An Episulfoxide and Episulfone by Oxidation of Dibenzoylstilbene Episulfide

D. C. DITTMER[1] AND G. C. LEVY[2]

Contribution No. 998 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington 98, Delaware, and Department of Chemistry, Syracuse University, Syracuse, New York 13210

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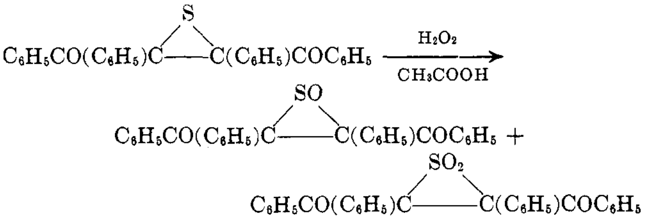
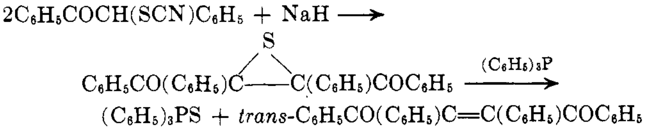
An episulfoxide and episulfone have been obtained by oxidation of dibenzoylstilbene episulfide with hydrogen peroxide in acetic acid. Two isomers of the episulfoxide were isolated. Dibenzoylstilbene episulfide was prepared by treatment of desyl thiocyanate with sodium hydride in dimethoxyethane.

Episulfoxides are rare; only one example has been reported, and its structure was not well characterized.[3] Although several episulfones are known,[4] none has been prepared by oxidation of an episulfide.[5]

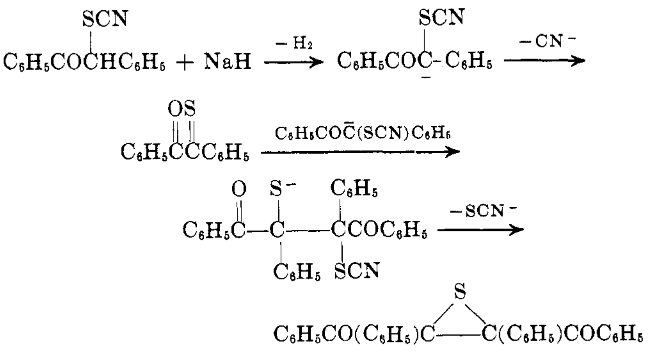
A new episulfoxide and episulfone have been prepared by oxidation of dibenzoylstilbene episulfide with 30% hydrogen peroxide in glacial acetic acid. The episulfoxide was obtained when the oxidation was done with a limited amount of hydrogen peroxide at room temperature; the episulfone was obtained when a greater quantity of hydrogen peroxide was used at steam-bath temperature.



The episulfide is prepared from desyl thiocyanate and sodium hydride in dimethoxyethane. This appears to be a new method whose generality is as yet unexplored. The episulfide is probably mainly the *trans* isomer since *trans*-dibenzoylstilbene was obtained on treatment of the episulfide with triphenylphosphine.

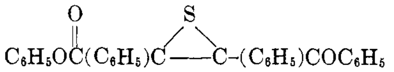


The formation of the episulfide may proceed *via* thiobenzil. Evidence for the formation of both cyanide ion and thiocyanate ion has been obtained.



The elimination of hydrogen cyanide from the thiocyanate is analogous to the elimination of nitrous acid from benzyl nitrite to yield benzaldehyde.[6] A deep blue color, presumably of thiobenzophenone, is obtained when benzhydryl chloride, sodium thiocyanate, and a base are mixed.

The structure of the episulfoxide is inferred from its composition and molecular weight, its mode of preparation, and strong sulfoxide absorption in the infrared at 1065 cm.$^{-1}$. Its ultraviolet absorption spectrum is similar to that of the episulfone, and its proton magnetic resonance spectrum is similar to that of the episulfide and the episulfone. The infrared absorption for the sulfoxide group is at a somewhat greater frequency than is usual for acyclic sulfoxides,[7] and may be attributed to a greater s-character in the S–O bond.[8] There is no evidence of an ester group in the infrared spectrum, which rules out an episulfide ester, a product from a Baeyer–Villiger reaction.



