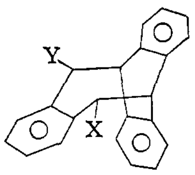
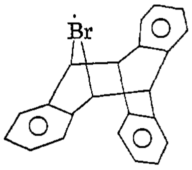
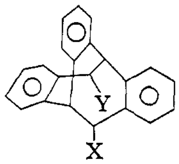
The reaction of I with 1 equiv of N-bromosuccinimide (NBS) in CCl$_4$ (tungsten lamp) gave the previously reported monobromide III, mp 183°.[5,6] Lithium aluminum hydride (LAH) reduction of III gave I, confirming the unrearranged skeletal structure of III. Acetolysis of III gave the monacetate IV, mp 172°,[1] assigned the rearranged structure IVb instead of the originally assigned structure IVa for the following reasons. Alkaline hydrolysis of IVb gave alcohol Vb (rather than Va), mp 191°,[1] converted by thionyl chloride (*via* the uncharacterized VIb) followed by LAH reduction to the new hydrocarbon 3,7-*o*-benzeno-1,2,5,6-dibenzocyclooctadiene ("semitriskelene," VII), mp 235°. Chromic acid oxidation of Vb gave monoketone VIIIb (rather than VIIIa), mp 193°;[1] further oxidation of VIIIb gave diketone IXb, mp 224–225°. The isomeric unrearranged diketone IXa, mp 213–214°, was obtained by direct chromic acid oxidation of hydrocarbon I.[7]

Bromination of I (tungsten lamp) with 2 equiv of NBS (or better, bromine) in CCl$_4$ gave the rearranged dibromide Xb, mp 235° (reported[1] as Xa, mp 216–217°). Further light-catalyzed bromination of Xb afforded tribromide XI, mp 217°, and finally tetrabromide XII, mp 224–225° dec; solvolysis of XII in moist methanol gave diketone IXb. Bromides Xb, XI, and XII were all reduced by LAH (or zinc) to give the same hydrocarbon, triskelene (II),[4] mp 207°. Zinc reduction of tetrabromide XII could be effected in two stages, allowing the isolation of 6,12-dibromotriskelene (XIII), mp 233°. The structure of XIII has been confirmed by a complete X-ray crystallographic analysis.[8]



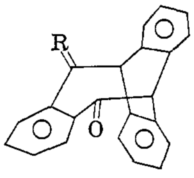


XIV

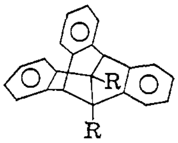


Series a
I, X = Y = H
III, X = Br, Y = H
IV, X = OCOCH$_3$, Y = H
V, X = OH, Y = H
X, X = Y = Br

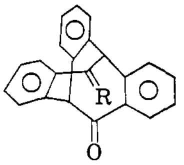
Series b
IV, X = OCOCH$_3$, Y = H
V, X = OH, Y = H
VI, X = Cl, Y = H
VII, X = Y = H
X, X = Y = Br



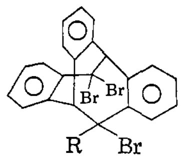
VIIIa, R = H$_2$
IXa, R = O



II, R = H
XIII, R = Br



VIIIb, R = H$_2$
IXb, R = O



XI, R = H
XII, R = Br

The bromination of I under free radical conditions takes place rapidly (within a few minutes) and cleanly to give only either the *unrearranged* monobromide III or the *rearranged* dibromide Xb. Clearly the bromine atom in III must play a critical part in the rearrangement to the semitriskelene skeleton which accompanies bromination of III to Xb. We suggest that the radical formed by abstraction of a hydrogen atom from III is stabilized considerably by neighboring group participation of the bromo substituent. The resulting strainless but rigid bridged radical (XIV) has a geometry particularly conducive to a transoid rearrangement to the energetically more favorable semitriskelene system.[9] Evidence has been reported previously in support of three-membered-ring bromine radical intermediates produced during photobromination.[10] The conversion of III to Xb is, to our knowledge, the first example of a reaction involving a five-membered-ring bridged bromine radical.

Acknowledgment. We thank the National Science Foundation for their general support of this work under Grants GP-3369 and GP-4931.

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[5] Satisfactory elemental analyses were obtained for all compounds reported in this paper except for tribromide XI which was not obtained entirely free of Xb.

[6] This melting point is at variance with that (141–142°) previously reported.

