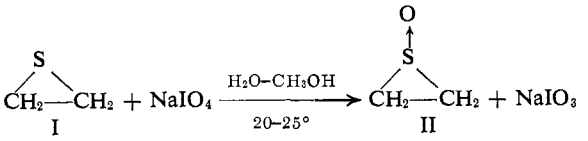
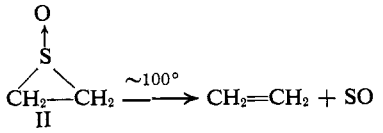
We have now prepared ethylene episulfoxide (II) in yields up to 65% by direct oxidation of ethylene episulfide (I) using sodium metaperiodate in aqueous methanolic solution.[5] The ethylene episulfoxide was



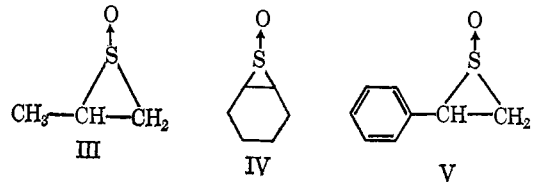
distilled at 46–48° (2.0 mm); $n^{25}D$ 1.5210. *Anal.* Calcd for C_2H_4SO: C, 31.6; H, 5.3; S, 42.1. Found: C, 31.7; H, 5.4; S, 42.2.

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.

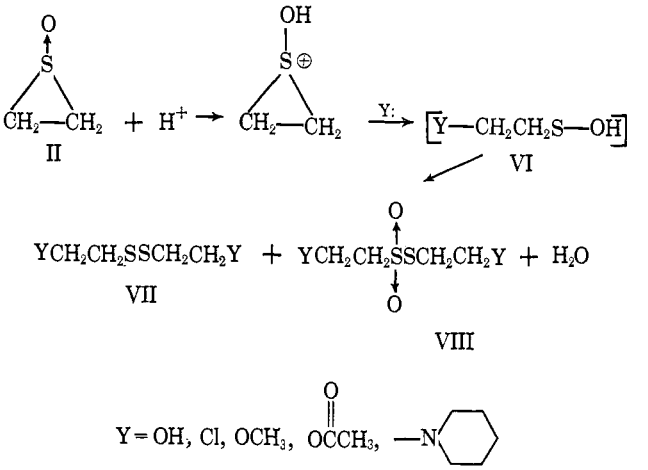
Ethylene episulfoxide has been found to undergo two significant types of reactions. At temperatures near 100°, dethionylation occurs to yield ethylene and sulfur monoxide.[6] Sulfur monoxide is thermodynamically unstable and disproportionates to elemental sulfur and sulfur dioxide.[7] The dethionylation 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.



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.

(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.

G. E. Hartzell, Janet N. Paige
Edgar C. Britton Research Laboratory
The Dow Chemical Company, Midland, Michigan
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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

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

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

caffeic acid in methanol or acetic acid was irradiated[3] at 2537 or 3500 A under nitrogen no other product was detected by thin layer chromatography over polyamide (in methanol–acetic acid–water, 8:2:1) or Avicel[4] cellulose (in 15% acetic acid). When the irradiation was performed in the presence of oxygen bubbled through the solution, a third compound was formed which was easily detected by tlc because of its bright fluorescence. Its mobility was intermediate between those of the two caffeic acid isomers.

As an example, after 14-hr irradiation at 2537 A in presence of oxygen, a solution of 440 mg of caffeic acid in 120 ml of glacial acetic acid was taken to dryness under vacuum. The residue was dissolved in ethyl acetate and the caffeic acids were extracted with the minimum amount of saturated sodium bicarbonate solution. The organic phase was dried and concentrated, yielding 44 mg of a solid. This product was recrystallized from dilute methanol and was found identical in all respects with an authentic sample of esculetin (6,7-dihydroxycoumarin).[5] The same reaction was observed in dilute acetic acid or in methanol. It also took place, but more slowly, at 3500 A.

Earlier workers had noted the presence of traces of esculetin during paper chromatography of caffeic acid solutions when it was performed in the presence of light or after short ultraviolet irradiation[2,6] and its absence when the chromatography was performed in the dark.[2] The primary effect was correctly ascribed to the partial isomerization of the caffeic acid to its *cis* isomer. It was further suggested that the *cis* isomer had undergone a metal ion catalyzed air oxidation to yield esculetin. We have now observed that mixtures of the *cis*- and *trans*-caffeic acid isomers are stable and can be analyzed by thin-layer or paper chromatography in the dark without formation of the coumarin. Furthermore, no esculetin was formed when a mixture of these isomers was neutralized with sodium bicarbonate and the latter mixture was reacidified. It must therefore be concluded that the formation of esculetin from *cis*-caffeic acid is also a photochemical process.

