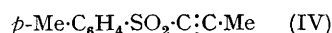
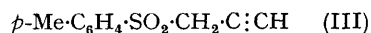
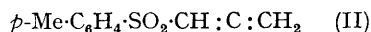
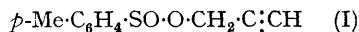


Rearrangement of an Acetylenic Sulphinic Ester to an Allenic Sulphone

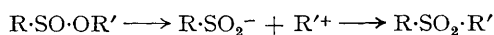
By C. J. M. STIRLING

(King's College, Strand, London, W.C.2)

PROP-2-YNYL TOLUENE-*p*-SULPHINATE (I) has been obtained by alcoholysis of toluene-*p*-sulphinyl chloride.¹ When a 2.5% solution of the ester in chlorobenzene is heated under reflux under nitrogen, rearrangement to propadienyl *p*-tolyl sulphone (II) is complete in 6 hr. Progress of the rearrangement is followed by disappearance of infrared spectral bands in the ester at 3300 cm.⁻¹ (C-H str.) and at 2130 cm.⁻¹ (C≡C str.) and the appearance of bands in the sulphone at 1960 cm.⁻¹ (C:C:C str.) and at 1325 and 1150 cm.⁻¹ (O:S:O str.). Evaporation of the solution gave the allene (80%), m.p. 79–81° alone or mixed with an authentic specimen,² m.p. 86.5–87.5°. The extent of the rearrangement is not appreciably affected when carried out in a darkened flask or in neutral conditions maintained by the presence of calcium carbonate (formation of acidic material accompanies rearrangement).



Alkyl³ and alkenyl⁴ sulphinic esters undergo acid-catalysed rearrangement to sulphones when the alkyl or alkenyl group is capable of forming a stable carbonium ion. Dissociation into sulphinic ion and carbonium ion with subsequent recombination appears probable:



This mechanism does not appear to account for the present observations as there is little evidence⁵ for rearrangement of prop-2-ynyl to allenyl carbonium ions. The isomeric sulphones, (III) and (IV), are stable under the conditions of the rearrangement. As the allene (II) is the thermodynamically most stable isomer,⁶ they can be excluded as intermediates. Ethyl toluene-*p*-sulphinate is also stable under the reaction conditions.

More detailed studies of the reaction are in progress. A related rearrangement, that of acetylenic to allenic acetates, is considered⁷ to involve a six-membered cyclic transition state.

(Received, January 4th, 1967; Com. 015.)

¹ Cf. C. J. M. Stirling, *J. Chem. Soc.*, 1963, 5741.

² S. T. McDowell and C. J. M. Stirling, *J. Chem. Soc. (B)*, 1967, in the press.

³ D. Darwish and R. McLaren, *Tetrahedron Letters*, 1962, 1231.

⁴ A. C. Cope, D. E. Morrison, and L. Field, *J. Amer. Chem. Soc.*, 1950, 72, 59.

⁵ G. R. Lappin, *J. Org. Chem.*, 1952, 17, 897.

⁶ C. J. M. Stirling, *J. Chem. Soc.*, 1964, 5856.

⁷ P. D. Landor and S. R. Landor, *J. Chem. Soc.*, 1956, 1015.