tials of I at 10.07, 12.23, and 13.07 eV, respectively, with those of III at 8.79, 9.96, and 12.26 eV.

According to this analysis, the ionization potential of I at 8.24 eV bears no relation to that of II at 8.47 eV. The former corresponds to ionization from an antisymmetric π MO concentrated entirely on carbon, the latter to ionization from a two-center π MO largely concentrated on nitrogen. In II, the nitrogen "lone pair" electrons occupy a single MO largely centered on nitrogen; in I, they are dispersed over the three symmetric π MO's.

We hope soon to establish suitable parameters for boron in our SCF MO treatments; it will be interesting to see if the calculated π-orbital energies in I agree with this interpretation of the photoelectron spectrum.

A New Mode of Decomposition of an Episulfone. Pyrolysis of the Episulfone of *cis*-Dibenzoylstilbene[1-3]

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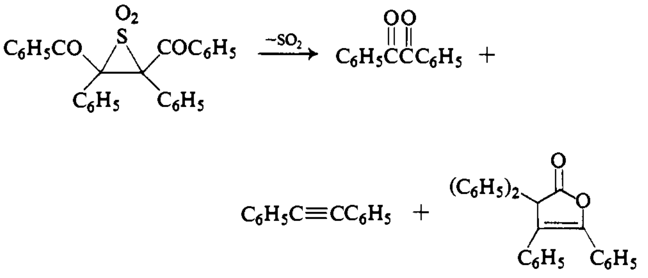
Contribution from the Department of Chemistry, Syracuse University, Syracuse, New York 13210. *Received August 27, 1968*

Abstract: Pyrolysis of the episulfone of *cis*-dibenzoylstilbene yields sulfur dioxide but unlike other episulfones does not yield the olefin but rather diphenylacetylene, benzil, and the lactone of 4-hydroxy-2,2,3,4-tetraphenyl-3-butenoic acid. These decompositions are rationalized on the basis of expansion of the three-membered episulfone ring to a four-membered cyclic sulfinate or a five-membered dioxathiolane ring. The possible significance of ring expansion of episulfones to 1,3,2-dioxathiolanes in determining the observed stereochemistry of decomposition of certain episulfones is discussed.

Two isomeric episulfoxides and one episulfone previously were reported to be obtained by oxidation of *cis*-dibenzoylstilbene episulfide by hydrogen peroxide in acetic acid.[4] Oxidation of an episulfide to an episulfoxide or episulfone in an acidic medium is rare; only a patent claims such a synthesis.[5] Several examples of oxidation of episulfides to episulfoxides by sodium metaperiodate in aqueous methanol have been reported, but these episulfoxides are unstable in acid.[6] No other example of oxidation of an episulfide to an episulfone is known. The episulfide, episulfoxide, and episulfone of dibenzoylstilbene represent the first examples of episulfide derivatives in which the thiirane ring is substituted by electron-withdrawing carbonyl groups.

Results and Discussion

Heating the episulfone at about 300° (25 mm) gave benzil (34, 31%), diphenylacetylene (26, 31%), the lactone (**1**) of 4-hydroxy-2,2,3,4-tetraphenyl-3-butenoic acid (3, 7%), and unreacted episulfone. These products are unusual because episulfones usually lose sulfur dioxide readily and stereospecifically to yield an olefin which in the above case would be *cis*-dibenzoylstilbene. In fact, the lactone may be derived from *cis*-dibenzoylstilbene because pyrolysis of the latter at 270° has been reported to give the lactone quantitatively.[7]



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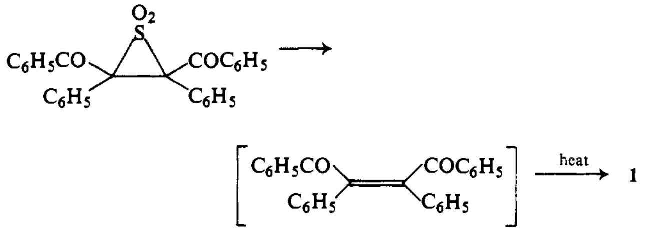

Although the stereospecific decompositions of episulfones by loss of sulfur dioxide have been investigated extensively[8] and have been useful in the synthesis of

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(1) This work was aided by Grant GP-5513 of the National Science Foundation and Grant CA08250 of the National Cancer Institute of the National Institutes of Health.

