

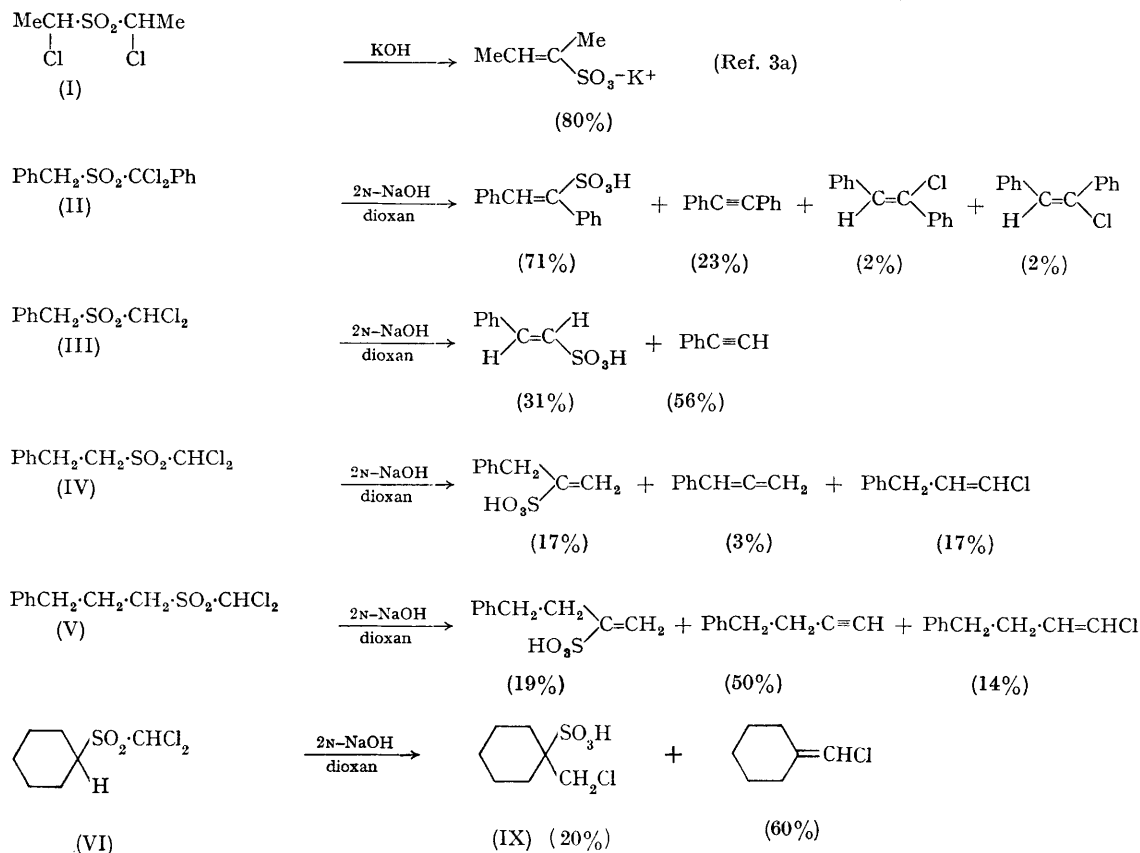
The *in situ* Generation of Thiiren Dioxides by the Base-induced Rearrangement of $\alpha\alpha$ -Dihalogeno-sulphones¹

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THE mechanistic pathways which are operative in the reaction of $\alpha\alpha$ -dichloro-sulphones with base have not been elaborated, except for the fact that chloro-episulphone intermediates are involved.² The problem has in part been complicated by the variety of products and product ratios which have been obtained in the limited number of examples

studied.^{2,3} We have now examined the rearrangements of $\alpha\alpha$ -dichloro-sulphones, (II—VI) in 2N-aqueous sodium hydroxide (dioxan as cosolvent, see Table) and in potassium *t*-butoxide/*t*-butyl alcohol and present evidence which demonstrates that the major products arise from thiiren 1,1-dioxide intermediates (VIII).

TABLE. *Rearrangements of dihalogeno-sulphones in aqueous base (87°)*

Progression down the Table from sulphone (I) to sulphone (V) reveals a gradual decrease in the yields of the sulphonic acids (isolated and characterized as their *p*-toluidine salts⁴) and a gradual increase in the proportion of the acetylenes (and also vinyl chlorides), except in the case of (IV) where the benzylacetylene is rapidly converted into phenylallene which is destroyed almost totally by polymerization.⁵ That the acetylenic products do not result from the dehydrohalogenation of intermediate vinyl chlorides has been established by the appropriate control experiments on independently prepared chloro-olefins. Furthermore, sulphite ion, liberated during the course of the reactions, does not interact with the acetylenic or halogenated products.

