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.$^{-1}$ (${\vdots}$C–H str.) and at 2130 cm.$^{-1}$ (C${\vdots}$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).

$p\text{-Me}\cdot\text{C}_6\text{H}_4\cdot\text{SO}\cdot\text{O}\cdot\text{CH}_2\cdot\text{C}{\vdots}\text{CH}$ (I)

$p\text{-Me}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{CH}:\text{C}:\text{CH}_2$ (II)

$p\text{-Me}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{C}{\vdots}\text{CH}$ (III)

$p\text{-Me}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{C}{\vdots}\text{C}\cdot\text{Me}$ (IV)

Alkyl[3] and alkenyl[4] sulphinic esters undergo acid-catalysed rearrangement to sulphones when the alkyl or alkenyl group is capable of forming a stable carbonium ion. Dissociation into sulphinate ion and carbonium ion with subsequent recombination appears probable:

$$\text{R}\cdot\text{SO}\cdot\text{OR}' \longrightarrow \text{R}\cdot\text{SO}_2^- + \text{R}'^+ \longrightarrow \text{R}\cdot\text{SO}_2\cdot\text{R}'$$

This mechanism does not appear to account for the present observations as there is little evidence[5] 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 considered[7] to involve a six-membered cyclic transition state.

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

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