Unusual Group Migrations attending the Thio-Claisen Rearrangement of Allyl 2,6-Dimethylphenyl Sulphide

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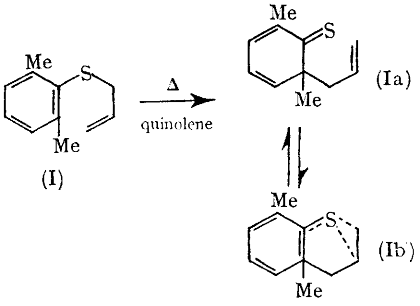
THE attempt to effect a *para*-thio-Claisen rearrangement[1] (in parallel with a *para*-oxy-Claisen[2]) results in an unprecedented reaction course. When allyl 2,6-dimethylphenyl sulphide (I) is heated in quinoline solution for 1·5 hr. at 350°, the volatile material which can be separated from the reacted mixture in *ca.* 65% yield is comprised of *ca.* 35% of the cleavage product 2,6-dimethylthiophenol and *ca.* 65% of a mixture of cyclic products.

Among the primary cyclic products[1,3] the formation of the *gem*-dimethyldihydrobenzothiophen (II) (8%)* must involve a 1–3 methyl shift accompanied by a 3–4 hydrogen shift from an initially formed *ortho* thio-Claisen intermediate. Formation of the 3-methylbenzothiopyran, (V) (16·5%) demands only a 1–3 methyl shift in the



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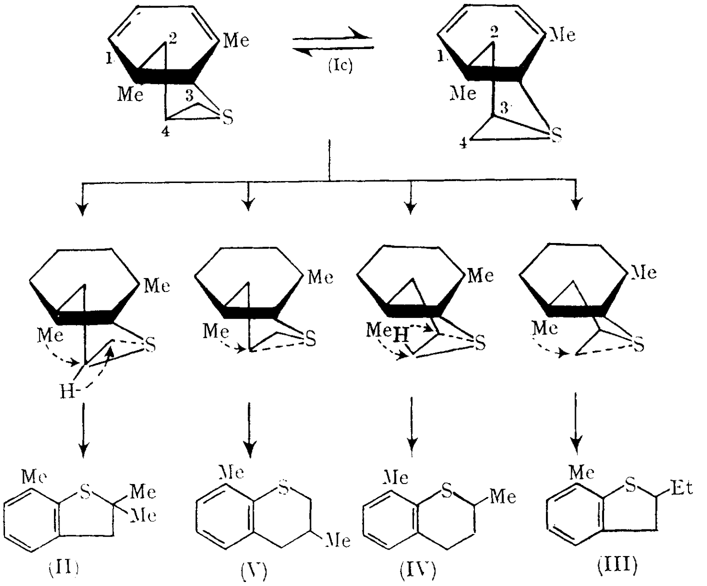
* All products were purified by g.l.c. and their structures established by n.m.r. and mass spectral analysis and direct synthesis.

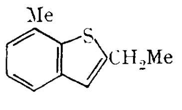
rearrangement of the same intermediate. Clearly, the 2-ethylbenzothiophen product, (III) (38%) must arise from a 1–4 methyl shift, and the 2-methylbenzothiopyran, (IV) (10%) can be perceived as a result of a 1–4 methyl shift in concert with a 4–3 hydrogen shift.

The course of all the primary cyclic migrations can be best visualized in the context of the previously suggested product-forming step of the *ortho* thio-Claisen rearrangement.[3] We assume the initial formation of a dienethione (Ia) product of thio-Claisen rearrangement† of (I) and subsequent events may be attributed to the ready interaction between the thiocarbonyl and the neighbouring olefin centres, establishing the equilibrium represented by (Ia) ⇌ (Ib).

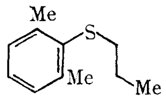


The thi-iran (Ib) in turn can exist in an equilibrium of conformations (Ic) (see Scheme). The nature of the charge distribution in this intermediate and the nature of the charge delocalizations in the methyl and hydrogen transfer steps, shown in the Scheme to proceed from the equilibrium (Ic) cannot yet be specified. The detailed electronic assignments in (Ib) must await the results of studies, now in progress in these laboratories, regarding the effect of substituents on the course and ease of rearrangement. The possibility that these migrations are sigmatropic[4] in character must also be considered.

The secondary products can be correlated with the occurrence of an ensuing disproportionation reaction. Among all the primary cyclic products, only (III) is capable of simple dehydrogenation to a fully aromatic structure, namely the benzo[*b*]thiophen (VII) (21%). The most probable oxidants to be recognized in the reaction mixture are the substrate (I) and the small amount of 2,6-dimethylphenyl propenyl sulphide (VI). Some propenylization of the substrate always tends to occur in the thio-Claisen.[3] The common reduction product was readily identified as (VI) (6·5%).



(VII)



(VI)

We thank the National Science Foundation for financial support.

(*Received, August 5th,* 1968; *Com.* 1067.)

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† The evidence for this assumption is based on results, obtained by J. L. Schwartz in these laboratories, to be presented in a forthcoming article.

[1] H. Kwart and M. C. Hackett, *J. Amer. Chem. Soc.*, 1962, **84**, 1754.

[2] For a review of such cases, see D. S. Tarbell, *Org. Reactions*, 1944, **2**.

[3] H. Kwart and M. H. Cohen, *J. Org. Chem.*, 1967, **32**, 3135.

[4] See for full discussion, R. B. Woodward and R. Hoffman, *Accounts Chem. Res.*, 1968, **1**, 17.