(2) Reported in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstracts of Papers, P-19.

(3) For further details see G. E. Kuhlmann, Ph.D. Thesis, Syracuse University, 1968, and G. C. Levy, A.B. Honors Thesis, Syracuse University, 1965.

(4) D. C. Dittmer and G. C. Levy, *J. Org. Chem.*, **30**, 636 (1965). Evidence has been obtained that the episulfide reported in this paper was *cis* (see ref 3).

(5) S. B. Soloway, U. S. Patent 2,694,073 (1954); *Chem. Abstr.*, **49**, 3465 (1955).

(6) G. E. Hartzell and J. N. Paige, *J. Am. Chem. Soc.*, **88**, 2616 (1966).

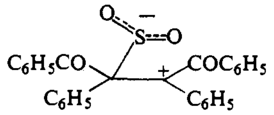
(7) D. R. Berger and R. K. Summerbell, *J. Org. Chem.*, **24**, 1881 (1959). However, when *trans*-dibenzoylstilbene is heated to its boiling point the lactone **1** is reported to be formed: N. Zinin, *Jahresber.*, 409 (1875). For definitions of the old terminology see F. R. Japp and F. Klingemann, *J. Chem. Soc.*, **57**, 662 (1890). We have found that *trans*-dibenzoylstilbene is stable at least to 250°.

(8) (a) N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.*, **85**, 1209 (1963); N. P. Neureiter, *ibid.*, **88**, 558 (1966); N. Tokura, T. Nagai, and S. Matsumura, *J. Org. Chem.*, **31**, 349 (1966); (b) L. A. Paquette and L. S. Wittenbrook, *J. Am. Chem. Soc.*, **89**, 4483 (1967); (c) F. G. Bordwell and J. M. Williams, Jr., *ibid.*, **90**, 435 (1968).

olefins,[9] the mechanism or mechanisms by which extrusion of sulfur dioxide occurs is not clearly understood. Freeman and Graham[10] pointed out that the stereospecific elimination of sulfur dioxide if concerted constitutes an apparent exception to the Woodward–Hoffmann rules,[11] and this has been discussed further by Paquette and Wittenbrook.[8b]

On the basis of a rate enhancement in polar solvents, Bordwell, Williams, Hoyt, and Jarvis in their study of the Ramberg–Bäcklund reaction favor a two-step mechanism for loss of sulfur dioxide involving a transition state with considerable polar character.[12] The ring-opened intermediate which results is supposed to lose sulfur dioxide faster than rotation occurs about the carbon–carbon bond originally in the three-membered ring.

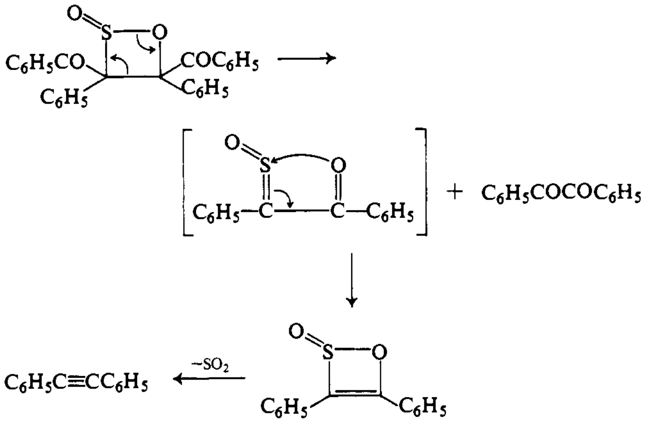
The episulfone of dibenzoylstilbene is unusually stable and yields relatively little olefin (found as lactone 1) on pyrolysis, which sets it apart from the other episulfones whose decomposition to olefin and sulfur dioxide has been studied. The relative stability of the episulfone of dibenzoylstilbene may be attributed to the instability of a dipolar intermediate in which there is a positive charge on a carbon adjacent to a carbonyl group.[13]



