Interception of Sulphenate Esters formed in the Rearrangement of Sulphoxides

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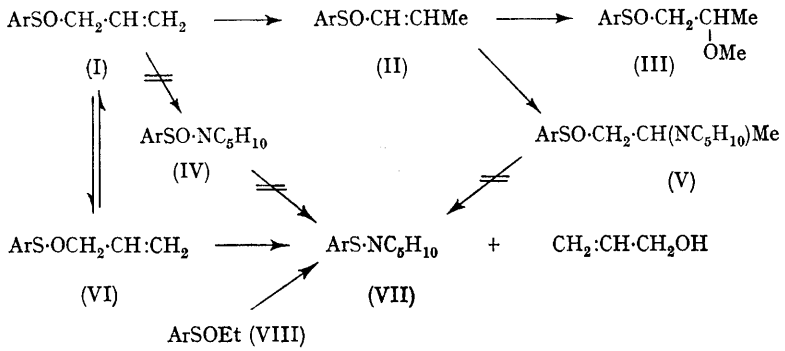
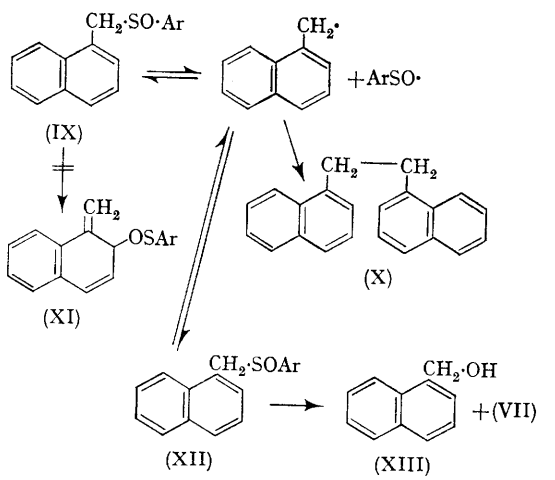
IN a study of reactions of unsaturated sulphoxides with nucleophiles, we found that allyl *p*-tolyl sulphoxide (I), on treatment with methanolic sodium methoxide at 65°, gave the adduct (III)† (84%) by the expected[1] sequence of isomerisation of (I) to the propenyl isomer (II) and subsequent addition. By contrast, treatment of the sulphoxide (I) with an excess of piperidine in chlorobenzene at 98° gave none of the adduct (V), although allylic alcohols and sulphenyl halides, are derived from the initially formed allylic sulphenates, which subsequently rearrange. Although no equilibrium amount of sulphenate has been detected, it is evident that piperidine, by nucleophilic displacement at S in the ester, diverts the sulphenate from regeneration of the sulphoxide. Formation of sulphenamides by reaction of sulphenates with amines does not appear to have been reported, and



similar treatment (in methanol) of the propenyl isomer‡ (II) gives the adduct§ (V) in high yield. Instead, the main products are allyl alcohol (77%) and toluene-*p*-sulphenopiperidide (VII) (68%), together with a trace of di-*p*-tolyl disulphide. With methanol as solvent, reaction at 60° gives the sulphenamide (46%), allyl alcohol (70%), a trace of disulphide, and the adduct (V) (8%).

The sulphenamide does not arise from (I) by displacement at sulphur followed by oxygen transfer (I → IV → VII); the sulphinamide (IV) is stable under the reaction conditions. The adduct (V) is also stable and no decomposition of the sulphoxide (I) occurs in the absence of piperidine.

Our observations are entirely in accord with the suggestion[2] that rapid racemisation of allyl *p*-tolyl sulphoxide proceeds *via* reversible cyclic rearrangement to the sulphenate (VI), and with the conclusion[3,4] that allylic sulphoxides, obtained from



† Mixture of diastereoisomers.

‡ *cis–trans*-Mixture (approximately 50 : 50) obtained by treatment of allyl *p*-tolyl sulphide with potassium t-butoxide in t-butyl alchohol and subsequent oxidation of the mixture of isomeric propenyl sulphides (C. C. Price and W. H. Snyder, *J. Org. Chem.*, 1962, **27**, 4639.)

§ Mixture of diastereoisomers from which that of m.p. 90° was isolated in 56% yield.

nucleophilic displacement in sulphenates has, in general, received little attention.[5] Because of its rapid rearrangement, allyl toluene-*p*-sulphenate is not available,[3] but we showed that ethyl toluene-*p*-sulphenate (VIII), on treatment with piperidine, readily gave the sulphenamide (VII) (84%) and ethanol (76%).

Formation of a small amount of adduct (V), when the reaction with piperidine is carried out in methanol, indicates that, in this solvent, prototropic isomerisation of the allylic sulphoxide to the propenyl sulphoxide and subsequent addition of piperidine can compete with attack of the amine on the sulphenate. When the more strongly basic methoxide ion is the nucleophile, prototropy is very rapid and the rearrangement pathway is not observed.

Preliminary work has shown that 1-naphthylmethyl *p*-tolyl sulphoxide (IX) also gives the sulphenamide (VII) on treatment with piperidine in chlorobenzene at 132°. This product is doubtless derived from an intermediate sulphenate ester which probably has structure (XII) as the alcohol (XIII) is also obtained. Formation of the ester (XII) is consistent with suggestions[2] that benzylic sulphoxides racemise *via* a homolytic dissociation[6]—recombination mechanism and isolation, in our work, of the dimer (X) is substantiative. We have excluded formation of the isomeric sulphenate (XI) which might result from a cyclic rearrangement and which would also give the sulphenamide (VII) on reaction with piperidine. In this case, the complementary product would be a tautomer of 1-methylnaphth-2-ol. No phenolic product was obtained.

(*Received, December 13th*, 1967; *Com.* 1335.)

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[4] S. Braverman and Y. Stabinsky, *Chem. Comm.*, 1967, 270.
[5] C. Brown and D. R. Hogg, *Chem. Comm.*, 1967, 38.
[6] W. Carruthers, I. D. Entwistle, R. A. W. Johnstone, and B. J. Millard, *Chem. and Ind.*, 1966, 342.