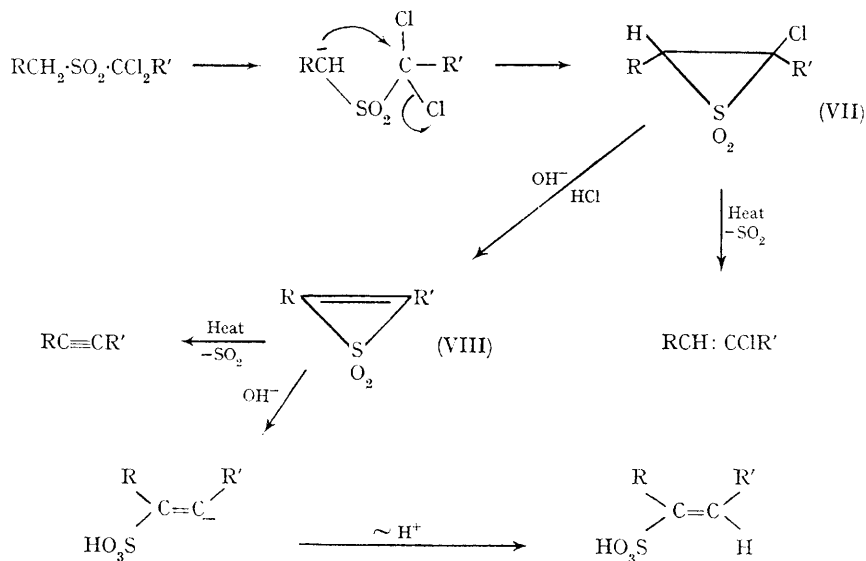
The observed data can be explained uniquely in terms of a mechanism which proceeds initially *via* a 1,3-elimination of hydrogen chloride to generate a chloro-episulphone such as (VII)² which, depending upon its stability under the reaction conditions,

may either undergo a thermal loss of sulphur dioxide (to produce the vinyl chloride) or a base-induced loss of hydrogen chloride. In the latter event, a thiiren dioxide (VIII) results; if this intermediate possesses appreciable stability, it would not be expected to suffer thermal loss of sulphur dioxide very readily (to yield acetylene),⁶ but would enjoy a lifetime sufficient to be attacked by base and produce sulphonic acid. If the assumption is made that the rates of reaction of the intermediate thiiren dioxides with hydroxide ion do not vary significantly within the series, then the results with compounds (I—V) suggest the following order of relative stabilities:

dimethyl > diphenyl > phenyl > benzyl \approx phenethyl.

Of particular interest is the observation that the stability order of the thiiren dioxides appears to parallel that of the cyclopropenone system.⁷

The direction of cleavage of such three-membered

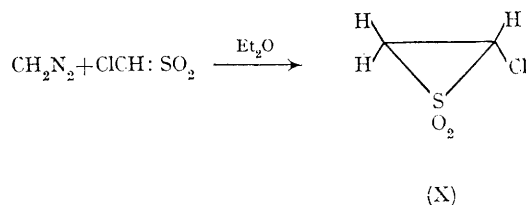


heterocycles (VIII) is such as to generate the more stable carbanion as demonstrated in the rearrangements of (IV) and (V). Interestingly, when potassium *t*-butoxide in dry *t*-butyl alcohol is used as the base, no sulphonic acids are obtained and acetylenes result almost exclusively.

Dichlorosulphone (VI) on solvolytic rearrangement leads to a spiro-chloro-episulphone which cannot undergo further loss of hydrogen chloride. This special feature is reflected in the nature of the derived products. Interestingly, the formation of (IX) suggests that the spiro-chloro-episulphone intermediate is likewise cleaved by hydroxide ion to generate the more stable carbanion.

In an ancillary study, treatment of an ethereal solution of diazomethane with chlorosulphene⁸ at -5° gives the unsubstituted chloro-episulphone (X) m.p. $53-54^\circ$ dec. Of particular relevance to the

above results, (X) is decomposed into vinyl chloride and sulphur dioxide on heating to 65° in



carbon tetrachloride solution. It is not, however, dehydrohalogenated by triethylamine at 0° .

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¹ For previous paper, see: L. A. Paquette, *J. Amer. Chem. Soc.*, 1964, **86**, 4383.

² L. A. Paquette, *J. Amer. Chem. Soc.*, 1964, **86**, 4089.

³ (a) L. Ramberg and B. Bäcklund, *Arkiv. Kemi Mineral. Geol.*, 1940, **13A**, No. 27 (b) F. Scholnick, Ph.D. Dissertation, Univ. of Pennsylvania, 1955.

⁴ Satisfactory analytical and spectral data were obtained for all new compounds described here. Certain of the acetylenes and vinyl chlorides were compared by means of v.p.c. retention times and infrared spectra with authentic samples.

⁵ M. Vo-Quang Yen, *Ann. Chim. (France)*, 1962, **7**, 785.

⁶ In this context, L. A. Carpino and L. V. McAdams, tert., (*J. Amer. Chem. Soc.*, 1965, **87**, 5804) independently have prepared diphenylthiirene dioxide and have demonstrated it to be a stable species which decomposes smoothly at its melting point with the formation of diphenylacetylene and sulphur dioxide.

⁷ R. Breslow, G. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Amer. Chem. Soc.*, 1965, **87**, 1320; R. Breslow, L. J. Altman, A. Krebs, E. Mohacs, I. Murata, R. A. Peterson, and J. Posner, *ibid.*, p. 1326; R. Breslow and L. J. Altman, *ibid.*, 1966, **88**, 504.

⁸ L. A. Paquette, *J. Org. Chem.*, 1964, **29**, 2854.