The result obtained in the pyrolysis of dibenzoylstilbene episulfone may provide insight into the mechanism of pyrolysis of episulfones generally; and a rationalization of this result provides an alternate explanation of the retention of the configuration of the episulfone by the alkene when sulfur dioxide is lost from ordinary episulfones. Scheme I accounts for the formation of diphenylacetylene, benzil, and lactone 1 from dibenzoylstilbene episulfone. The three-membered episulfone ring may expand to a less strained four-membered ring[14] (a cyclic sulfinate or 1,2-oxathietane 2-oxide) followed by further expansion (and relief of strain) to a five-membered ring (a 1,3,2-dioxathiolane). If these ring expansions are stereospecific as appears possible,[15] then the dioxathiolane can lose sulfur dioxide concertedly and yield olefin stereospecifically.[16] The intermediate 3 may decompose analogously to a molozonide[17] to give benzil and diphenylacetylene. Barriers to rotation in the transition states for ring expansion preserve the stereochemistry[18]

In support of this reaction scheme, certain four-membered cyclic sulfones undergo ring expansion to cyclic sulfinate esters on heating[19] or on treatment with *t*-butoxymagnesium bromide.[20] Cyclic sulfinate esters have been suggested as intermediates occurring in the mass spectra of certain sulfones.[21] A ring expansion of the episulfoxide of dibenzoylstilbene has been suggested as an intermediate in its photolysis and pyrolysis in which monothiobenzil and benzil were obtained.[22]

Benzil and diphenylacetylene also could be formed



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[9] L. A. Paquette, *J. Am. Chem. Soc.*, **86**, 4383 (1964); G. Opitz and K. Fischer, *Angew. Chem.*, **77**, 41 (1965).

[10] J. P. Freeman and W. H. Graham, *J. Am. Chem. Soc.*, **89**, 1761 (1967).

[11] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968), and references cited therein.

[12] F. G. Bordwell, J. M. Williams, Jr., E. B. Hoyt, Jr., and B. B. Jarvis, *J. Am. Chem. Soc.*, **90**, 429 (1968).

[13] The relative inertness of olefins substituted with acyl groups to attack by electrophilic reagents such as bromine bespeaks the instability of positively charged intermediates in such reactions.

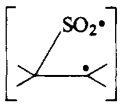
[14] The reverse rearrangement of acyclic sulfinates to sulfones by an ionic mechanism is well known: J. Kenyon and H. Phillips, *J. Chem. Soc.*, 1676 (1930); D. Darwish and R. McLaren, *Tetrahedron Letters*, 1231 (1962); D. Darwish and E. A. Preston, *ibid.*, 113 (1964); E. Ciuffarin, M. Isola, and A. Fava, *J. Am. Chem. Soc.*, 90, 3595 (1968).

[15] In the formation of the transition states for ring expansion the bonding sulfur–carbon σ orbital can smoothly go over to a nonbonding sulfur orbital and a nonbonding orbital on oxygen can be converted to a bonding oxygen–carbon σ orbital.

[16] (a) We had at first considered the possibility that the decomposition of the episulfone of dibenzoylstilbene could be explained solely by way of the cyclic sulfinate 2. In a discussion with Professor Roald Hoffmann he pointed out to us that intermediate 3 should lose sulfur dioxide concertedly and stereospecifically as can be shown by construction of orbital energy diagrams. We are grateful for his suggestion which provides an explanation for the formation of *cis*-dibenzoylstilbene from the *cis*-episulfone and possibly for the stereochemistry of other episulfone decompositions. As shown, 3 also can lead to the other products observed. The possibility exists that sulfur dioxide might be lost concertedly and stereospecifically from the cyclic sulfinate 2. Although this loss of sulfur dioxide seems to be a high-energy 2 + 2 process, the process may not be as unlikely as it is in the strictly carbon system. Because of the involvement of the sulfur atom, the orbital energies, and amplitude of orbital overlap may permit a lower energy transition state for the concerted loss of sulfur dioxide (L. Salem, 12th Conference on Reaction Mechanisms, Brandeis University, June 1968). (b) Pertinent to the stereospecific loss of sulfur dioxide from 2 is the observation that carbon dioxide is lost stereospecifically from β-lactones on heating them: D. S. Noyce and E. H. Banitt, *J. Org. Chem.*, **31**, 4043 (1966); O. L. Chapman and W. R. Adams, *J. Am. Chem. Soc.*, **90**, 2333 (1968).

