Thione Photochemistry: Cyclopropanethiol Formation from Arylalkyl Thiones

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Summary Excitation into the $\pi^* \leftarrow n$ band of arylalkyl thiones having an activated β position leads to the formation of cyclopropanethiols.

The formation of cyclopropyl derivatives by cyclisation has rarely been documented in the photochemistry of ketones or thiones. With ketones it is restricted to a very few complex systems,[1] and the mechanisms of these are unclear. Hydrogen abstraction from the β position has also been reported in certain allylic systems where stereochemical rigidity facilitates transfer, but the abstraction is not followed by cyclopropanol formation.[2] On the other hand photochemical cyclopropanethiol formation, a synthetically valuable process since access to these substances is difficult, has only been reported following specific excitation into the S_2 state in alicyclic, rigid, bridged, bicyclic systems.†[3] We report here examples of the cyclisation of arylalkyl thiones having an activated β position following excitation into the $\pi^* \leftarrow n$ band.

All irradiations were performed through a filter permitting the passage of light $\lambda > 460$ nm.[4] The thione (**1a**),‡ when irradiated for 12 h in benzene solution, gave, in virtually quantitative yield, the thiol (**2a**), m.p. 56 °C, which was characterised as the 3,5-dinitrobenzoate (**2b**). Similarly, the 2-naphthyl derivative (**1b**) gave the thiol (**2c**), m.p. 116 °C.

The formation of a fused system is illustrated by the conversion of (**3**) into (**4a**). In this instance the opening

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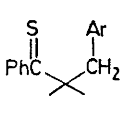
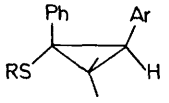
† An exception is the formation of cyclopropanethiol itself by the photolysis of carbon disulphide in cyclopropane: A. R. Knight, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, 1963, **85**, 1207.

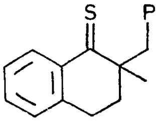
‡ Adequate analyses of precise mass determinations and consonant i.r., u.v., n.m.r., and mass spectroscopic data were obtained for all new substances.



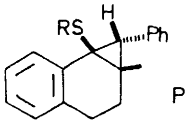
(1) a; Ar = Ph
b; Ar = β-naphthyl



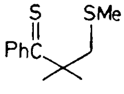
(2) a; Ar = Ph; R = H
b; Ar = Ph; R = 3,5-$(NO_2)_2C_6H_4CO$-
c; Ar = β-naphthyl; R = H



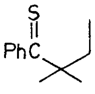
(3)



(4) a; R = H
b; R = Ac



(5)



(6)

of the thiol (presumably because of increased strain) was indicated by the formation of a blue colour on standing. The substance was characterised after acetylation (AcCl–pyridine at −50 °C) to (**4b**), m.p. 75 °C. The low-field chemical shift of one of the tetralin benzylic protons in (**4b**) clearly indicates its proximity to the phenyl group and hence the indicated stereochemistry.

The cyclisation is not, apparently, limited to substances where the β position is activated by an aromatic nucleus. The thione (**5**) gave the corresponding thiols as a mixture of stereoisomers (1 : 3). On the other hand activation of the β position is required for reaction to occur; the thione (**6**) is known to be unreactive.[5]

The reason for the difference in behaviour between thiones and ketones is not clear, except for the ketone related to (**1b**), which could be inactive because of triplet energy transfer. However, the ketone related to (**1a**), for instance, undergoes only a slow Type I cleavage. Quenching by addition to, and elimination from, the aromatic rings is conceivable (a form of chemical internal conversion) but such a process is equally conceivable for thiones since a related addition has already been observed.[6] Electron-transfer processes,[7] whilst not excluded, seem unlikely at least for (**1a**) and, assuming the reaction proceeds in all cases by the same mechanism, a simple rationalisation may be that the greater size of the *n* 3*p* orbital makes H abstraction more easy.

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[3] D. S. L. Blackwell, and P. de Mayo, *J.C.S. Chem. Comm.*, 1973, 130; D. S. L. Blackwell, Thesis, University of Western Ontario, 1975.

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[7] S. G. Cohen and S. Ojanpera, *J. Amer. Chem. Soc.*, 1975, **97**, 5633, and references therein.