Triethylenediamine-induced Ramberg–Bäcklund Rearrangement of αα-Dichlorodibenzyl Sulphones

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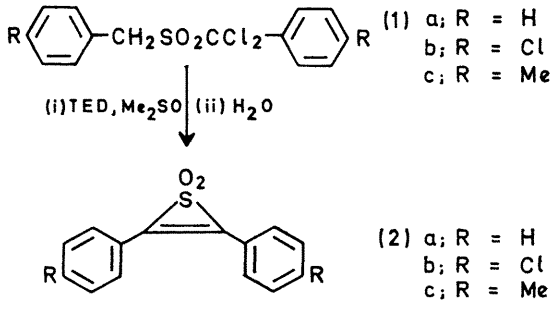
Summary Diphenylthiiren 1,1-dioxides or diphenylacetylenes may be isolated in high yields from the triethylenediamine-induced Ramberg–Bäcklund rearrangement of αα-dichlorodibenzyl sulphones.

THE Ramberg–Bäcklund rearrangement[1] of αα-dichlorodibenzyl sulphones with aqueous sodium hydroxide results in the formation of complex mixtures consisting of 1-chloro-*cis*-1,2-diphenylethylenes, 1-chloro-*trans*-1,2-diphenylethylenes, diphenylacetylenes, and vinylsulphonic acid salts.[2] The intermediacy of 2,3-diphenylthiiren 1,1-dioxides in this rearrangement has been postulated previously, but attempted isolation of such intermediates from αα-dichlorodibenzyl sulphones has been unsuccessful.[2,3]

We have investigated the triethylenediamine(TED)-induced rearrangements of three αα-dichlorodibenzyl sulphones and find that the formation of vinylsulphonic acid salts can be avoided with this base. In addition, appropriate conditions have been discovered that allow conversion of αα-dichlorodibenzyl sulphones into 2,3-diphenylthiiren 1,1-dioxides and hence to diphenylacetylenes[3] in high yields. The reaction of αα-dichlorodibenzyl sulphones (**1a—c**) with an excess of TED in dimethyl sulphoxide at ambient temperature results in the rapid disappearance of the dichloro-sulphones (by t.l.c.) and the formation of 2,3-diphenylthiiren 1,1-dioxides (**2a—c**). The thiiren 1,1-dioxides may be isolated in >90% yields simply by pouring the reaction mixture into water and collecting the precipitate.



Thermal decomposition of the thiiren 1,1-dioxides results in the extrusion of sulphur dioxide and the formation of the corresponding diphenylacetylenes in >90% yields.

The reaction of αα-dichlorodibenzyl sulphones (**1a—c**) with TED in less polar solvents is more complicated. For example, the reaction of (**1a**) with TED in refluxing *p*-xylene results in the formation of a mixture that consists of diphenylacetylene (**3**), 1-chloro-*trans*-1,2-diphenylethylene (**4**), and 1-chloro-*cis*-1,2-diphenylethylene (**5**). Subsequent treatment of this mixture with potassium hydroxide in triethylene glycol afforded an 85% overall yield of (**3**). Independently prepared samples of vinyl chlorides (**4**) and (**5**)[4] could be recovered in high yield after treatment with TED in refluxing *p*-xylene, and hence the initially observed (**3**) could not have resulted from dehydrohalogenation of either vinyl halides (**4**) or (**5**). In a similar manner *pp'*-dichlorodiphenylacetylene could be isolated in 90% yield upon dehydrohalogenation of the Ramberg–Bäcklund mixture obtained from (**1b**) in *p*-xylene. In refluxing methylene chloride, dichloro-sulphone (**1a**) also reacts with TED to yield the corresponding thiiren 1,1-dioxide (**2a**), but the transformation is further complicated by slow conversion of (**1a**) under these conditions and by competing reaction of the solvent with TED.

Satisfactory elemental analyses and spectra were obtained for all new compounds reported.

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[1] F. G. Bordwell, "Organosulfur Chemistry," ed. M. J. Janssen, Interscience, New York, 1967, ch. 16; L. A. Paquette, *Accounts Chem. Res.*, 1968, **1**, 209; L. A. Paquette, "Mechanisms of Molecular Migrations," Vol. 1, ed. B. S. Thyagarajan, Interscience, New York, 1968, pp. 121—156.

[2] L. A. Paquette and L. S. Wittenbrook, *J. Amer. Chem. Soc.*, 1967, **89**, 4483.

[3] The isolation of 2,3-diphenylthiiren 1,1-dioxide (**2a**) from the more acidic αα'-dibromodibenzyl sulphone has been accomplished with triethylamine in methylene chloride. See: L. A. Carpino and L. V. McAdams, III, *J. Amer. Chem. Soc.*, 1965, **87**, 5804. We thank Dr. M. Rosen of CIBA, Summit, New Jersey for an authentic sample of (**2a**).

[4] S. J. Cristol and R. S. Bly, jun., *J. Amer. Chem. Soc.*, 1960, **82**, 142.