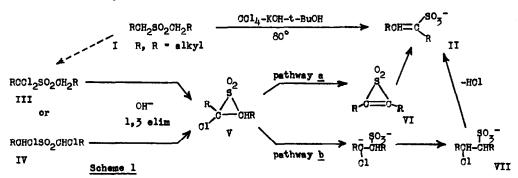
MECHANISM OF THE DIRECT FORMATION OF ALKENESULFONIC ACIDS FROM THE REACTION OF SULFONES WITH COLA-KOH. INTERMEDIACY OF GEM-C4-DICHLORO SULFONES AND THIREME 1,1-DICXIDES

Cal Y. Meyers, Laurence L. Ho, Gregory J. McCollum, and John Branca Department of Chemistry and Biochemistry, Southern Illinois University Carbondale, Illinois 62901

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The direct conversion of primary dialkyl sulfones (I) into dialkylethylenesulfonic acids (II) by treatment with  $COl_4$ -KOH was recently reported. 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 and the conversion of III as well as IV with alkali into II (and other products) via a common chlorothiirane 1,1-dioxide (V);  $\alpha$ , and conversion of V either into a thiirene 1,1-dioxide (VI, pathway a) or a  $\alpha$ -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. 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 ethylenesulfonic acids remained an open question.



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

Secondary dialkyl sulfones similarly treated are converted into mono-«-chloro sulfones which rapidly undergo 1,3 elimination leading to simple clefins. These results suggested that monochloro-I must undergo geminal chlorination and at a rate faster than 1,3 elimination. The sequence of «chlorination - gem-c(dichlorination - 1,3 elimination was established by a series of independent and competitive reactions: 6a 1) cis-4-octene-4-sulfonic acid (IIs) was produced by the reaction of COl4-KCH-t-BuOH with dibutyl sulfone (Ia) at 80°, yields of 45% requiring 2 hr and yields of 75% requiring at least 5 hr; 2a but IIa was produced in>90% yield in a simi-

lar reaction of «-chlorobutyl butyl sulfone (VIIIa) at 25-40° within minutes. 2) When VIIIa was treated with COl<sub>4</sub>-KOH-t-BuOH at 0° for 1 hr, 31% of gem-«-dichlorobutyl butyl sulfone (IIIa), 25% of IIa, and 34% of unchanged VIIIa were isolated. 3) Treatment of an equimolar mixture of Ia and VIIIa with COl<sub>4</sub>-KOH-t-BuOH at 25° for 5 min provided 14% of IIIa and 80% of IIa while >90% of Ia and 6% of VIIIa were recovered. 6b 4) Treatment of IIIa with KOH-t-BuOH at 0° for 1 hr provided about 90% of IIa. 5) Treatment of an equimolar mixture of VIIIa and IIIa with KOH-t-BuOH at 0° for 1 hr gave >80% of IIa while 70% of VIIIa was recovered. 6) Conversion of VIIIa into 4-octane (IX) by treatment with KOH-t-BuOH at 80° was complete within 1 hr. The sequence and relative rates of the reactions suggested by these data are presented in Scheme 2.

The formation of II via pathway <u>a</u> was established by two different but mutually supporting methods. Although the geometry of the alkenesulfonic acids produced in similar reactions was not determined by other workers, our recent study proved that II is formed exclusively in the <u>cis</u>-alkene structure. This fact should preclude the intermediacy of VII (pathway <u>b</u>), but it is consistent with the direct formation of the <u>cis</u>-alkenyl anion (X) from VI (pathway <u>a</u>). To

Definitive evidence that pathway a is followed was derived from the observation that the identical mixture of cis-2-pentene-2-sulfonic acid (IIb) and cis-2-pentene-3-sulfonic acid (IIb') was obtained when a-chlorosthyl propyl sulfone (VIIIb) or a-chloropropyl ethyl sulfone (VIIIc) was treated with CCl4-KOH-t-BuOH. These results are tenable only if both reactions proceeded through a common intermediate. While a different gem-a-dichloro sulfone (IIIb and IIIc) and chlorothirane 1,1-dioxide (Vb and Vc) would be formed in each reaction, 2-ethyl-3-methylthi-irene 1,1-dioxide (VIb) would be formed in both reactions and lead to the observed results. Moreover, IIb and IIb' were obtained in a ratio close to 1:1 from both reactions, which is consistent with the similar stabilities expected of the alkenyl anions Xb and Xb' formed from VIb. On the contrary, if these products were formed via pathway b a different isomer would be expected from each substrate since the cleavage of Vb and Vc into the respective chloro carbanion is product determining. The conversion of ethyl propyl sulfone (Ib) also into about 1:1 IIb and IIb' was previously reported 2s and, based on the data presented here, is undoubtedly initiated by the formation of VIIIb and VIIIc. These results and conclusions are summarized in Scheme 3.

The dichlorination of I was unexpected since dibenzyl sulfone, also a primary sulfone, is simply monochlorinated and converted into stilbene under these conditions. This surprising difference arises from the fact that the «-chlorodialkyl sulfones undergo gem- « dichlorination faster than 1,3 elimination (viz. Scheme 2) while the opposite order is exhibited by «-chlorodibenzyl sulfone. The factors responsible for this contrast will be reported shortly.

II 
$$\leftarrow$$
 ROOl<sub>2</sub>SO<sub>2</sub>OH<sub>2</sub>R  $\leftarrow$  ROHOlSO<sub>2</sub>OH<sub>2</sub>R  $\leftarrow$  ROH—CHR  $\leftarrow$  RO

Conversion of I or the monochloro derivative into II was essentially quantitative, exclusive dichlorination precluding the formation of simple alkenes. The absence of chloroalkenes and alkynes, however, was unexpected: No further chlorination occurred and treatment of related dichloro sulfones with base has been reported to provide significant amounts of both products apparently via thermally induced extrusion of SO<sub>2</sub> from the subsequently formed chlorothirane dioxides and thirene dioxides, respectively. <sup>4,5,9</sup> The powerful "base effect" of KOH-t-BuOH on sulfones together with the indication that the relative rate of thermal decomposition of dialkylthirene dioxides is substantially lower than that of the monoalkyl or the aryl derivatives could account for the specificity of our reactions (Scheme 4).

## NOTES AND REFERENCES

- 1. National Science Foundation Grant GF-36746 is gratefully acknowledged.
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- 6. (a) Generally for 1 g (ca. 0.01 mol) of substrate, 4 g of powdered ROH (85%), 10 ml of COl4, 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.
- 7. Presumably pathway b would lead to both diastereoisomers of VII and, therefore, to <u>cis</u> and <u>trans</u>-II since base-catalyzed dehydrohalogenation of diastereomeric mixtures of β-halo sulfones analogous to VII provided <u>cis</u>-trans mixtures while the reaction was stereospecific for each diastereoisomer [P. S. Skell and J. H. McNamers, J. Amer. Chem. Soc., 79, 85 (1957)].
- 8. 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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