

carbazone, m.p. 220–222° dec., mixture m.p. 219–220° dec. (lit.,<sup>2,3</sup> m.p. 220–221° dec., 220.5–221.5°) (Anal. Calcd. for C<sub>8</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub>: C, 53.03; H, 6.12. Found: C, 52.86; H, 6.17).

The juxtaposition of the methyl groups in the rearrangement product suggests that the photochemical reaction may proceed initially by a route analogous to that followed in the case of compounds possessing the corresponding carbocyclic system, *i.e.*, the 2,5-cyclohexadienones,<sup>4</sup> with the "lumisantonin" rearrangement product III as an intermediate.

(3) T. Reichstein, and A. Grüssner, *Helv. Chim. Acta*, **16**, 28 (1933).

(4) D. H. R. Barton, *ibid.*, **42**, 2604 (1959); H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962).

(5) This work was supported by a grant from the National Research Council of Canada, which is gratefully acknowledged.

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### MECHANISM FOR THE FORMATION OF *cis*-ALKENES FROM $\alpha$ -CHLORO SULFONES

Sir:

In a previous paper<sup>1</sup> the rate of release of chloride ion during the formation of alkenes from  $\alpha$ -chloro sulfones on treatment with alkali was shown to be consistent with the formation of an episulfone intermediate. One puzzling feature of the reaction was the formation of *cis*-2-butene, rather than *trans*-2-butene, in the reaction of  $\alpha$ -chloroethyl ethyl sulfone.<sup>2</sup> This result cast a shadow on the postulate of an episulfone intermediate, and suggested that another mechanism might pertain. One such possibility is initial cleavage of a carbon-sulfur bond, rather than a carbon-chlorine bond, giving an intermediate MeCH(SO<sub>2</sub><sup>-</sup>)CH(Cl)Me, which then loses SO<sub>2</sub> and Cl<sup>-</sup>. (By making the proper assumptions, one can rationalize the stereochemistry using this mechanism.) We now wish to report further evidence for the formation of an episulfone intermediate.

Reaction of diazoethane in ether with sulfur dioxide<sup>3</sup> gave a mixture from which the postulated intermediate episulfone (*cis*-2,3-dimethylthiirane 1,1-dioxide) was isolated in pure form. The corresponding *trans* isomer was obtained admixed with a smaller amount of the *cis* form. (Microanalyses, n.m.r. spectra, and infrared spectra are consistent with these structure assignments.) The *cis* episulfone underwent rapid decomposition when warmed neat, or in solution, to give 100% *cis*-2-butene. The episulfone mixture decomposed to a mixture of 78% *trans*- and 22% *cis*-2-butenes, which composition is identical with the episulfone isomer distribution in the mixture, as determined by n.m.r.

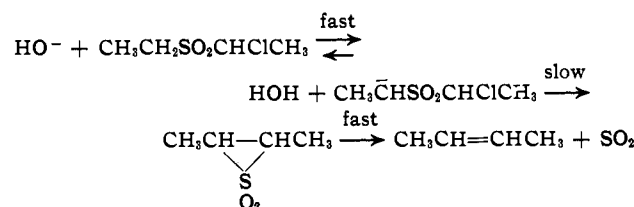
Starting from  $\alpha$ -chloroethyl ethyl sulfone the percentages of *cis* isomer in the 2-butene mixture (g.l.c. analysis) using various alkaline media were: 78.8% (2 *N* NaOH), 78.2% (2 *N* KOH), 74.6% (1 *M* BuONa in BuOH), 77.9% (BuLi in heptane-hexane), and 78.1% (C<sub>6</sub>H<sub>5</sub>Li in C<sub>6</sub>H<sub>6</sub>). However, when 1 *M* *t*-BuOK in *t*-BuOH was used, the ratio was almost reversed, being now 18.6% *cis* and 81.4% *trans*. Significantly, the *cis* episulfone behaved similarly, giving only *cis*-2-

(1) F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **73**, 5187 (1951).  
(2) L. Ramberg and B. Bäcklund, *Arkiv. Kemi Mineral. Geol.*, **1314**, No. 27 (1940), concluded from physical constant measurements made on the 2-butene dibromides that *cis*-2-butene predominated. An infrared analysis of the 2-butene mixture (N. P. Neureiter, Ph.D. Dissertation, Northwestern University, 1957) gave the composition as about 80% *cis*, and this result has been confirmed by gas-liquid chromatographic (g.l.c.) analysis (both by the present authors and, independently, by T. A. Whitney).