[7] The diketone (mp 213–214°) previously assigned structure IXa (ref 1) must be regarded as a slightly impure sample of our diketone IXb (mp 224–225°). The ultraviolet spectrum reported for this material is identical with that of our rearranged diketone IXb. In contrast, the ultraviolet spectrum of our unrearranged diketone IXa shows the following values in isooctane solution: $\lambda_{\max}$ 203 mμ (log ϵ 4.69), 221 (4.34), 230 (4.25), and 273 (4.14). Apparently, the carbonyl groups of diketone IXa show very little conjugation with the adjacent aromatic ring, indicating a bent structure for the *o*-phthaloyl system.

(8) This work was carried out by R. Henriques, F. Paton, and R. Gosling at the Department of Physics, University of the West Indies. A complete analysis of the structure of XIII will be published elsewhere.

(9) Molecular models indicate that no appreciable nonbonded interactions exist in semitriskelene (VII). On the other hand, such interactions are present in hydrocarbon I (see ref 1).

(10) P. S. Skell, D. L. Tuleen, and P. D. Readio, *J. Am. Chem. Soc.*, **85**, 2849 (1963); P. S. Skell and P. D. Readio, *ibid.*, **86**, 3334 (1964).

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Ethylene Episulfoxide[1]

Sir:

Reported attempts to oxidize ethylene episulfide to either the episulfoxide or the episulfone have consistently failed.[2] Several examples of ethylene episulfones are now known, but these were prepared by reaction of a diazomethane with sulfur dioxide.[3] The only characterized examples of an episulfoxide or an episulfone obtained by oxidation of the corresponding episulfide are those resulting from the hydrogen peroxide oxidation of dibenzoylstilbene episulfide.[4]

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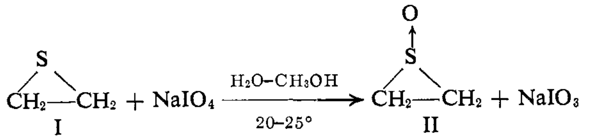
(1) Thiirane 1-oxide.

(2) (a) G. Hesse, E. Reichold, and S. Majmudar, *Chem. Ber.*, **90**, 2106 (1957); (b) C. C. J. Culvenor, W. Davies, and N. S. Heath, *J. Chem. Soc.*, 282 (1949).

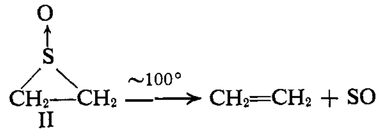
(3) (a) G. Hesse, E. Reichold, and S. Majmudar, *Chem. Ber.*, **90**, 2106 (1957); (b) H. Staudinger and F. Pfenninger, *ibid.*, **49**, 1941 (1916); (c) N. Tokura, T. Nagai, and S. Matsumura, *J. Org. Chem.*, **31**, 349 (1966); (d) N. P. Neureiter, *J. Am. Chem. Soc.*, **88**, 558 (1966).

We have now prepared ethylene episulfoxide (II) in yields up to 65% by direct oxidation of ethylene episulfide (I) using sodium metaperiodate in aqueous methanolic solution.[5] The ethylene episulfoxide was distilled at 46–48° (2.0 mm); $n^{25}D$ 1.5210. *Anal.* Calcd for C_2H_4SO: C, 31.6; H, 5.3; S, 42.1. Found: C, 31.7; H, 5.4; S, 42.2.

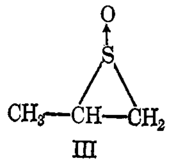


Infrared, nmr, ultraviolet, and mass spectra were all consistent with the structure of ethylene episulfoxide. The infrared spectrum showed C–H stretching at 3000 and 3100 cm^{-1}, indicative of the three-membered ring system, and intense absorption at 1080 cm^{-1}, attributed to the sulfoxide group. One ultraviolet maximum was exhibited in methanol at 220 mμ (ϵ_{max} 795). The nmr spectrum consisted of a complex A_2B_2 multiplet at −1.80 to −2.58 ppm (internal TMS), indicating the oxygen atom to lie out of the plane of the ring. The C^{13}–H coupling constant was 172.3 cps, typical of a three-membered ring system. The mass spectrum of ethylene episulfoxide obtained at 50–100° exhibited a parent peak corresponding to mass 76.