Two isomeric episulfoxides, m.p. *ca.* 170° and *ca.* 145°, respectively, were obtained. The total number of stereoisomers possible for the episulfoxide is four: one DL-*trans* pair and two *meso-cis* forms. The stereochemistry of the two isomers obtained has not been determined. It is possible that solid solutions of the isomers are involved since the melting points of different preparations of pure episulfoxide show some variability. The melting points reported above are for samples on which an elemental analysis had been done.

The structure of the episulfone is supported by its composition and molecular weight, proton magnetic resonance spectrum, infrared spectrum, and ultraviolet spectrum. The infrared absorption for the sulfone group (1315, 1145 cm.$^{-1}$) is not unusual and is similar to the absorption of ethylene sulfone (1310, 1168 cm.$^{-1}$).[4a] During recrystallization the episulfone tends to absorb ether which is not removed in a vacuum. Sulfur dioxide is obtained from the episulfone on heating and was identified in the mass spectrum of the sulfone.

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(1) To whom inquiries should be addressed at the Department of Chemistry, Syracuse University, Syracuse, N. Y. 13210.

(2) National Science Foundation Undergraduate Research Scholar, Syracuse University.

(3) S. B. Soloway, U. S. Patent 2,694,073; *Chem. Abstr.*, **49**, 3465 (1955).

(4) (a) G. Hesse, E. Reichold, and S. Mayundar, *Chem. Ber.*, **90**, 2106 (1957). (b) H. Staudinger and F. Pfenninger, *Ber.*, **49**, 1941 (1916); L. v. Vargha and E. Kovacs, *ibid.*, **75**, 794 (1942); G. P. Hager and R. M. Burgison, *J. Am. Pharm. Assoc.*, **39**, 7 (1950); N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.*, **85**, 1209 (1963).

(5) Previous attempts to oxidize episulfides to episulfoxides or episulfones have failed: H. Staudinger and J. Siegwart, *Helv. Chim. Acta*, **3**, 833 (1920); C. C. J. Culvenor, W. Davies, and N. S. Heath, *J. Chem. Soc.*, 282 (1949).

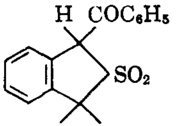
(6) J. U. Nef, *Ann.*, **309**, 175 (1899).

(7) The range for the infrared absorption of sulfoxides is given as 1060–1040 cm.$^{-1}$ in solution, and 10–20 cm.$^{-1}$ lower in the solid state: L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, p. 359.

(8) The carbonyl stretching frequency of what was presumed to be cyclopropanone is greater than that of other cyclic or acyclic ketones: W. B. DeMore, H. O. Pritchard, and N. Davidson, *J. Am. Chem. Soc.*, **81**, 5874 (1959).

The organic material from the pyrolysis seems complex and is currently under investigation.

Structures such as **1** or **2**, analogous to products derived from tetraphenylethylenesulfone,[9] are not considered likely for the sulfone because no absorption caused by an aliphatic proton could be detected in the proton magnetic resonance spectrum. There was no evidence of enol formation (**1** might be expected to enolize readily) in the infrared spectrum. A structure like **2** would be expected to absorb at longer wave lengths in the ultraviolet spectrum than was actually observed. The infrared spectrum also shows no evidence for the triene structure in **2**.



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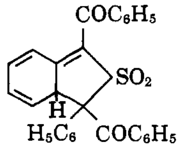

2

Further work on the properties of the episulfoxide and sulfone is in progress.

Experimental

Desyl thiocyanate (2-thiocyanato-2-phenylacetophenone) was prepared by refluxing desyl chloride with potassium thiocyanate in acetone. Desyl chloride (132 g., 0.572 mole) was dissolved in 500 ml. of acetone and was added to potassium thiocyanate (dried, 60 g., 0.62 mole) in 250 ml. of hot acetone in a 1-l., three-neck flask equipped with stirrer and reflux condenser. The mixture was refluxed for 4.5 hr. after which it was filtered while hot. To the filtered solution was added about 200 ml. of benzene. Inorganic salts were extracted with three 100-ml. portions of water. The benzene solution was dried over Molecular Sieves and then concentrated. Petroleum ether was added to the cloud point and the solution was chilled. The desyl thiocyanate was recrystallized from benzene–ligroin to give 123 g. (0.486 mole, 85%) of light pink or white crystals, m.p. 109–110° (lit.[10] m.p. 110–111°).