(3) The procedure was adapted from that for ethylene sulfone: G. Hesse, E. Reichold and S. Majmudar, *Chem. Ber.*, **90**, 2106 (1957).

butene with NaOH and predominantly *trans*-2-butene with *t*-BuOK. Furthermore, with *t*-BuOK in *t*-BuOH the 2-butene produced from the *cis* episulfone was over 90% CH<sub>3</sub>CD=CDCH<sub>3</sub> (19% *cis*) whereas with 2 *N* NaOD in D<sub>2</sub>O, the *cis* episulfone gave CH<sub>3</sub>CH=CHCH<sub>3</sub> (100% *cis*), with less than 5% deuterium exchange. Finally, the 2-butene produced from  $\alpha$ -chloroethyl ethyl sulfone with 2 *N* NaOD in D<sub>2</sub>O was 98% CH<sub>3</sub>CD=CDCH<sub>3</sub> (78% *cis*).

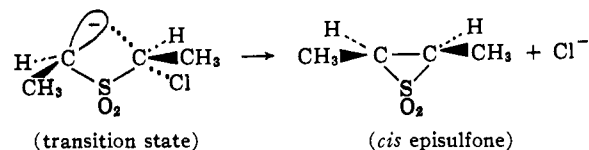
These results are consistent with the mechanism originally proposed,<sup>1</sup> the final step being a thermal elimination of sulfur dioxide.<sup>4</sup>



The deuterium exchange experiments show that with hydroxide ion all the  $\alpha$ -hydrogen atoms in the  $\alpha$ -chloro sulfone are rapidly exchanged, but that those in the episulfone are not exchanged prior to its decomposition. With the stronger base, *t*-butoxide ion, hydrogen exchange and epimerization precede decomposition of the episulfone. The latter experiment also shows that, as expected, the *trans* episulfone is favored over the *cis* episulfone at equilibrium.

When the reaction was carried out using 2 *N* KOH and  $\alpha$ -chloropropyl ethyl sulfone 72.3  $\pm$  0.3% of *cis*-2-pentene was produced, as compared to 65.7  $\pm$  0.2% of *cis*-2-pentene from  $\alpha$ -chloroethyl propyl sulfone. In contrast, the same per cent of *cis*-2-pentene (15.8%) was obtained from either chloro sulfone when *t*-BuOK in *t*-BuOH was used. These results are consistent with and support the interpretation given above. In 2 *N* KOH the *cis* episulfone is formed preferentially, a slightly different *cis/trans* ratio being obtained from the two chloro sulfones. When formed in the presence of the stronger base, *t*-BuOK, the episulfones are epimerized to the same *cis/trans* mixture with the *trans* isomer now predominating.

Although the present evidence does not completely rule out other mechanisms for the first stage in the reaction (carbene or dipolar ion rather than strictly carbanion), it does appear to provide conclusive evidence for the formation of an episulfone intermediate. A likely transition state for the formation of the preferred episulfone is then



Assuming this representation, the question immediately arises as to why this transition state is preferred to the alternative one in which the methyl groups are on opposite sides. One intriguing possibility is that the methyl groups may actually attract one another. In the transition state shown, the methyl groups have a relationship similar to that for the methyl groups in the skew conformation of butane, except that the central C-C bond distance is somewhat greater. In skew butane Pitzer and Catalano<sup>5</sup> estimate that steric repulsive forces amounting to about 2.5 kcal. per mole

(4) Thermal decomposition of the episulfone is very rapid, but we have not excluded the possibility that the rate of cleavage may be accelerated by hydroxide ion.