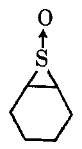
Ethylene episulfoxide has been found to undergo two significant types of reactions. At temperatures near 100°, dethionylation occurs to yield ethylene and sulfur monoxide.[6] Sulfur monoxide is thermodynamically unstable and disproportionates to elemental sulfur and sulfur dioxide.[7] The dethionylation reaction was observed by mass spectrometry, differential thermal analysis, and cracking in a glpc column. Preliminary kinetic experiments carried out in chlorobenzene solution indicate the dethionylation of ethylene episulfoxide to be first order and to possess an activation energy of 35 kcal/mole.



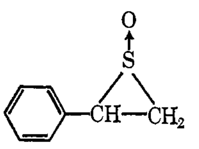
Three additional episulfoxides, propylene episulfoxide (III), cyclohexene episulfoxide (IV), and styrene episulfoxide (V), were also prepared and found to pyrolyze to the corresponding olefins. These episulfoxides could not be distilled without decomposition. In each case, the crude episulfoxide was analyzed by infrared spectroscopy and found to possess strong S–O absorption at 1070–1085 cm^{-1} and to be completely free of olefin. Pyrolysis of each episulfoxide in a glpc column afforded isolation of a significant quantity of decomposition product which possessed an infrared spectrum identical with that of an authentic sample of the appropriate olefin.



III

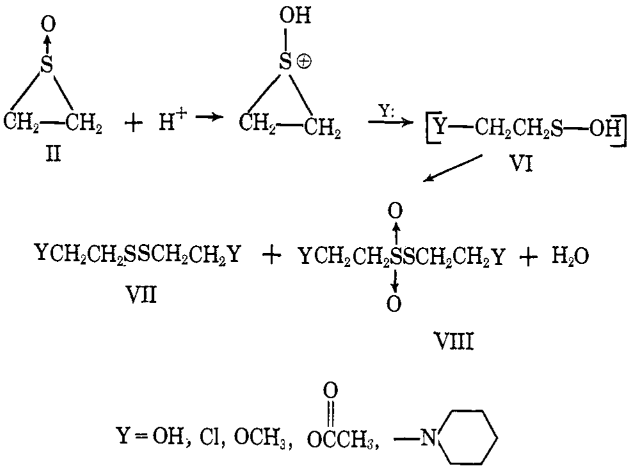


IV



V

Ethylene episulfoxide was also found to undergo acid-catalyzed nucleophilic attack, with opening of the three-membered ring. It is postulated that protonation of the sulfoxide oxygen occurs, followed by attack of the nucleophile to form a sulfenic acid (VI). Due to the instability of alkylsulfenic acids, the ultimate products observed were a disulfide (VII) and a thiolsulfonate (VIII).[8] Ring-opening reactions of ethylene episulfoxide were carried out using water, hydrogen chloride, methanol, acetic acid, and piperidine. The crude disulfide–thiolsulfonate mixture obtained from the reaction of ethylene episulfoxide in methanol solution acidified with sulfuric acid was subsequently reduced with triphenylphosphine to give an 88% over-all yield of 2-methoxyethanethiol.



Based on one known exposure, ethylene episulfoxide can cause burns upon contact with the skin. We suspect that it could cause serious eye injury as well. The material should be handled with caution.

Acknowledgment. The authors wish to acknowledge the assistance of M. Dilling, J. C. Gavan, A. W. Douglas, and F. L. Beman for spectrometric analyses, and J. L. Fookes for technical help.

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(4) D. C. Dittmer and G. C. Levy, *J. Org. Chem.*, **30**, 636 (1965).

(5) The sodium metaperiodate oxidation of sulfides to sulfoxides has been previously reported: (a) N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962); (b) P. Friedman and P. Allen, Jr., *ibid.*, **30**, 780 (1965).

(6) Stereospecific elimination of sulfur dioxide from episulfones has been recently reported.[3c,d]

(7) P. W. Schenk and R. Steudel, *Angew. Chem.*, **4**, 402 (1965).

(8) H. Gilman, "Organic Chemistry," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p 920.

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Received February 21, 1966

The Photochemical Conversion of Caffeic Acid to Esculetin. A Model for the Synthesis of Coumarins *in Vivo*

Sir:

We wish to report the first example of the photochemical oxidative cyclization of a cinnamic acid to a coumarin.

The photochemical *trans* → *cis* isomerization of caffeic acid (3,4-dihydroxycinnamic acid) has been reported.[1,2] We have observed that when a solution of

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(1) A. H. Williams, *Chem. Ind.* (London), 120 (1955).

(2) W. L. Butler and H. W. Siegelman, *Nature*, **183**, 1813 (1959).