Pyrolysis of Styryl Sulphoxides and Sulphides. Formation of Benzothiophen Derivatives *via* Intramolecular Cyclization of Thiyl Radicals

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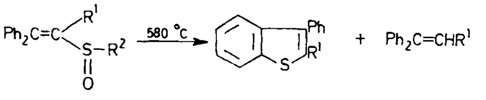
Summary The pyrolysis of styryl sulphoxides yields benzothiophens in 40—50% yield, indicating that intramolecular cyclization of the styrylthiyl radical, which may be formed by homolysis of the S–OH bond of an intermediate sulphenic acid, is a favourable process; pyrolysis of styryl sulphides, and bis-(β-methyl styryl) disulphide also gave benzothiophens under similar conditions.

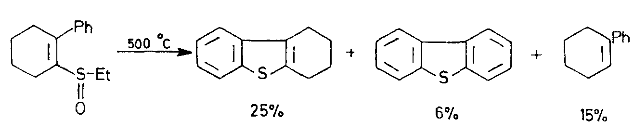
ALTHOUGH thiyl radicals add readily to various olefinic systems, additions to aromatic systems occur only under special circumstances. The failure to obtain addition can be ascribed to the unfavourable energetics involved in disrupting the aromatic system. Several examples of addition of thiyl radicals to aromatic systems are now known, but these were all additions to the 9,10-position of anthracenes.[1]

Recently, we found that pyrolyses of styryl sulphoxides produced benzothiophen derivatives, probably *via* formation



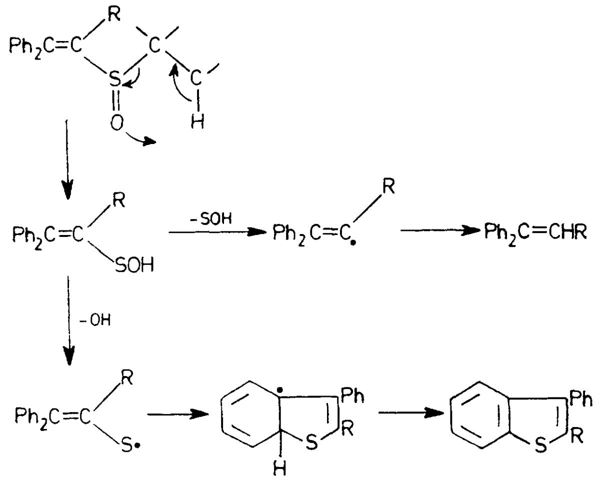
(I) (II) (III)

a, R^1=H, R^2=Et; b, R^1=Me, R^2=Et; c, R^1=Me, R^2=Pr^i



(IV)

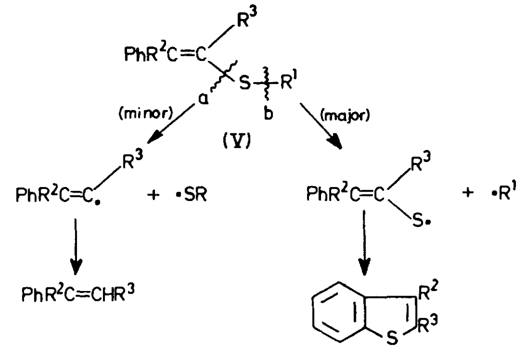
of a sulphenic acid[2] followed by cleavage to styrylthiyl and hydroxyl radicals, the benzothiophen being formed finally by addition of intermediate thiyl radicals to the benzene ring. If this mechanism is correct, this is the first example of intramolecular addition of thiyl radicals to a benzene ring.



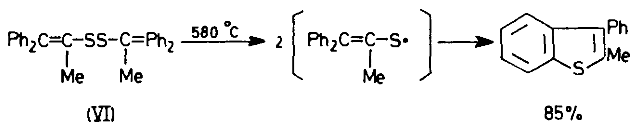
Ethyl α-phenylstyryl sulphoxide (Ia) in excess of benzene was pyrolysed in a nitrogen flow system (30 ml/min; 580 °C) and the pyrolysate was collected at —78 °C. Analysis of the pyrolysate by g.l.c. revealed two major products and absence of the starting sulphoxide (Ia). Separation of the products by preparative chromatography afforded 3-phenylbenzothiophen (IIa) (47% yield) and 1,1-diphenylethylene (IIIa) (12%). The structures of these products were confirmed by comparison of their i.r. and n.m.r. spectra with those of authentic samples.

Similar pyrolyses of the ethyl (Ib) and isopropyl (Ic) sulphoxides gave the benzothiophen (IIb) in 42 and 47% yields, respectively, together with some 1,1-diphenyl-2-methylethylene and other olefins. Under the same conditions, pyrolysis of the sulphoxide (IV) with benzene at 500 °C gave tetrahydrodibenzothiophen (25% yield), dibenzothiophen (6%), and 1-phenylcyclohexene (15%).

The large amount of benzothiophen obtained from the pyrolysis of styryl sulphoxides indicates that the intramolecular cyclization of the styrylthiyl radical, which may be formed by homolysis of the sulphur–hydroxy bond of the intermediate sulphenic acid, is a favourable process.† The radical resulting from addition to the aromatic ring can be stabilized not only by the two remaining double bonds in the original aromatic ring but also by the double bond and sulphur atom in the five-membered ring. The minor product, 1,1-diphenylethylene, no doubt arose from hydrogen abstraction by the styryl radical obtained in the homolysis of the carbon-sulphur bond.



a; $R^1 = R^3 = Me$, $R^2 = Ph$
b; $R^1 = Pr^i$, $R^2 = Ph$, $R^3 = Me$
c; $R^1 = Et$, $R^2R^3 = -[CH_2]_4-$
d; $R^1 = Et$, $R^2 = Ph$, $R^3 = H$
e; $R^1 = Et$, $R^2 = H$, $R^3 = Me$



The intramolecular addition of the thiyl radical is supported further by the results of the pyrolyses of alkyl styryl sulphides and styryl disulphide. Pyrolysis of the sulphide (Va) with excess of benzene at 580 °C gave 2-methyl-3-phenylbenzothiophen in 33% yield together with a trace of diphenylethylene. A number of styryl sulphides were then examined, all of which gave the corresponding benzothiophen derivatives in 50—70% yield, and a trace of styrene derivatives. The *cis*- and *trans*-β-ethylthio-β-methylstyrenes (Ve) also gave 2-methylbenzothiophen in 40—50% yields. The styryl disulphide (VI) under similar conditions gave 2-methyl-3-phenylbenzothiophen in 85% yield.

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† In view of the various resonance structures possible for the original thiyl radical one can also regard the reaction as not necessarily being an addition of a thiyl radical to the ring, but, alternatively, as addition of a carbon radical to a >C=S group.

[1] A. L. J. Beckwith and B. S. Low, *J. Chem. Soc.*, 1964, 2571; *Austral. J. Chem.*, 1967, **17**, 109; R. M. Kellog, M. B. Groen, and H. Wynberg, *J. Org. Chem.*, 1967, **32**, 3903.

[2] J. R. Shelton and K. E. Davis, *J. Amer. Chem. Soc.*, 1968, **89**, 718; E. Block and J. O'Connor, *ibid.*, 1974, **96**, 3929 and references cited therein.