(5) K. S. Pitzer and E. Catalano, *J. Am. Chem. Soc.*, **78**, 4844 (1956).

slightly outweigh attractive electronic correlation (London) forces amounting to about 2 kcal. per mole. It seems possible that, at the slightly greater bond distance existing in the transition state of the present reaction, the order of importance of these repulsive and attractive forces may be reversed.<sup>6</sup> If so, we are provided with an explanation for the preferential formation of the less stable episulfone.

(6) London forces between atoms are believed to fall off with the reciprocal sixth power of the internuclear distance.<sup>5</sup> Repulsive forces between atoms have been described by a function involving the reciprocal twelfth power of the distance (Lennard-Jones 6-12 potential).<sup>7</sup>

(7) J. O. Hirschfelder, C. F. Curtis and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 1070-1075.

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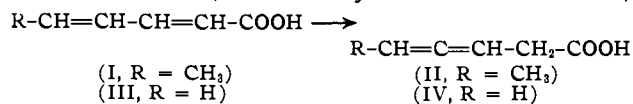
### PHOTOCHEMICAL FORMATION OF ALLENES IN SOLUTION

Sir:

Srinivasan has reported<sup>1</sup> the vapor phase photoisomerization of 1,3-butadiene to 1,2-butadiene and of 1,3,5-hexatriene to 1,2,4-hexatriene. As part of an investigation of the extent of photochemical production of cyclobutenes,<sup>2</sup> systems containing dienes present in extendedly conjugated systems are being examined in this Laboratory. It is here reported that sorbic acid (I) and the homologous acid III, in dilute solution, are isomerized by light to the corresponding allenes, II and IV.

Irradiation<sup>3</sup> of a 3% solution of sorbic acid in dry diethyl ether until almost no starting material remained (ultraviolet absorption) gave, after fractional distillation, the acid II (20%), b.p. 63° (0.4 mm.), m.p. 23°,  $n_D^{20}$  1.4770. This product showed no ultraviolet maximum, but had  $\epsilon$  460 at 220  $m\mu$ ,  $\epsilon$  4200 at 192  $m\mu$  (in  $C_6H_{18}$ ), while its infrared spectrum possessed the characteristic allene maximum at 1972  $cm^{-1}$ ; its methyl ester (from diazomethane,  $n_D^{20}$  1.4595) and its *p*-bromophenacyl ester (m.p. 68.5°) both showed this peak at 1972  $cm^{-1}$ . The acid (II) in ethyl acetate, over Adams catalyst, absorbed two equivalents of hydrogen to yield caproic acid, and, on ozonolysis followed by oxidation of the ozonide with hydrogen peroxide in formic acid, gave malonic acid (76%). When heated with 10% aqueous sodium hydroxide<sup>4</sup> at 70° during 15 min., the photoproduct was re-isomerized to sorbic acid (48%).

Irradiation of 2,4-pentadienoic acid (III)<sup>5</sup> under similar conditions, followed by fractional distillation,



gave 3,4-pentadienoic acid (IV)<sup>4</sup> in 32% yield. This product (m.p. 1.5°) was identified by its infrared maximum at 1965  $cm^{-1}$ , by its low ultraviolet absorption, and by alkali catalyzed isomerization<sup>4</sup> to the starting material (83%).

(1) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 5063 (1960); **83**, 2806 (1961).

(2) K. J. Crowley, *Proc. Chem. Soc.*, 334 (1962); cf. R. Srinivasan, *J. Am. Chem. Soc.*, **84**, 4141 (1962).

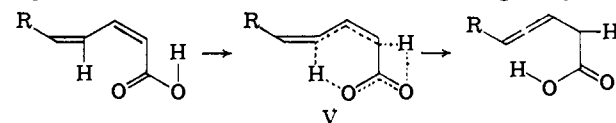
(3) A 450-watt Hanovia high-pressure mercury vapor lamp was used in a double walled water-cooled Vycor glass immersion well; rather more than 1 hr. irradiation was required per gram of sorbic acid. Non-allenic monomeric products were obtained in only minor amounts in all irradiations described.

