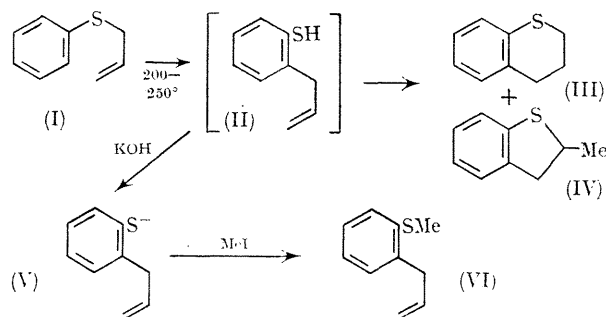


Evidence substantiating a Thiophenolic Intermediate in the Thio-Claisen Rearrangement

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EARLIER,¹ we suggested that *o*-allylthiophenol (II), was the precursor of the major products (III) and (IV) on thio-Claisen rearrangement² of allyl phenyl sulphide (I); we have now detected and trapped this elusive intermediate.



o-Allylthiophenol is unstable at room temperature and cyclizes exclusively to 1,2-dihydro-2-methylbenzo[b]thiophen (IV). An aqueous solution (strongly basic) of potassium *o*-allylbenzenethiolate (V), however, was unchanged for extended periods of time. This suggested two alternative approaches, both of which resulted in trapping the intermediate thiol (II) during the rearrangement.

In the first, the reaction in refluxing quinoline was carried out for 1 hr., a time considerably shorter than that

required for completion; the mixture was then quenched by addition to 3*N*-aqueous KOH. Neutral and water-insoluble compounds were removed and methyl iodide was added to the basic solution. An immediate reaction occurred to give a small amount of *o*-allylphenyl methyl sulphide (VI), as a pale yellow liquid; this accounted for ca. 5% of the product.

In the second approach, the sulphide (I) was heated under reflux with lithium methoxide (1 mol.) in quinoline. The mixture was quenched after one half-life and treated (as above) with methyl iodide. In this reaction the sulphide (VI) obtained accounted for ca. 50% of the total thio-Claisen product. We treated compound (I) in refluxing methanol containing lithium methoxide and found only phenyl propenyl sulphide as product. This excluded the possibility that methoxide was effecting the rearrangement.

Additional evidence for the intermediacy of the thiol (II) in the thio-Claisen rearrangement was obtained as follows. In refluxing quinoline, conditions under which compound (I) affords a nearly equimolecular mixture of (III) and (IV), *o*-allylthiophenol gave an *identical product ratio*. This highly reproducible result conflicts with our earlier report² that, in the presence of a high-boiling amine, the thiol (II) cyclized to a mixture (III) and (IV) in a ratio of 4:1. We conclude that the earlier result² was mistaken and the consequence of an inadequate analytical technique.

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¹ H. Kwart and M. H. Cohen, *J. Org. Chem.*, 1967, **32**, 3135.

² H. Kwart and E. R. Evans, *J. Org. Chem.*, 1966, **31**, 413.