

Thio-Claisen Rearrangement of Allyl Aryl Sulphoxides

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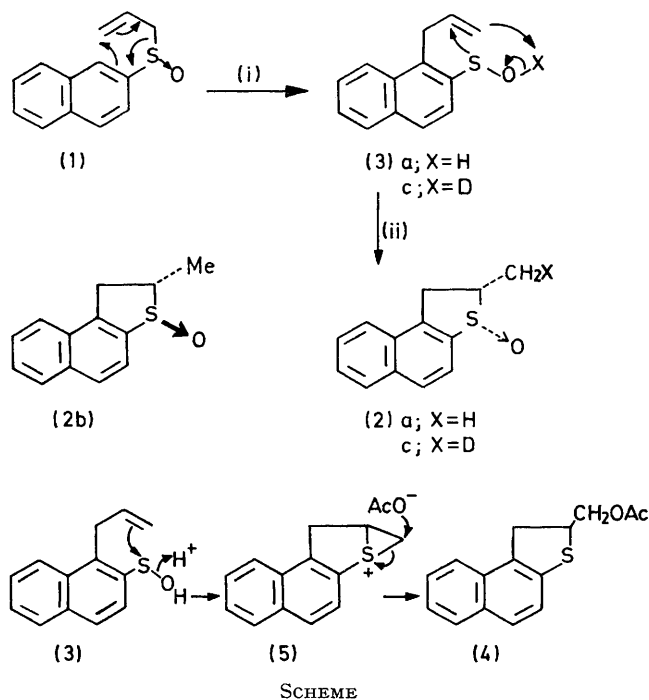
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Summary Allyl 2-naphthyl sulphoxide undergoes thermal rearrangement to give a dihydronaphthothiophen derivative.

THE thio-Claisen rearrangements of allyl aryl sulphides¹ and sulphonium salts² have been reported. However, there have been no reports of successful thio-Claisen rearrangement of allyl aryl sulphoxides, although recent communications³ have described the allyl sulphoxide \rightleftharpoons allyl sulphenate equilibrium by [2,3] sigmatropic rearrangement. We now present the first example of thio-Claisen rearrangement of allyl aryl sulphoxides.

Allyl 2-naphthyl sulphoxide (**1**), † m.p. 70–71°, obtained by periodate oxidation of the corresponding sulphide, was heated at 120° for 2 h in dimethylaniline or dimethylformamide to give quantitatively the isomeric product (**2a**), m.p. 149–151°; $\nu_{S \rightarrow O}$ (CHCl₃) 1030 cm⁻¹. This product was identical with the *cis*-isomer of the *cis*- and *trans*-S-oxides (**2a, b**) which were prepared by the oxidation of 2-methyl-1,2-dihydronaphtho[2,1-*b*]thiophen with *m*-chloroperbenzoic acid (1 mol. equiv.) at 0°. The configuration of the sulphoxide bond in the *cis*- and *trans*-isomers (**2a, b**) was established by the benzene-induced shift⁴ of the methyl signals in the n.m.r. spectra [(**2a**), 1.63 p.p.m. (in CDCl₃) and 1.29 p.p.m. (in C₆D₆); (**2b**), m.p. 81–82°, 1.56 p.p.m. (in CDCl₃) and 1.04 p.p.m. (in C₆D₆)].

A possible pathway for the formation of (**2a**) from (**1**) is shown in the Scheme, involving a [3,3] sigmatropic rearrangement of the sulphoxide (**1**) and intramolecular *cis*-addition of the resulting sulphenic acid (**3**) by a six-electron electrocyclic process.⁵ Heating (**1**) in D₂O-dimethylformamide gave an S-oxide (**2c**) with incorporation of only one deuterium atom on the methyl group of (**2a**), supporting the intervention of the sulphenic acid intermediate (**3**). The rearrangement of (**1**) to (**2a**) was shown to be a first-order reaction by preliminary n.m.r. kinetic studies ($t_{1/2}$ ca. 50 min at 100° in dimethylaniline), and the reaction rate at 100° was ca. 50 times faster than that of the corresponding sulphide.⁶



Heating (**1**) at 110° for 3 h in acetic acid–dimethylformamide gave the thiophen (**4**) (liquid; m.p. of its S-dioxide, 129–130°) in 48% yield, although the reaction of (**1**) in protic solvents generally afforded bis-2-naphthyl disulphide by solvolysis and a subsequent coupling reaction of the allyl 2-naphthyl sulphinate resulting from equilibrium with (**1**). The structure of (**4**) was proved by chemical correlation with 2-methylnaphtho[2,1-*b*]thiophen.⁷ The formation of (**4**) can be explained in terms of an episulphonium intermediate (**5**)⁸ derived from the [3,3] sigmatropic product (**3**).

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† The n.m.r. and i.r. spectra and elemental analyses of all new compounds were consistent with the structures assigned.

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² B. W. Bycroft and W. Landon, *Chem. Comm.*, 1970, 967.

³ P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, 90, 4869; D. A. Evans, G. C. Andrews, T. T. Fujimoto, and D. Wells, *Tetrahedron Letters*, 1973, 1385, 1389; P. A. Grieco, *J.C.S. Chem. Comm.*, 1972, 702.

⁴ J. J. Rigau, C. C. Bacon, and C. R. Johnson, *J. Org. Chem.*, 1970, 35, 3655.

⁵ R. D. G. Cooper and F. L. José, *J. Amer. Chem. Soc.*, 1970, 92, 2575.

⁶ Y. Makisumi and A. Murabayashi, unpublished result, $\Delta H^\ddagger = 21.6$ kcal mol⁻¹, $\Delta S^\ddagger = -26.1$ cal K⁻¹ mol⁻¹ at 130 °C.

⁷ K. Clarke, G. Rawson, and R. M. Scowston, *J. Chem. Soc. (C)*, 1969, 1274.

⁸ D. H. R. Barton, F. Comer, D. G. T. Greig, G. Lucente, and P. G. Sammes, *Chem. Comm.*, 1970, 1059.