Stereochemistry of the Decomposition of 2-Butene Episulfoxides

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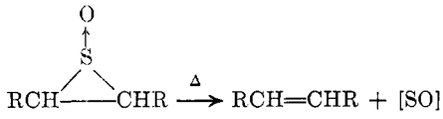
Recent studies on the decomposition of episulfones have demonstrated the elimination of sulfur dioxide to be stereospecific.[1] For example, *cis*-1,2-diphenylethylene episulfone decomposes at 85° to yield *cis*-stilbene[1a] and *cis*-2-butene episulfone pyrolyzes to give *cis*-2-butene.[1b]

We have studied the stereochemistry of an analogous reaction, the dethionylation of episulfoxides. Episulfoxides, prepared by oxidation of the corresponding episulfides, are pyrolyzed readily to form olefins and sulfur monoxide.[2] No additional organic products



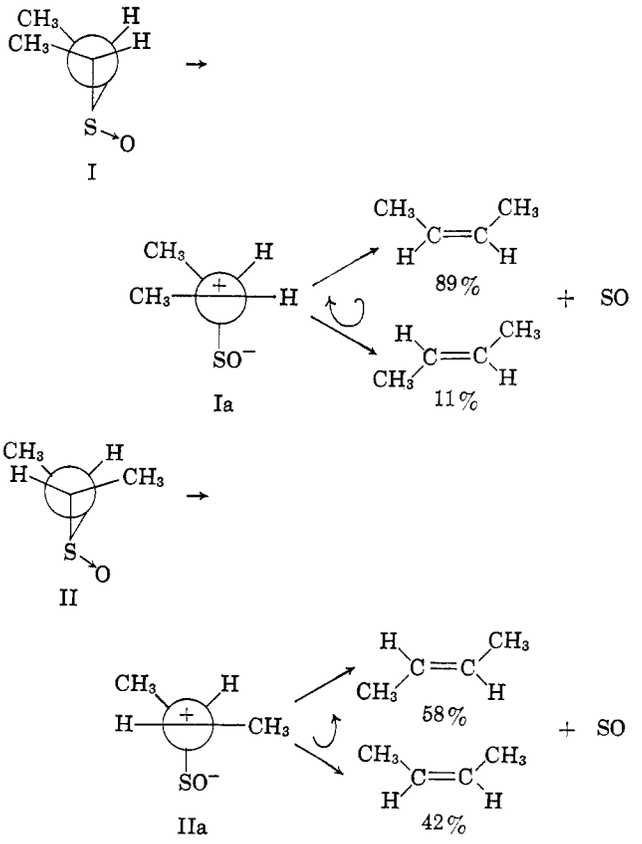
have been detected from the dethionylation reaction.[3] Yields of ethylene from pyrolysis of ethylene episulfoxide have been estimated from glpc data to be at least 70%.[4]

cis- and *trans*-2-butene episulfoxides were obtained by the sodium metaperiodate oxidation of the corresponding episulfides which had been prepared by known methods,[5] and were found to be isomerically pure by gas–liquid partition chromatography (glpc). The *cis*- and *trans*-2-butene episulfoxides could not be distilled owing to their thermal instability, but each was found to be free of its stereoisomer by infrared analysis.

The 2-butene episulfoxides were each pyrolyzed in the injection port of a glpc instrument at 150°. *cis*-2-Butene episulfoxide (I) decomposed to yield 89% *cis*-2-butene and 11% *trans*-2-butene. *trans*-2-Butene episulfoxide (II) gave only 58% *trans*-2-butene and 42% *cis*-2-butene. Moreover, in independent experiments, no evidence could be found by infrared analysis of solutions of partially pyrolyzed *cis*- and *trans*-2-butene episulfoxides that isomerization occurs prior to dethionylation. The elimination of sulfur monoxide does not, therefore, appear to be completely stereospecific as would be predicted from a mechanism involving cleavage of the two carbon–sulfur bonds simultaneously with formation of the olefin.

The experimental results can be explained by the steric requirements of an intermediate resulting from a two-step mechanism in which breakage of one carbon–sulfur bond precedes breakage of the other.