[17] R. Criegee, *Record Chem. Progr.*, **18**, 11 (1957). The zwitterionic intermediate is written with a polarity different from the usual zwitterion derived from a primary ozonide in order to avoid a positive charge next to a carbonyl group. Sulfur is less electronegative than oxygen so that making it positive in the intermediate seems reasonable. The intermediate, 1,3,2-dioxathiolane (3), is analogous to the unstable 1,3,2-dioxazolidine formed when cyclohexene and nitrobenzene are irradiated: J. L. Charlton and P. de Mayo, *Can. J. Chem.*, **46**, 1041 (1968); G. Büchi and D. E. Ayer, *J. Am. Chem. Soc.*, **78**, 689 (1956).

[18] Trimethylene is calculated to have a barrier to internal rotation: R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 1475 (1968). A ring-opened intermediate from the episulfone may also have some barrier.



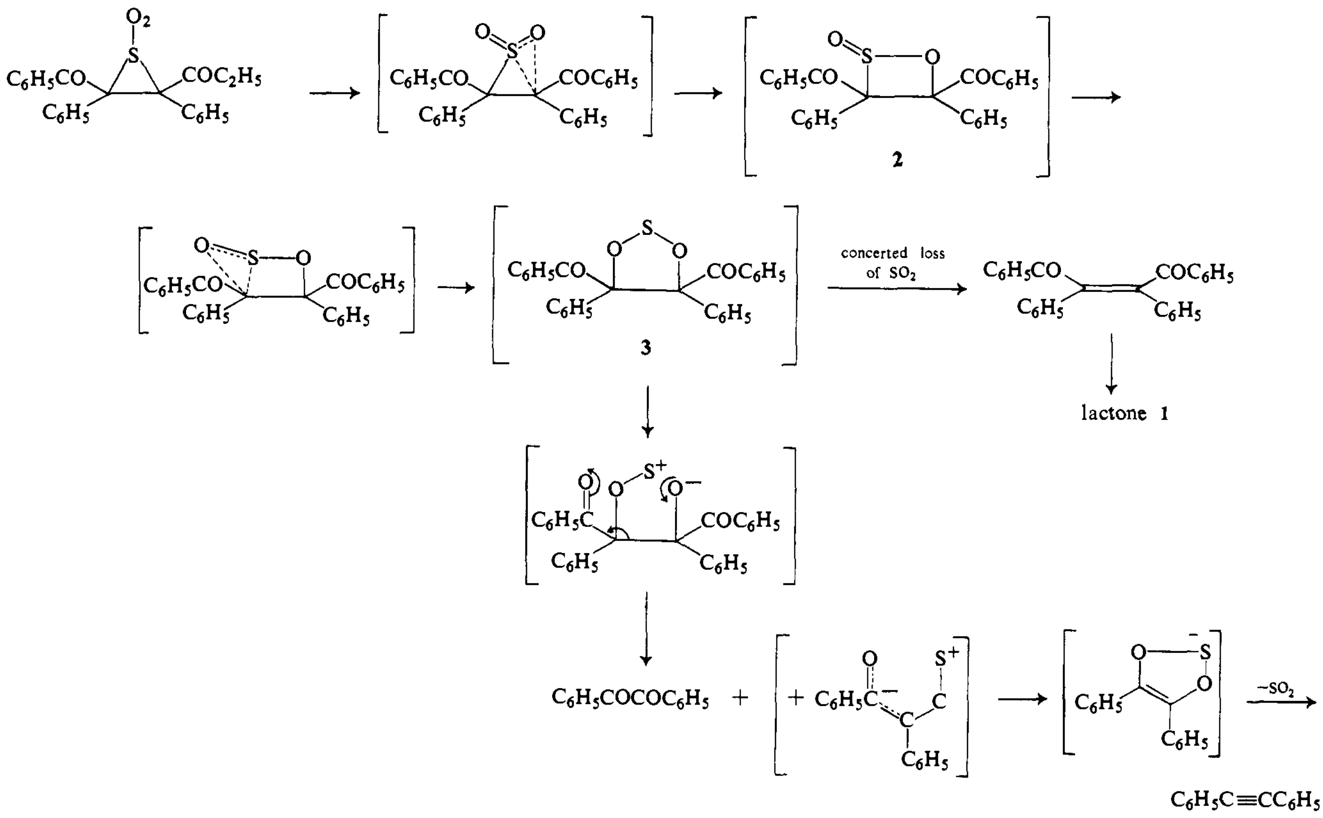
[19] R. S. Henion, Ph.D. Thesis, Syracuse University, Syracuse, N. Y., 1967; D. C. Dittmer, R. S. Henion, and N. Takashina, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Abstracts of Papers, p 101-O; R. W. Hoffmann and W. Sieber, *Ann. Chem.*, **703**, 96 (1967); D. C. Dittmer and R. S. Henion, *J. Org. Chem.*, in press.

