The Rearrangement of Allylic Trichloromethanesulphenates

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THE recent communication[1] on the spontaneous rearrangement of allylic toluene-*p*-sulphenates to allylic *p*-tolyl sulphoxides has prompted us to report some of our results on this subject. Our interest in the behaviour of allylic sulphenates originated from a study of allylic arenesulphinates which revealed some unique features.[2] It has been found that even under solvolytic conditions, the sulphinate esters undergo rearrangement in high yields to sulphones, and that the rearrangement of unsymmetrically substituted allylic esters involves simultaneous isomerisation of the allylic group (Equation 1).

$$\mathrm{CH_2{:}CH{\cdot}CHR{\cdot}O{\cdot}SO{\cdot}Ar} \rightarrow \mathrm{Ar{\cdot}SO_2{\cdot}CH_2{\cdot}CH{:}CHR} \qquad (1)$$

A kinetic study of the rearrangement indicated[2] a relatively low sensitivity of the rate to the nature of the substituent and the solvent. On the basis of these observations and other pertinent data, it has been suggested[2] that the rearrangement to sulphone occurs by a cyclic intramolecular mechanism. In view of the behaviour of allylic sulphinates, we investigated the predictable analogous rearrangement of allylic sulphenates to sulphoxides (Equation 2).

$$\mathrm{CH_2{:}CH{\cdot}CHR{\cdot}O{\cdot}SR'} \rightarrow \mathrm{R'{\cdot}SO{\cdot}CH_2{\cdot}CH{:}CHR} \qquad (2)$$

The project was initiated by the preparation of the claimed "allyl trichloromethanesulphenate" using the method of Sosnovsky.[3] This method involved the reaction between trichloromethanesulphenyl chloride and allyl alcohol in ether at 0°, in the presence of pyridine. The product was distilled under reduced pressure (b.p. 122—125°/9 mm. Hg; yield 60%). The compound[†] showed a strong infrared absorption band at 1115 cm.$^{-1}$ in carbon disulphide, which was assigned to the sulphoxide group.[4] The n.m.r. spectrum[†] showed a multiplet between τ 3·8—4·7 and an octet[‡] between τ 5·9—6·7, with relative peak areas of 3 : 2. These spectral data indicate that the structure of the compound is allyl trichloromethyl sulphoxide,[§] and not allyl trichloromethanesulphenate as claimed.[3] The fact that the infrared spectrum of the crude product was practically identical with that of the distilled material excluded the suspicion

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[*] The two new sulphoxides gave satisfactory analyses.

[†] The n.m.r. spectra were recorded on a Varian A-60 spectrophotometer. $CDCl_3$ was used as solvent.

[‡] The two methylenic protons are nonqeuivalent owing to the effect of the adjacent sulphoxide group.

[§] The original assignment (ref. 3) of the biological activity of this compound to the trichloromethylthio-radical attached to oxygen atom should be revised accordingly.

that rearrangement occured during distillation. Similarly, allyl trichloromethyl sulphoxide was obtained even when the reaction was carried out at $-70°$. These observations are consistent with those reported by Mislow and his co-workers[1] on allyl, crotyl, and α-methylallyl toluene-*p*-sulphenates. The sulphoxides obtained by the spontaneous rearrangement of the last two esters indicated that a simultaneous allylic rearrangement had also taken place.

In contrast to the results mentioned so far, we have found that cinnamyl trichloromethanesulphenate can be isolated and is relatively stable. We have prepared this compound (yield 72%) by using the above mentioned method at $-70°$. Its infrared spectrum showed no sulphoxide group absorption; in chloroform solution a band at 925 cm.$^{-1}$ is assigned to the sulphenate group. The n.m.r. spectrum exhibited a singlet at τ 2·8 (5H), a quartet at τ 3·5—3·8 (2H), and a doublet at τ 5·2 (2H). This compound was found to undergo rearrangement to cinnamyl trichloromethyl sulphoxide (*i.e.*, without allylic shift) at a relatively slow rate. A solution of the ester in chloroform over anhydrous sodium carbonate as buffer, was heated under reflux for 5 days, after which time the reaction was practically completed. Cinnamyl trichloromethyl sulphoxide (m.p. 110—110·5°) was identified by its infrared spectrum (*i.e.*, strong sulphoxide absorption at 1100 cm.$^{-1}$, in chloroform), and by its n.m.r. spectrum which displayed an unresolved doublet at τ 2·7 (5H), a multiplet at τ 3·1—3·9 (2H), and an octet at τ 5·8—6·5 (2 methylenic H).

Apparently, the rearrangement of cinnamyl trichloromethanesulphenate to cinnamyl trichloromethyl sulphoxide proceeds by a mechanism different from that of the rearrangement of other allylic sulphenates examined to date.

The data presented here are reminiscent of those reported[5] on the rearrangement of allylic thiocyanates to allylic isothiocyanates. This rearrangement is accompanied by an allylic shift in the case of alkyl-substituted allylic thiocyanates, but not in the case of cinnamyl thiocyanate, which is converted into cinnamyl isothiocyanate.

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[2] S. Braverman, Ph.D. Thesis, University of Alberta, Edmonton, Canada, 1963; D. Darwish and S. Braverman, 48th Chemical Institute of Canada Conference, Montreal, Canada, May 30—June 2, 1965.

[3] G. Sosnovsky, *J. Chem. Soc.*, 1956, 3139.

[4] L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Wiley, New York, 1958, pp. 357—360; K. Nakanishi, "Infrared Absorption Spectroscopy", Holden-Day, San Francisco, 1962, p. 54.

[5] References and discussion in "Organic Sulphur Compounds", vol. 1, ed. N. Kharasch, Pergamon, Oxford, 1961, p. 312; vol. 2, ed. N. Kharasch and C. Y. Meyers, 1966, p. 86.