Coumarins are widely distributed in plants, but their biosynthesis has not been firmly established. Cinnamic acids are generally considered to be precursors, undergoing a combination of *cis* isomerization, *ortho* hydroxylation and/or glucosylation, followed by lactonization.[7]

G. W. Kenner, *et al.*, have already described oxidative cyclization reactions leading from cinnamic acids to coumarins through carboxylate cations or free radicals,[8,9] but these authors suggested that it was unlikely that such reactions would compete with enzymatic processes in plants.[9]

The results herein reported strongly suggest that a photochemically induced oxidative cyclization, so easily accomplished *in vitro*, could account, at least in part, for the synthesis of coumarins from cinnamic acids *in vivo*.

Work is in progress designed to elucidate the mechanism of the reaction and to determine its relevance to the biosynthesis of coumarins.

Jacques Kagan

Department of Biological Sciences and Department of Chemistry
University of Illinois at Chicago Circle, Chicago, Illinois 60680

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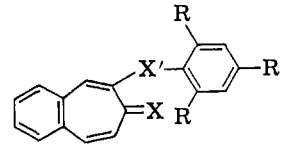
Electron Impact Induced 1,4-Phenyl Migration

Sir:

The study of electron impact induced rearrangements of substituents other than hydrogen is particularly important, not only for their contribution to mass spectral theory, but also practically for the possible limitations these rearrangements might impose on Biemann's elegant element-mapping technique.[1,2] The ejection of stable neutral molecules from the interior portion of some linear molecules with rebonding of the termini constitutes the most common type of rearrangement.[3] The other type, of which only two documented examples have been reported,[4] is the intrinsically more interesting 1,2 migration of an alkyl substituent. We now wish to describe the 1,4 transfer of an aryl group from one oxygen atom to another in a process which competes efficiently with fragmentation even at the lowest electron energies at which fragmentation occurs.

The mass spectrum of 2-phenoxy-4,5-benztropone (I, $M^+ = 248$; 100%) shows two fragment ions of substantial interest at *m/e* 231 (M − 17; 26%) and 220 (M − 28; 60%). The *m/e* 231 ion is due to the loss of –OH and the *m/e* 220 ion is due to the loss of carbon monoxide. Separate examination of carbonyl-^{18}O-labeled (II) and ether-^{18}O-labeled (III) benztropones (containing 29 and 18% of ^{18}O, respectively) shows



I, R = H; X = X′ = ^{16}O
II, R = H; X = ^{18}O; X′ = ^{16}O
III, R = H; X = ^{16}O; X′ = ^{18}O
IV, R = D; X = X′ = ^{16}O

(1) K. Biemann, P. Bommer, and D. M. Desiderio, *Tetrahedron Letters*, 1725 (1964).
(2) H. Achenbach and K. Biemann, *J. Am. Chem. Soc.*, **87**, 4944 (1965).
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(4) (a) F. Komitsky, Jr., J. E. Gurst, and C. Djerassi, *ibid.*, **87**, 1398 (1965); (b) C. Djerassi, A. M. Duffield, F. Komitsky, Jr., and L. Tokes, *ibid.*, **88**, 860 (1966).

(3) A Rayonet photochemical reactor from the Southern New England Ultraviolet Co., Middletown, Conn., was used in this work.
(4) (a) American Viscose Co., Newark, Del.; (b) M. L. Wolfrom, *Chem. Ind.* (London), 1065 (1964).
(5) We wish to thank Professor T. J. Mabry, Department of Botany, The University of Texas, who kindly provided this sample.
(6) C. F. van Sumere, F. Parmentier, and M. van Poucke, *Naturwiss.*, **46**, 668 (1959).
(7) References to the earlier studies may be found in: (a) D. J. Austin and M. B. Meyers, *Phytochemistry*, **4**, 255 (1965); (b) S. A. Brown, G. H. N. Towers, and D. Chen, *ibid.*, **3**, 469 (1964); (c) T. Kosuge in "Proceedings of Symposium, Plant Phenolics Group of North America," V. C. Runeckeles, Ed., Imperial Tobacco Co., Montreal, Canada, 1964, p 83.
(8) G. W. Kenner, M. A. Murray, and C. M. B. Tylor, *Tetrahedron*, **1**, 259 (1957).
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