Dibenzoylstilbene Episulfide.—Sodium hydride (36.1 g. of 53% dispersion in oil, 0.75 mole) in a 2-l., three-neck flask fitted with a mechanical stirrer, a condenser, and addition funnel was washed under dry nitrogen three times with 50-ml. portions of dry petroleum ether to remove the mineral oil. Dry dimethoxyethane (250 ml.) was added. Desyl thiocyanate (185 g., 0.73 mole) in 600 ml. of dry dimethoxyethane was added in one portion to the slurry of sodium hydride which was cooled in an ice–salt bath. The temperature rose to about 45° at once, and there was considerable frothing as hydrogen was evolved. The reaction mixture became red, then yellow as the addition was completed. Stirring was continued at room temperature for 5 hr. The reaction mixture was filtered of a solid which was a mixture of sodium cyanide and sodium thiocyanate (it gave a Prussian blue and also the red ferric complex of thiocyanate). Ether (800 ml.) was added to the filtered reaction solution and this was extracted with three 150-ml. portions of water to remove any potassium thiocyanate. The ether solution was dried over Drierite, filtered, and evaporated on a rotary evaporator to yield a semicrystalline yellow-orange oil. The oil was dissolved in the minimum amount of ether (800–1000 ml.) and methanol (2–3 l.). The solution was concentrated to about two-thirds of the original volume and then chilled. Bright yellow crystals (132 g., 0.486 mole, 85%), m.p. 106–112°, were collected. Frequently, lower melting samples were obtained at first.

A sample [m.p. 107–110°; λ_{max} (CH_3CN) 330 mμ (ϵ 6.8 × 10^3), 250 (shoulder), and 230] from a similar run was analyzed after it had been recrystallized several times from methanol.

Anal. Calcd. for $C_{28}H_{20}O_2S$: C, 79.97; H, 4.80; S, 7.63; mol. wt., 421. Found: C, 79.69; H, 4.73; S, 7.68; mol. wt., 446, 451 (boiling point elevation in ethylene chloride).

Dibenzoylstilbene episulfide (2 g., 0.005 mole) and triphenylphosphine (2 g., 0.008 mole) were dissolved in 50 ml. of xylene and the solution was refluxed for 21 hr. Water was added and the white solid (1.7 g.) which appeared at the water–xylene interface was removed by filtration and washed with benzene. It was recrystallized twice from 150 ml. of glacial acetic acid to give a white solid, m.p. 230° (lit.[11] m.p. 230.3–230.6° for *trans*-dibenzoylstilbene), λ_{max} (CH_3CN) 254 mμ (ϵ 3.3 ×10^4) [lit.[12] λ_{max} (C_2H_5OH) 254 mμ (ϵ 3.3 × 10^4)].

Anal. Calcd. for $C_{26}H_{20}O_2$: C, 86.58; H, 5.19; O, 8.24. Found: C, 86.48; H, 5.25; O, 8.24.

Triphenylphosphine sulfide (m.p. 148–155°, lit.[13] m.p. 157.5°) was isolated also from the reaction mixture. Its infrared spectrum was identical with that of an authentic sample.

Dibenzoylstilbene Episulfoxide.—Dibenzoylstilbene episulfide (3.6 g., 0.0086 mole) was dissolved in 30 ml. of glacial acetic acid with heating (not over 50°). Hydrogen peroxide (30%, 2.5 ml.) was added and the reaction mixture was allowed to stand overnight. A white solid was removed by filtration and washed with a little ether. The material remaining on the filter was recrystallized from ether to give 0.3 g. of a white solid, m.p. 169–173°. Its proton n.m.r. spectrum (60 Mc. in $CDCl_3$) had complex multiplets at 425 and 445 c.p.s. relative to tetramethylsilane.

In another run, 1 ml. of 30% hydrogen peroxide was used and crystals, m.p. 163–165°, were obtained.

Anal. Calcd. for $C_{28}H_{20}O_3S$: C, 77.04; H, 4.62; S, 7.41; mol. wt., 437. Found: C, 77.26; H, 4.75; S, 6.99; mol. wt., 438 (osmometric in acetone).

In another experiment, dibenzoylstilbene episulfide (4.2 g., 0.01 mole) was dissolved in 75 ml. of glacial acetic acid on a steam bath. Hydrogen peroxide (30%, 3.5 ml.) was added, and the bright yellow reaction mixture was heated. After 8 min. the color was very pale. The acetic acid solution was poured into 400 ml. of water to give 6.3 g. of a buff precipitate. The precipitate was washed on the filter with 50% sodium bicarbonate solution and with water. The material was dried and washed with ether to give a white solid, m.p. 145–147°.

