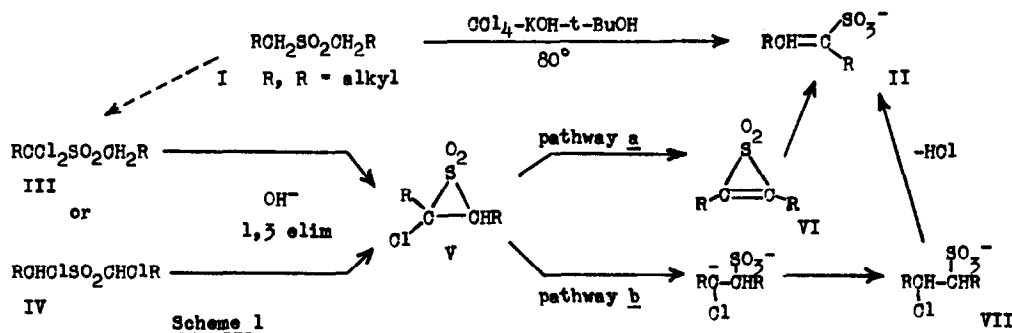


MECHANISM OF THE DIRECT FORMATION OF ALKENESULFONIC ACIDS FROM THE REACTION OF SULFONES WITH  $\text{COCl}_4$ -KOH. INTERMEDIACY OF GEM- $\alpha$ -DICHLORO SULFONES AND THIURENE 1,1-DIOXIDES

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The direct conversion of primary dialkyl sulfones (I) into dialkylethylsulfonic acids (II) by treatment with  $\text{COCl}_4$ -KOH was recently reported.<sup>2</sup> Various routes, with precedence from related studies, could lead to these results (Scheme 1): Initial formation either of gem- $\alpha$ -dichloro sulfones (III) or  $\alpha,\alpha'$ -dichloro sulfones (IV), based on the  $\alpha$  chlorination of sulfones under these conditions<sup>3</sup> and the conversion of III as well as IV with alkali into II (and other products) via a common chlorothiirane 1,1-dioxide (V);<sup>4,5</sup> and conversion of V either into a thiurene 1,1-dioxide (VI, pathway a) or a  $\beta$ -chloro sulfonate (VII, pathway b) as the direct precursor of II. Paquette proved that pathway a is followed in the formation of II via V in which R, R = aryl.<sup>4c</sup> But he also showed that cleavage via pathway b can occur with alkyl chlorothiirane 1,1-dioxides, and from these facts and other considerations he concluded that the pathway leading from alkylated V to ethylsulfonic acids remained an open question.<sup>4b</sup>

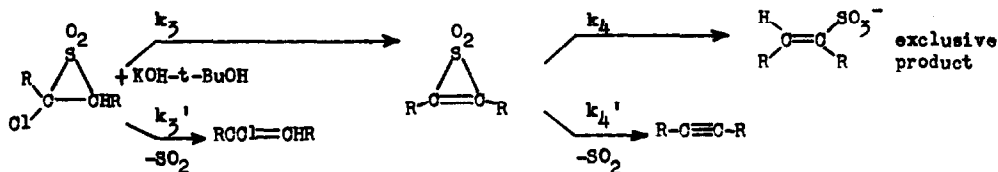


We have now shown that under these conditions gem- $\alpha$  dichlorination of I is favored over  $\alpha,\alpha'$  dichlorination and other competing reactions, and that the formation of II from V in which R, R = alkyl requires the intermediacy of a thiurene 1,1-dioxide (VI), i.e., pathway a is followed when R = alkyl or aryl. Thus,  $\text{I} \rightarrow \text{III} \rightarrow \text{V} \rightarrow \text{VI} \rightarrow \text{II}$ .

Secondary dialkyl sulfones similarly treated are converted into mono- $\alpha$ -chloro sulfones which rapidly undergo 1,3 elimination leading to simple olefins.<sup>3</sup> These results suggested that monochloro-I must undergo geminal chlorination and at a rate faster than 1,3 elimination. The sequence of  $\alpha$  chlorination - gem- $\alpha$  dichlorination - 1,3 elimination was established by a series of independent and competitive reactions:<sup>6a</sup> 1) Cis-4-octene-4-sulfonic acid (IIa) was produced by the reaction of  $\text{COCl}_4$ -KOH-t-BuOH with dibutyl sulfone (Ia) at 80°, yields of 45% requiring 2 hr and yields of 75% requiring at least 5 hr;<sup>2a</sup> but IIa was produced in >90% yield in a simi-







Scheme 4

R, R = alkyl

 $k_3 \gg k_3'$  $k_4 \gg k_4'$ 

## NOTES AND REFERENCES

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- (a) Generally for 1 g (ca. 0.01 mol) of substrate, 4 g of powdered KOH (85%), 10 ml of  $\text{CCl}_4$ , and/or 10 ml of t-BuOH were used. The % yields are based on the original substrate charge.  
(b) The % yields of IIIa and IIa in this run are based on their formation only from VIIIa.
- Presumably pathway b would lead to both diastereoisomers of VII and, therefore, to cis- and trans-II since base-catalyzed dehydrohalogenation of diastereomeric mixtures of  $\beta$ -halo sulfones analogous to VII provided cis-trans mixtures while the reaction was stereospecific for each diastereoisomer [P. S. Skell and J. R. McNamara, *J. Amer. Chem. Soc.*, **79**, 85 (1957)].
- The yield of II directly from I is diminished by the competitive autoxidation of I in hot KOH-t-BuOH. Much faster base-catalyzed autoxidations of benzylic sulfones have now been investigated (C. Y. Meyers and G. J. McCollum, results to be published shortly).
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