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.

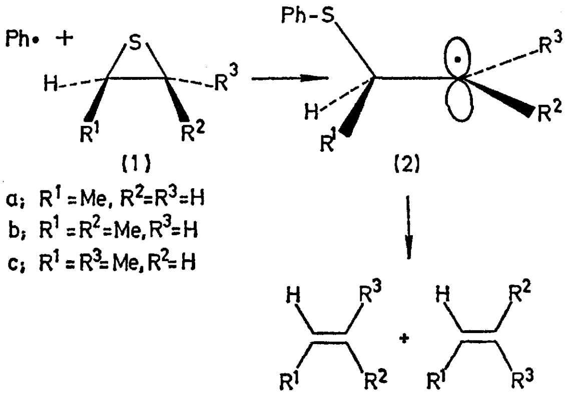
FORMATION of β-phenylthio-radicals (**2**), by abstraction of β-protons in alkyl phenyl sulphides[1] or by homolysis of carbon–sulphur bonds in 1,2-bis(phenylthio)ethanes,[2,3] often results in the production of alkenes *via* the elimination of thiophenoxy-radicals. A major question in these studies 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]

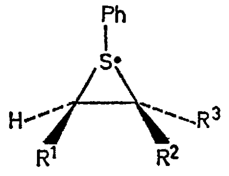
In order to test whether this reaction proceeds *via* the open-chain radical (**2**) or directly from a bridged intermediate (**3**), the stereochemistry of desulphurization of the *cis*- and *trans*-but-2-ene episulphides (**1b**) and (**1c**) has been measured. The results (see Table) show that the 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.

TABLE. Alkene yields in the reaction of phenyl radicals with sulphides; [PAT] = 0·19M

Sulphide	[Alkene] [PAT]	Alkene[a] (% 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)
$\mathrm{Pr^nSPh}$	0·10	(**A**) (100)
$\mathrm{Pr^iSPh}$	0·04	(**A**) (100)
$\mathrm{Bu^sSPh}$	0·16	(**D**) (14); (**B**) (28); (**C**) (58)

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





(3)

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