

Desulphurization of Episulphides by Phenyl Radicals

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Summary Reaction of phenyl radicals with episulphides results in the formation of alkenes with loss of the thiophenoxy-radical.

FORMATION of β -phenylthio-radicals (2), by abstraction of β -protons in alkyl phenyl sulphides¹ or by homolysis of carbon-sulphur bonds in 1,2-bis(phenylthio)ethanes,^{2,3} often results in the production of alkenes *via* the elimination of thiophenoxy-radicals. A major question in these studies concerns the intermediacy of a symmetrically bridged radical (3). We report here a similar free-radical

elimination in which the intermediate is generated by reaction of a phenyl radical with an episulphide. Phenyl radicals were generated by the thermolysis of phenylazotriphenylmethane (PAT) in the episulphide. The volatile alkenes were swept from the reaction mixture in a stream of nitrogen and trapped at -195° . The Table gives the yields of alkenes resulting from these reactions and from the reactions of phenyl radicals with selected alkyl phenyl sulphides. Thiophenoxy-radicals were trapped primarily as phenyl disulphide and phenyl tritylsulphide. Strausz and his co-workers have reported the gas-phase desulphurization of episulphides by methyl radicals.⁴

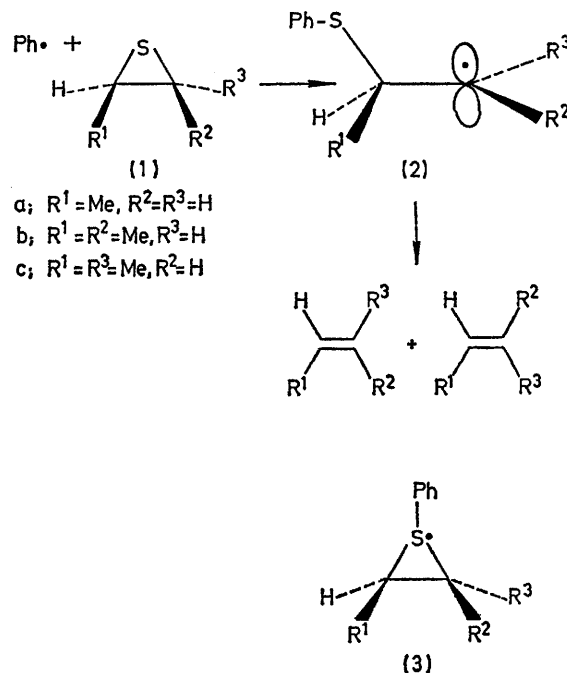
In order to test whether this reaction proceeds *via* the open-chain radical (2) or directly from a bridged intermediate (3), the stereochemistry of desulphurization of the

TABLE. Alkene yields in the reaction of phenyl radicals with sulphides; [PAT] = 0.19M

Sulphide	[Alkene] [PAT]	Alkene* (% of total)
(1a)	1.09	(A) (100)
(1b)	0.84	(B) (74.1); (C) (25.9)
(1c)	1.01	(B) (18.3); (C) (81.7)
Pr ⁿ SPh	0.10	(A) (100)
Pr ⁱ SPh	0.04	(A) (100)
Bu ^s SPh	0.16	(D) (14); (B) (28); (C) (58)

* Alkene yields were determined by gas chromatography. (A) = propene; (B) = *cis*-but-2-ene; (C) = *trans*-but-2-ene; (D) = but-1-ene.

cis- and *trans*-but-2-ene episulphides (1b) and (1c) has been measured. The results (see Table) show that the alkenes are not formed stereospecifically. This indicates that desulphurization must proceed *via* an intermediate such as (2) in which rotation about the central carbon-carbon bond is possible. A control experiment in which *cis*-but-2-ene was slowly bubbled through a reacting mixture of phenyl radicals and propylene episulphide shows no isomerization of the recovered butene. Hence, the *cis*- and *trans*-but-2-enes are not isomerized after formation. These stereochemical results are in direct contrast to the anionic desulphurization of episulphides which is not thought to involve an open-chain intermediate and is completely stereospecific.⁵ Intermediate (2) may also be generated by



abstraction of a β -hydrogen from the appropriate alkyl phenyl sulphide. The Table shows that production of (2) by this pathway also results in elimination.

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