Unusual *ortho*-Claisen Rearrangements of Aryl Prop-2-ynyl Sulphoxides†

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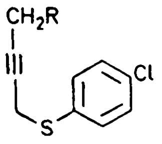
Summary 4-Aryl-1-aryloxysulphinylbut-2-ynes undergo a totally new mild thermal rearrangement resulting in the formation of dihydrobenzothiophen derivatives

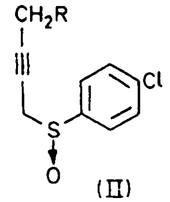
We report a totally new *ortho*-Claisen rearrangement involving an aryl allenyl sulphenate, itself generated from the thermal reorganization of an aryl prop-2-ynyl sulphoxide.

Compound (I), m.p. 73—74° was synthesized from 4-chloro-1-(*p*-chlorophenoxy)but-2-yne and potassium *p*-chlorothiophenoxide. Oxidation of (I) with one equivalent of *m*-chloroperbenzoic acid, MCPBA, at 0° gave the corresponding sulphoxide (II) in quantitative yield, m.p. 82—83°.

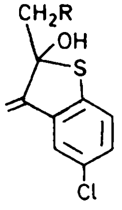
When (II) was heated under reflux in CCl_4 for 2 h, a clean liquid (III) was obtained in quantitative yield. Treatment of (III) with 20% aqueous KOH at room temperature afforded within 3 min a colourless crystalline solid (IV),‡ (90% yield), m.p. 118°, [2,4-dinitrophenylhydrazine derivative m.p. 208° (decomp)]. The structure of (IV) is assigned on the basis of the spectral data and the chemical reactions described later.



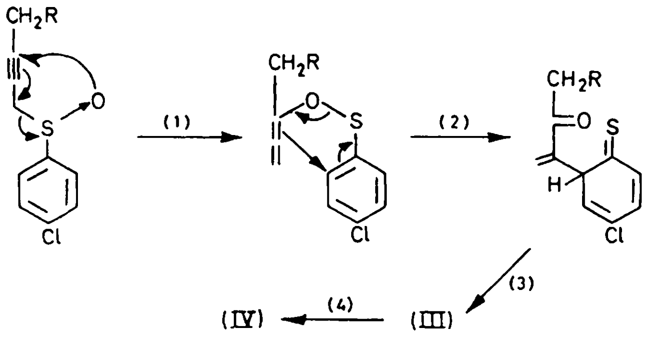
(I)



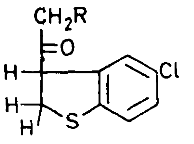
(II)



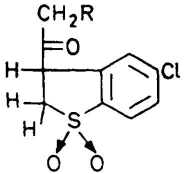
(III)



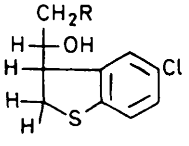
Scheme. R = *p*-chlorophenoxy



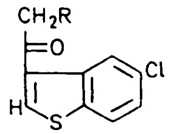
(IV)



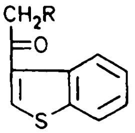
(V)



(VI)



(VII)



(VIII)

R = *p*-chlorophenoxy

That the molecule has two methylene functions—one flanked by a carbonyl and the other by a sulphide group—was proved by an oxidation and a reduction effected separately. Oxidation with two equivalents of MCPBA converted (IV) into the benzothiophen dioxide (V), m.p. 140—141°. Following this, the $-CH_2$ protons adjacent to the sulphone showed a downfield shift in the n.m.r. while the other protons were almost unchanged. Reduction of (IV) with sodium borohydride in THF gave the alcohol (VI). The $O-CH_2$ protons as expected showed a complicated multiplet consequent on the reduction. Dehydrogenation of (IV) with chloranil afforded by loss of two

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† This work was presented at the recent U.S.-Japan Organosulfur seminar held at Takarazuka, Japan between August 29 and September 4, 1971.

‡ New compounds were characterized by elemental analysis, high-resolution mass measurements on the molecular ion, together with the usual spectroscopic techniques.

hydrogens, compound (VII), m p 119°. A possible pathway for the formation of (IV) from (II) is given in the Scheme.

Many analogies are known in recent literature for step 1 from the stereomutation studies of aryl allyl sulphoxides,[1] and in the rearrangements of alkyl allyl sulphoxides[2] and aryl prop-2-ynyl sulphinates.[3] However, step 2 is novel in that the present work is the first example of an *ortho*-Claisen rearrangement with the bonds Ar–S–O–C=C=C. Step 3, the ketolization, and step 4, an intramolecular Michael addition of the thiophenolate to the enone system, take place as a result of the favourable position of the relevant functional groups.

As further structural proof, (VIII) was prepared in a way analogous to (VII), and its structure confirmed by synthesis from 3-(ω-bromoacetyl)thianaphthen.[4,5]

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