Anal. Calcd. for $C_{28}H_{20}O_3S$: C, 77.04; H, 4.62; S, 7.41; mol. wt., 437. Found: C, 77.10; H, 4.71; S, 6.99; mol. wt., 440 (osmometric in acetone).

The ultraviolet spectrum in dioxane has shoulders at 255 and 230 mμ. The episulfoxide became green on exposure to ultraviolet light.

The infrared spectra in Nujol of the two isomers are rather different. The high melting isomer had absorption at 1670 (s), 1620 (m), 1590 (m), 1570 (w), 1495 (m), 1445 (s), 1315 (m), 1305 (m), 1245 (m), 1220 (m), 1180 (w), 1160 (w), 1145 (m), 1110 (m), 1100 (m), 1065 (s), 1050 (s), 1035 (w), 1025 (m), 1005 (m), 1000 (w), 960 (m), 940 (w), 930 (w), 912 (w), 848 (w), 810 (w), 775 (s), 755 (m), 740 (m), 705 (sh), and 693 (s) cm.$^{-1}$. The low melting isomer had absorption at 1670 (s), 1600 (m), 1580 (m), 1565 (w), 1480 (m), 1440 (s), 1315 (w), 1300 (m), 1260 (s), 1215 (s), 1180 (w), 1115 (m), 1100 (m), 1065 (s), 1045 (m), 1030 (m), 1000 (w), 950 (s), 884 (w), 857 (m), 820 (w), 785 (m), 777 (m), 760 (s), 745 (s), 705 (s), and 695 (s) cm.$^{-1}$.

When the episulfoxide was heated in a vacuum (0.02 mm.), the sulfur content decreased.

Dibenzoylstilbene Episulfone.—Dibenzoylstilbene episulfide (8.4 g., 0.02 mole) was dissolved in 100 ml. of glacial acetic acid with warming. Hydrogen peroxide (30%, 11 ml.) was added and the reaction was heated on a steam bath at 70–90° for 3 hr. It was allowed to stand at room temperature overnight, and 5 g. (56%) of white crystals, m.p. 75–80°, was obtained. The solid was washed four times with petroleum ether (b.p. 30–60°). A sample of this material was heated in a test tube equipped with an outlet which passed into 30% hydrogen peroxide. A gas was evolved, and the odor of sulfur dioxide was apparent. When aqueous barium chloride was added to the solution of hydrogen peroxide, an acid-insoluble, white precipitate of, presumably, barium sulfate was obtained.

A sample of the episulfone was heated to 300° and the evolved gas was determined to be ether and sulfur dioxide by mass spectrometry. The gas evolved also was shown to be sulfur dioxide

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[9] H. Kloosterziel and H. J. Backer, *Rec. trav. chim.*, **71**, 1235 (1952).

[10] H. L. Wheeler and T. B. Johnson, *Am. Chem. J.*, **26**, 202 (1901).

[11] N. M. Bikales and E. I. Becker, *J. Org. Chem.*, **21**, 1405 (1956).

[12] L. P. Kuhn, R. E. Lutz, and C. R. Bauer, *J. Am. Chem. Soc.*, **72**, 5058 (1950).

[13] A. Michaelis and H. V. Soden, *Ann.*, **229**, 307 (1885).

by its infrared spectrum which was identical with the spectrum of known sulfur dioxide.[14]

The sulfone was recrystallized from ether to give white crystals, m.p. 75–78°. Further recrystallizations gave material melting at 82–84°. The substance crystallized with 0.5 mole of ether which was not removed completely even on pumping at 0.05-mm. pressure with gentle heating. The ether was detected by a proton n.m.r. spectrum of the episulfone. A typical ether spectrum was observed in deuterioacetone in addition to complex multiplets centered at 425 and 445 c.p.s. (relative to tetramethylsilane at 60 Mc.). The relative areas of the absorption peaks for the aromatic protons *vs.* the ether protons were 20:5 corresponding to the empirical formula $C_{28}H_{20}O_4S \cdot 0.5C_4H_{10}O$. The areas under the two absorptions for the methylene protons in the ether were in the ratio of 6:4.

Anal. Calcd. for $C_{28}H_{20}O_4S \cdot 0.5C_4H_{10}O$: C, 73.59; H, 5.15; S, 6.55; mol. wt. (assume dissociation), 326. Found: C, 73.45; H, 5.26; S, 6.66; mol. wt., 339, 348 (boiling point elevation in acetone).