This suggested mechanism is an E1-type elimination, in which the resulting intermediates Ia and IIa are



more or less capable of limited internal rotation about the carbon–carbon bond.[6] Intermediate Ia, obtained from *cis*-2-butene episulfoxide (I) would be essentially locked in the initially formed conformation. Rotation about the internal carbon–carbon bond would be restricted owing to one of the methyl groups having to eclipse either another methyl group or the S–O group. The result would be a high degree of stereospecificity leading predominately to *cis*-2-butene. *trans*-2-Butene episulfoxide (II) would lead to the formation of intermediate IIa, which would be expected to possess somewhat greater rotational freedom than intermediate Ia, since partial rotation would involve eclipsing only of a methyl group and a hydrogen atom. Partial rotation about the internal carbon–carbon bond would result in loss of stereospecificity, with the result being formation of a considerable amount of *cis*-2-butene. Since the isomeric 2-butene episulfoxides do not yield identical product compositions, intermediates Ia and IIa cannot be equivalent and free rotation does not occur. It is implied in this argument that the activation energy for elimination of sulfur monoxide from the intermediate is comparable with the internal rotation energy barrier.

Experimental Section

***cis*-2-Butene Episulfoxide (I).**—*cis*-2-Butene episulfide was prepared in 43.2% yield by the reaction of thiourea with *cis*-2,3-epoxybutane (99% minimum isomer purity).[7] The episulfide was distilled at 52.5–53° at 130 mm (lit.[5] bp 51–51.5° at 130 mm) and was determined to be free of the *trans* isomer by glpc analysis. A solution of 3.7 g (0.042 mole) of *cis*-2-butene episulfide in 90 ml of methanol was added dropwise to a stirred solu-

(1) (a) N. Tokura, T. Nagai and S. Matsumura, *J. Org. Chem.*, **31**, 349 (1966); (b) N. P. Neureiter, *J. Am. Chem. Soc.*, **88**, 558 (1966).

(2) G. E. Hartzell and Janet N. Paige, *ibid.*, **88**, 2616 (1966).

(3) The corresponding episulfides are stable under the conditions for dethionylation of episulfoxides and would have been detected if formed.

(4) G. E. Hartzell and J. N. Paige, unpublished results.

(5) (a) G. K. Helmkamp and D. J. Pettitt, *J. Org. Chem.*, **25**, 1754 (1960); (b) F. G. Bordwell and H. M. Andersen, *J. Am. Chem. Soc.*, **75**, 4959 (1953).

(6) The postulation of an E1 initial ionization of the episulfoxide is analogous to the unimolecular elimination reactions of sulfonium compounds. See D. J. Cram in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 6, p 314.

(7) N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.*, **81**, 578 (1959).

tion of 11.3 g (0.053 mole) of sodium metaperiodate in 125 ml of water at 0–5° over a period of 30 min. After stirring for 1 hr, the cold reaction mixture was filtered. The aqueous solution was extracted with 5–30-ml portions of chloroform. The combined chloroform extracts were dried over sodium sulfate. The chloroform was substantially removed by distillation under reduced pressure. The crude product, weighing 2.0 g, possessed an infrared spectrum showing absorption at 1078 cm^{-1} for the S–O bond.[8]

trans-**2-Butene Episulfoxide (II).**—*trans*-2-Butene episulfide, prepared from *trans*-2,3-epoxybutane (99% minimum isomer purity), was distilled at 45–45.5° at 155 mm (lit.[5] bp 43–43.2° at 140 mm) and was found by glpc to be free of the *cis* isomer. *trans*-2-Butene episulfoxide was prepared by oxidation of the episulfide according to the procedure described for the *cis* isomer. The crude product, weighing 0.6 g, showed infrared absorption at 1090 cm^{-1} for the S–O bond.[8]

Pyrolysis of *cis*- and *trans*-2-Butene Episulfoxides.—Samples of each of the isomeric 2-butene episulfoxides were pyrolyzed in the injection port (150°) of an F & M Model 300 glpc instrument. A 30 ft × 1/8 in. column of 30% dimethylsulfolane on Chromosorb P jacketed in an ice bath at 0° was used for separation of the *cis*- and *trans*-2-butenes. Retention times of 31.2 min for *trans*-2-butene and 36.7 min for *cis*-2-butene were determined using known mixtures of the isomeric 2-butenes. Pyrolysis product analyses were determined as peak area per cent of the total column effluent.

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(8) Although isomer purity was established at the episulfide step of the synthesis, it was reconfirmed on the episulfoxides. Using known mixtures of the *cis*- and *trans*-2-butene episulfoxides as infrared standards, it was determined that each isomer possessed a minimum purity of 97%.

