Electron Impact Induced Chemistry of Styryl Sulphoxides

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ELECTRON impact induced structural rearrangements involving migration of an aryl group from sulphur to oxygen as well as SO and/or SOH loss have been noted in the same spectra of aryl sulphoxides,[1] sulphones[1-3] and sulphonamides.[4] Alkyl sulphoxides do not appear to undergo these rearrangements.[5] It is not clear from the mass spectrum of methyl vinyl sulphoxide, the only acyclic vinyl sulphoxide reported,[6] how important either of the above mentioned rearrangement processes is since the elemental composition of the *m/e* 42 ion was not determined.†

We have investigated the series of methyl styryl sulphoxides (I), only recently made conveniently available,[7] with two major aims, (i) to assess the relative importance of vinyl group migration compared to the rearrangement loss of SO, or a migration of the aryl group to oxygen, (ii) to compare the gas-phase ion chemistry of the styryl sulphoxide group with the structurally similar styryl nitro-compounds,[8] azoxy-compounds,[9] and nitrones,[10] particularly with regard to attack of the oxygen atom on the aromatic ring.

The fragmentation pattern of (Ia) is shown in the Scheme. The intense $M-$CO, $M-$CHO, and $M-$SMe ions require that extensive structural rearrangement occur in the molecular ion. The spectra of the deuteriated compounds (If) and (Ig) clearly establish that the *m/e* 118 ion of (Ia) is due entirely to $M-$SMe$-$HMe rather than $M-$SO as has been observed in aryl sulphoxides.[1] The sulphenate ion (II) is the most likely intermediate ion in this process, since the alternative ion (III) exhibits a completely different fragmentation pattern.

The structure of the *m/e* 119 ion ($M-$SMe) is of considerable interest. The benzyl acylium ion (IV) must be considered unlikely since this ion, when generated from (III), does not lose a hydrogen atom as does the *m/e* 119 ion from (Ia). Furthermore, since *only* H (as opposed to some D) loss occurs in the analogous process (121 → 120) in (Ig), ion (V) is considered likely, with *m/e* 118 having the benzofuran structure.

The carbon atom contained in the CHO radical lost from the molecular ion of (Ia) is undoubtedly the vinyl carbon atom β to the benzene ring, since this ion shifts cleanly to $M-$CDO in (Ib) and (Ig). The same carbon is presumably lost as CO, since little CO is lost from (VI). This behaviour contrasts with that of similar systems[8-10] in which an aromatic ring carbon is lost.

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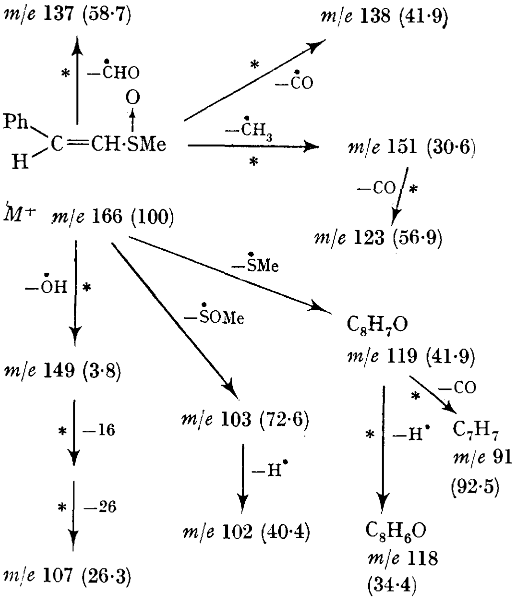
† Loss of SO would produce a C_3H_6 ion, while vinyl migration to form a C–O bond, followed by loss of SMe and H would produce a C_2H_2O ion.

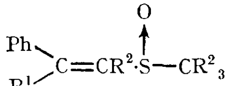
Such an aromatic carbon might well be lost in the process producing CO loss from the $M-15$ ions of (I).

In the remaining important fragmentation of (Ia), that is, the loss of OH from the molecular ion, the source of the hydrogen atom must be the aromatic ring, based on the spectra of (Ib), (If), and (Ig). This behaviour parallels that of similar compounds,[8-10] although the greatly enhanced intensity of the $M-OH$ ions in the spectra of (Ic) and (Id) indicate hydrogen abstraction is also occurring from the alkyl group in these cases.

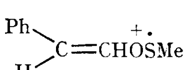
Spectra were measured using an Atlas CH4 mass spectrometer‡ with a direct solid inlet system. With heated inlet systems, pronounced thermal effects were noted. We are at present studying the thermolysis of (I). Preliminary results indicate that benzofuran is formed from (Ia), suggesting a close parallel with electron impact behaviour.

SCHEME

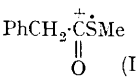




	R¹	R²
(I)a	H	H
b	D	H
c	Me	H
d	Et	H
e	Ph	H
f	H	D
g	D	D



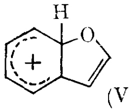
(II)



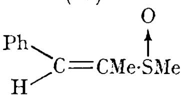
$PhCH_2\cdot\overset{+\bullet}{C}SMe$ with $\overset{\|}{O}$ (III)

$PhCH_2\cdot C\equiv\overset{+}{O}$

(IV)



(V)



(VI)

(*Received, June 10th, 1968; Com. 760.*)

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‡ We thank the National Science Foundation for financial assistance in the purchase of this instrument.

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