Thiirenium Ion as Intermediate in Unimolecular Reactions of β-Arylthiovinyl Sulphonic Esters

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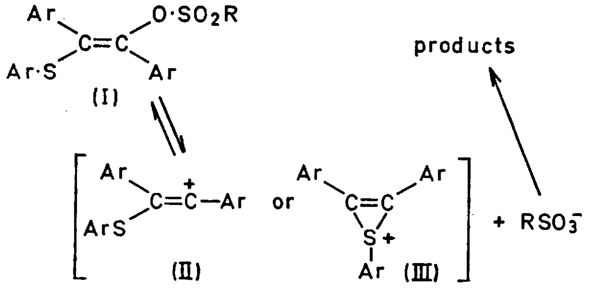
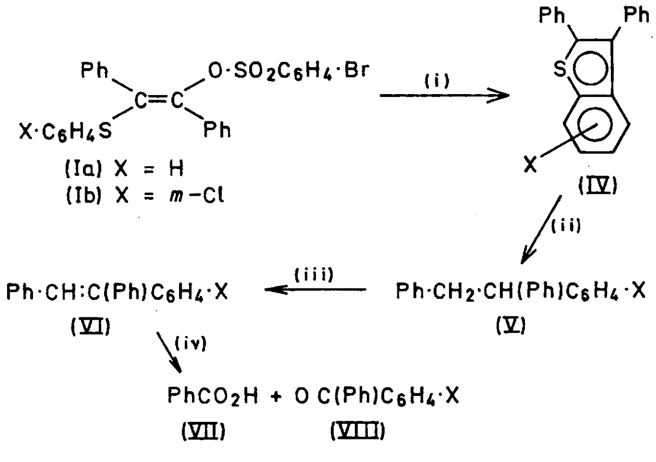
Summary The equilibration of the two ethylenic carbons and the stereospecificity observed in unimolecular reactions of β-arylthiovinyl sulphonates (I) are explained by the intermediacy of a thiirenium cation (III).

WE showed on the basis of chemical and kinetic arguments[1] that β-arythiovinyl sulphonic esters (I) react *via* an S_N1-type mechanism to generate a cationic intermediate which was indicated either as an open vinyl cation (II) or as a thiirenium cation (III).



We now present compelling evidences that along the reaction path from (I) to the products, the cyclic cationic species (III) is formed. This is the first demonstration of the existence, at least as an intermediate, of thiirenium cations. They have been postulated as intermediates of the addition of sulphenyl halides to acetylenes.[2] Volpin[3] suggested that rings of this kind may be stabilized by *p–p–d* interaction.

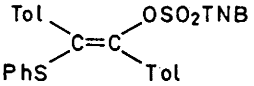
Three experimental approaches were followed. (i) We prepared by an unambiguous route the *p*-bromobenzenesulphonates (Ia) and (Ib) labelled with ^{14}C at the α-position.

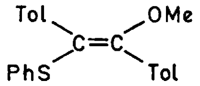


i; BF_3–CH_2Cl_2, $-Br{\cdot}C_6H_4{\cdot}SO_3H$. ii; Raney nickel. iii; *N*-bromosuccinimide, −HBr. iv; $KMnO_4$.

The fate of the label in the cyclization products, the benzo[*b*]thiophen derivatives (IV), was determined through the reaction sequence below.

Vitrually the same ^{14}C content was found in the benzoic acid (VII) and in the benzophenone derivative (VIII). Since careful control experiments showed that no scrambling occurs in the sequence from (V) to (VII) and (VIII), the two ethylenic carbons must become equivalent during the cyclization reaction. (ii) The trinitrobenzenesulphonate (Ic) obtained as described elsewhere[1a] in one geometric form, presumably of *trans*-configuration, afforded in 4 : 1 acetone–methanol at 25° the solvolysis product, the vinyl methyl ether (IXc) as a pure (at least 97% by ^1H n.m.r.) geometric isomer in 80—90% yield. This isomerizes easily in weakly acidic media to give a 1 : 1 mixture of the two geometric isomers, as measured by ^1H n.m.r. spectroscopy. Hence (IXc) is the kinetically controlled product.

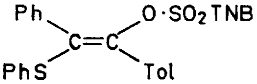




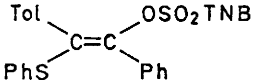
(Ic) TNB = 2,4,6-trinitrophenyl (IXc)

At variance with the above results, Rappoport[4] recently showed that the unimolecular solvolysis of triarylvinyl halides occurs with complete "racemization" and without any substantial β-aryl assistance. The stereospecificity here observed, plausibly involving "retention" of configuration, suggests that the β-sulphur acts as configuration holder through structures of type (III).

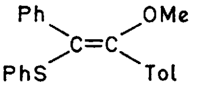
(iii) The pair of structural isomers (Id) and (Ie) were obtained by stereospecific addition of benzenesulphenyl trinitrobenzenesulphonate to *p*-methyltolan in a ratio of about 3—4 : 1.† Mixtures enriched in (Ie) were obtained by partial destruction of the more reactive (Id) under controlled conditions. Solvolysis in 4 : 1 acetone–methanol at 25° of two different mixtures of (Id) and (Ie) (3·1 : 1 and 1 : 2 respectively) gave the same mixture of the two isomeric vinyl ethers (IXd) and (IXe) in the ratio of 4·5 : 1 (by ^1H n.m.r.) in 80—85% overall yield.



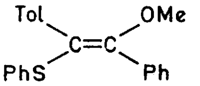
(Id)



(Ie)



(IXd)



(IXe)

Clearly, the solvolysis of both (Id) and (Ie) occurs *via* the same cationic species. It is remarkable that a similar

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† Measured by a kinetic technique[5] on recrystallized material. Since crystallizations involve loss of the more reactive isomer (Id), the ratio in the crude product is estimated as nearly 4—5 : 1.

ratio of α-tolyl to β-tolyl derivatives is obtained both in the solvolysis of the asymmetric sulphonates and in the addition of sulphenyl sulphonate to the methyltolan and that both reactions are stereospecific; these facts would suggest that the same cation is involved in the two processes.

A cyclic structure (III) for this cationic entity reasonably explains all the above experimental facts. Alternatively they could be interpreted in terms of a very fast equilibrium among almost isoenergetic cationic structures (IId), (IIe), and (III). In fact, there is no definite proof that the thiirenium ion is the only kinetically relevant intermediate in the reaction of (I). However, as far as the demonstration of the formation of (III) is concerned the difference is more one of degree than of kind.

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[2] For a review: G. Modena and G. Scorrano in "Mechanisms of Reactions of Sulfur Compounds," ed. N. K. Kharasch, B. S. Thyagarajan, and A. I. Khodair, Intra-Science Research Foundation, Santa Monica, California, 1969, vol. 3.

[3] M. E. Volpin, Yu. D. Koreshkov, V. G. Dulova, and D. N. Kursanov, *Tetrahedron*, 1962, **18**, 107.

[4] Z. Rappoport and A. Gal; Z. Rappoport and Y. Apeloig, papers submitted for publication in *J. Amer. Chem. Soc.*; we thank these authors for providing preprints.

[5] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd edn., Wiley, New York, 1961, pp. 162—164.