ring system increases when one or two sulfur atoms are introduced in the ring. The formation of the [C₅H₄]⁺ ion is discussed.

As a part of our investigation of organic arsenic compounds 1-3 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 communication 4 the electron impact-induced fragmentation of IV, VI, and VIII has been reported to give rise to the formation of a 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 pₚ—pₚ interaction of the lone pair electrons on arsenic with the benzene nucleus and consistent with our previous findings 4. In the mass spectrum (Fig. 2) of 2-phenyl-1,3,2-dioxarsolane (IV) the [C₅H₄As]⁺ ion thus gives rise to the base peak whereas the five-membered cyclic [M—C₅H₄]⁺ ion has an abundance of only 12%. The corresponding six-membered arsenium ion forms in the fragmentation of 2-phenyl-1,3,2-dioxasenane the base peak. In this case the [C₅H₄As]⁺ 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—C₅H₄]⁺ 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—C₅H₄]⁺ ions (Figs. 3 and 4). The difference between the As—O and As—S bond is clearly reflected in the fragmentation of the [M—C₅H₄]⁺ ion. Thus the oxathiarsolanes (VI and VII) are forming the abundant [AsS]⁺ ion (m/e 107) by elimination of R'C₅H₄O (R'=H, CH₃). The corresponding loss of R'C₅H₄S (to yield the [AsO]⁺ ion at m/e 91) is here almost
negligible. However, in the spectra of the dithiarsolanes elimination of this fragment leads to the formation of the prominent [AsS]$^+$ ion.

Formation of [C$_3$H$_7$]$^+$. Although [C$_3$H$_7$]+ (most probably the tropylium ion) is formed in all cases when R = C$_4$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 [M-RCHO]+ ion. This suggests that

the primary bond scission occurs at the C–C bond in the heterocyclic ring (Scheme 1). Accordingly, the high abundance (100 %) of the $[{\text{C}_7\text{H}_8}\text{H}]^+$ 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 \( \cdot\text{AsO} \) yields the \( [{\text{C}_7\text{H}_8}\text{H}]^+ \) ion. However, in case of V the ion corresponding to the loss of CH$_3$O is much more pronounced than that corresponding to the elimination of CH$_3$CHO, and a direct formation of the \( [{\text{C}_7\text{H}_8}\text{H}]^+ \) ion from the molecular ions of IV and V was not ob-

Scheme 1.

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 CH₂S 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 CH₃CHS in IX). The spectrum of IX exhibit in addition to the
[CH₃H₂]⁺ ion a possible methyltropylium ion (m/e 105).

The different ability of the three types of 2-phenyl substituted arsolenes to form the
[CH₃H₂]⁺ 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 CH₂O and CH₂CHO as compared to CH₂S⁺ is probably also reflected in the activation energies for the various fragmentations pathways.

It is interesting that the corresponding 2-phenylborolanes give rise to the formation of
[CH₃H₂]⁺ in analogous processes. However, in these cases CH₂S is lost preferentially to CH₂O.
As pointed out by the authors, 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. Subsequent ejection of AsO leads in these cases to the formation of an [CH₃H₂]⁺ 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 [CH₃H₂AsS₂]⁺ ions. The corresponding [CH₃H₂AsOS]⁺ ion is formed in less abundance in the spectra of VI and VII, whereas the [CH₃H₂AsO₃]⁺ ion could not be detected (Fig. 2).

The [CH₃H₂AsS₂]⁺ 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 [AsS]⁺ ion (m/e 107).

EXPERIMENTAL

The mass spectra were all recorded with an AEI MS-802 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 heptacosaffluorotributylamine. 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 was established by elemental analysis. The various arsolenes were prepared according to well known methods, and were purified by fractional distillation.

REFERENCES

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Received July 1, 1974.

* The heat of formation of CH₂S and CH₂O are 24 ² and —27 ² kcal/mol, respectively.