The molecular weight of a sample (m.p. 128–129°) recrystallized from water–acetic acid, *in which the etherate did not form,* was determined from the elevation of the boiling point of ethylene dichloride.

Anal. Calcd. for $C_{28}H_{20}O_4S$: C, 74.31; H, 4.48; S, 7.09; mol. wt., 453. Found: C, 74.83; H, 4.80; S, 6.79; mol. wt., 428, 426, 453.

The ultraviolet spectrum had no defined maxima, λ (dioxane) 260 and 235 mμ.

Acknowledgment.—We wish to thank Dr. W. A. Sheppard and Dr. E. A. LaLancette for helpful discussion.

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[14] "Sadtler Standard Spectra," Midget Edition, The Sadtler Research Laboratories, Philadelphia, Pa., 1962, No. 841.

Notes

Preparation of 1,2,3-Triazoles from 7-Azido-1,3,5-cycloheptatriene. A Displacement from Nitrogen

J. J. LOOKER

Research Laboratories, Eastman Kodak Company,
Rochester, New York 14650

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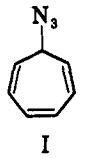
Tropylium azide (7-azido-1,3,5-cycloheptatriene) has been prepared previously,[1] and its n.m.r. spectrum shows that it has the covalent structure I. The ionic form II may exist in ionizing solvents.[2] The covalent structure is also suggested by its physical state (liquid); ionic cycloheptatrienylium compounds are high-melting solids. The observation that no solid separated from a mixture of methyl tropyl ether and hydrazoic acid in ether further supports this assignment since separation of ionic tropylium bromide occurred when hydrogen bromide was passed into a solution of ditropyl ether.[3]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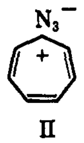
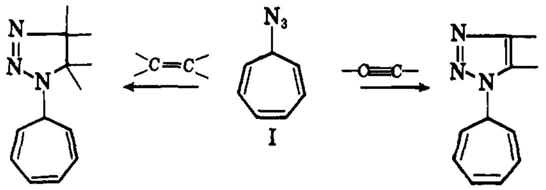
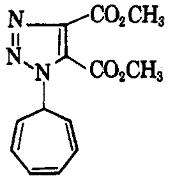

II

Phenyl and benzyl azide can be added to a variety of acetylenes and olefins to produce triazoles and triazolines, respectively.[4-6] Tropylium azide, with the covalent structure I, should undergo addition in a similar manner to form adducts with the seven-membered ring attached to nitrogen.



Addition of the azide I to acetylenes did occur when an electron-attracting group was attached to the triple bond. Dimethyl acetylene dicarboxylate, dibenzoylacetylene, and propargyl aldehyde condensed smoothly and gave triazoles III, IV, and V, respectively. Diacetylacetylene afforded only tar under the same conditions. Without a strong electron-withdrawing group present on the triple bond (phenylacetylene or diphenylacetylene), addition did not occur.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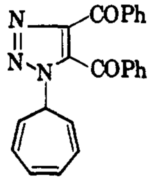
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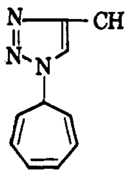
V

Two attempts were made to prepare triazolines from tropylium azide. 1,4-Naphthoquinone was recovered unchanged when heated with azide I. Maleic anhydride gave an unresolvable mixture which may have resulted from a competing Diels–Alder addition of the dienophile to the cycloheptatriene ring.

The structures of adducts III, IV, and V are supported by their n.m.r. spectra. Each spectrum has a triplet, representing one proton, between τ 5.2 and 5.4 which is due to the proton at position 7 of the 1,3,5-cycloheptatriene ring. The remaining bands in each spectrum also agree with the proposed structures. The formyl group in structure V was assigned to the 4-

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(1) C. E. Wulfman, C. J. Yarnell, and D. S. Wulfman, *Chem. Ind.* (London), 1440 (1960).

(2) D. S. Wulfman, L. Durham, and C. E. Wulfman, *ibid.*, 859 (1962).

(3) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **76**, 3203 (1954).

(4) A. Michael, F. Luehn, and H. H. Higbee, *Am. Chem. J.*, **20**, 377 (1898).

(5) F. Moulin, *Helv. Chim. Acta*, **35**, 167 (1952).

(6) W. Kirmse and L. Horner, *Ann.*, **614**, 1 (1958).