The Chemical Shift of the Hydroxyl Proton of Oximes in Dimethyl Sulfoxide

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In the solvents most frequently used in determination of pmr spectra (*i.e.*, $CDCl_3$ or CCl_4) the chemical shift of the OH proton of a hydroxylic substance generally exhibits a very considerable concentration dependence and is therefore not readily correlated with molecular structure; moreover, the OH signal may be quite broad. These phenomena are caused by self-association through hydrogen bonding and by the facile proton exchange among aggregate species catalyzed by the traces of acid almost always present in these solvents. Oximes appear to constitute no exception to this behavior,[1] and this normally precludes the detection of separate OH proton signals due to *syn* and *anti* oxime isomers in mixtures of the two.

We have found that in ≤5 mole % solution in dimethyl sulfoxide most simple oximes and many containing an additional functional group exhibit a hydroxyl proton resonance signal whose chemical-shift value is essentially concentration independent and thus characteristic of the particular oxime. This phenomenon is presumably attributable to the solvent's pronounced tendency to act as a strong hydrogen-bond acceptor which enables it to solvate strongly the oxime monomer. Similar observations have been reported in the case of alcohols[2] and phenols[3] dissolved in this same solvent.

We have now determined the hydroxyl proton chemical shift of some sixty oximes varying widely in type, and have found the signals to range from 8.6 to 13.3 ppm downfield from tetramethylsilane. The data show that the OH proton chemical shift often constitutes a valid basis for assigning *syn*[4] or *anti*[4] configuration to aldoximes and methyl ketoximes and also provides useful information concerning the nature of substituent groups bonded to the oxime trigonal carbon. Other investigators have focused chiefly upon the chemical shift of CH protons in developing criteria for configurational assignment,[5–7] although separate OH proton signals have previously been observed for *syn* and *anti* isomers of isophorone oxime in deuterated dimethyl sulfoxide solution.[8] With few exceptions we have found the OH proton signal rather sharply defined. In no case was splitting of the signal owing to spin–spin coupling detected. More than one oxime OH proton peak invariably signified either (a) the presence of a mixture of *syn* and *anti* isomers or (b) the presence in the molecule of two or more nonequivalent oxime groupings.

Table I summarizes our results with aliphatic aldoximes and methyl ketoximes, two alicyclic ketoximes being included for comparison. In common with other investigators[5–7] we find that most aliphatic oximes isolated and purified by distillation are obtained as mixtures of *syn* and *anti* isomers. In fact the data for all eight isomeric pairs of Table I were obtained from samples containing both geometric isomers. Thus in these instances two separate OH proton signals of unequal intensity were observed. The pure solid *anti* isomer of *n*-heptaldoxime (mp 54–56°) was partially isomerized to the *syn* isomer by heating the neat substance for some time a little above its melting point. This procedure failed entirely to produce detectable amounts of the sterically unfavored and so far unreported *anti* isomers of pivaldoxime and pinacolone oxime from their well-known *syn* isomers.

From Table I it can be seen that for simple aliphatic aldoximes the OH proton signals for the *syn* isomers range from δ = 10.25 to 10.31 ppm, while the range for the corresponding *anti* isomers is δ = 10.60 to 10.68 ppm. Formaldoxime constitutes an exception with δ = 11.01 ppm. Thus, owing to magnetic anisotropy effects, the hydroxyl proton is some 0.4 ppm more shielded in *syn*- than in *anti*-aldoximes. Unequivocal assignment of these signals to *syn*- and *anti*-aldoxime isomers was accomplished by correlating each OH signal with the corresponding trigonal CH signal for the same isomer. Phillips[5] and Lustig[6] had earlier demonstrated that the proton attached to the oxime

(1) N. S. Bhacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, "NMR Spectra Catalog," Vol. 2, Varian Associates, Palo Alto, Calif., 1963, Spectra No. 373, 420.

(2) O. L. Chapman and R. W. King, *J. Am. Chem. Soc.*, **86**, 1257 (1964).

(3) R. J. Ouelette, *Can. J. Chem.*, **43**, 707 (1965).

(4) Throughout this communication *syn*-aldoxime means that isomer in which H and OH are *cis* to one another; analogously the *syn*-methyl ketoxime has CH_3 and OH *cis* to one another.

(5) W. D. Phillips, *Ann. N. Y. Acad. Sci.*, **70**, 817 (1958).

(6) E. Lustig, *J. Phys. Chem.*, **65**, 491 (1961).

(7) (a) G. J. Karabatsos, R. A. Taller, and F. M. Vane, *J. Am. Chem. Soc.*, **85**, 2326 (1963); (b) *ibid.*, **85**, 2327 (1963).

(8) G. Slomp and W. J. Wechter, *Chem. Ind.* (London), 41 (1962).