(4) E. R. H. Jones, G. H. Whitham and M. C. Whiting, *J. Chem. Soc.*, 3201 (1954).

(5) E. P. Kohler and F. R. Butler, *ibid.*, **48**, 1041 (1926).

The yield of allene (II) was considerably increased and the irradiation time reduced by the addition of 1% of formic acid. No allene-type product was detected on irradiation of 5% aqueous potassium sorbate. Irradiation of a 1% solution of methyl sorbate in ether containing 10% formic acid resulted in an 8% yield of the methyl ester of II. This product could not be detected when the irradiation was carried out in the absence of formic acid, although a low (0.1%) yield of the allene ester was indicated when the concentration of methyl sorbate was increased to 5%.

Thus the non-ionized carboxyl group appears to play a part in the isomerization, so that the change may take



place as generalized in V, after preliminary conversion to the 2,3-*cis* isomer. The mechanism and the possibility of extending this reaction are being investigated.

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### AN INVERSE CARBON ISOTOPE EFFECT ON THE IONIZATION OF TRIPHENYLMETHYL CHLORIDE. KINETIC ISOTOPE EFFECTS ON $S_N1$ AND $S_N2$ REACTIONS<sup>1</sup>

Sir:

The carbon kinetic isotope effect on bimolecular nucleophilic substitution in methyl halides ( $S_N2$  reaction) is known to be large: reported  $C^{12}:C^{13}$  rate ratios at 25° range from 1.04 to 1.09<sup>2</sup> and  $C^{12}:C^{14}$  ratios are correspondingly higher.<sup>3</sup> In contrast, to this, the only reported carbon isotope effect on unimolecular heterolysis of a carbon-halogen bond ( $S_N1$  reaction) is small. The  $C^{12}:C^{14}$  rate ratio for the solvolysis of *t*-butyl chloride at 25° is 1.027,<sup>4</sup> this corresponds to a carbon-13 isotope effect of just over 1.01. We wish to report an isotope effect on an equilibrium closely related to  $S_N1$  heterolysis which supports this low rate ratio: the  $C^{12}:C^{13}$  equilibrium constant ratio for the ionization of triphenylmethyl chloride in liquid sulfur dioxide at 0° is 0.983. Analysis of this system suggests that carbon isotope effects on  $S_N1$  reactions may in general be smaller than those on  $S_N2$  reactions.

The isotope effect on this ionization was measured by comparing the conductances of sulfur dioxide solutions of triphenylmethyl chloride and triphenylmethyl- $\alpha$ - $C^{13}$  chloride. The labeled material was prepared from barium carbonate- $C^{13}$  with a nominal carbon-13 content of 66%. This carbonate was converted to benzoic- $\alpha$ - $C^{13}$  acid. The acid, *via* its ester, was transformed to triphenylmethanol- $\alpha$ - $C^{13}$  and the chloride was obtained directly from this alcohol. The carbon-13 content of the chloride and of two of its precursors was 65.6 atom % at the labeled position (direct analysis). The ratio of ionization constants in liquid sulfur dioxide solution at 0° was determined by measuring conductivities of separate solutions of normal and isotopic chlorides at very nearly the same concentrations.<sup>5</sup>

(1) Research supported in part by the U. S. Atomic Energy Commission under USAEC Contract AT(11-1)-1025 to the Illinois Institute of Technology and at Brookhaven National Laboratory.

(2) K. R. Lynn and P. E. Yankwich, *J. Am. Chem. Soc.*, **83**, 53, 790, 3220 (1961).

(3) M. L. Bender and D. F. Hoeg, *ibid.*, **79**, 5649 (1957); G. J. Buist and M. L. Bender, *ibid.*, **80**, 4308 (1958).

(4) M. L. Bender and G. J. Buist, *ibid.*, **80**, 4304 (1958).

(5) See N. N. Lichtin, E. S. Lewis, E. Price and R. R. Johnson, *ibid.*, **81**, 4520 (1959), for the basic principles of the method.