[20] R. M. Dodson, P. D. Hammen, and R. A. Davis, *Chem. Commun.*, 9 (1968).

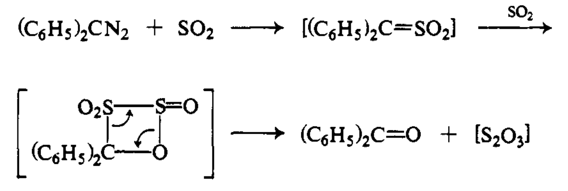
[21] S. Meyerson, H. Drews, and E. K. Fields, *Anal. Chem.*, **36**, 1294 (1964); E. K. Fields and S. Meyerson, *J. Am. Chem. Soc.*, **88**, 2836 (1966); D. C. Dittmer and F. A. Davis, *J. Org. Chem.*, **32**, 3872 (1967); R. D. Chambers and J. A. Cunningham, *Chem. Commun.*, 583 (1967).

[22] D. C. Dittmer, G. C. Levy, and G. E. Kuhlmann, *J. Am. Chem. Soc.*, **89**, 2793 (1967).

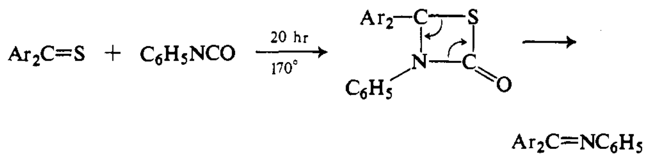
Scheme I



directly from the cyclic sulfinate **2** *via* a thiocarbonyl S-oxide. The S-oxide of monothiobenzil has been suggested as an intermediate in the synthesis of *cis*-dibenzoylstilbene from deoxybenzoin N-sulfinyl-*p*-toluenesulfonamide and aluminum chloride.[23] The S-oxide of 9-thiofluorenone decomposes with loss of sulfur dioxide to difluorenylidene.[24] Treatment of diphenyldiazomethane with excess sulfur dioxide was reported to yield benzophenone *via* a cyclic intermediate somewhat



analogous to **2**.[25] Addition of diaryl thioketones to phenyl isocyanate yields Schiff bases which were suggested to be formed *via* a cyclic intermediate which decomposed with loss of carbon oxysulfide.[26]



The pyrolysis of the episulfone could proceed by simultaneous loss of two benzoyl radicals (which recombine to give benzil) with the formation of 2,3-diphenylthiirene 1,1-dioxide which is known to yield diphenylacetylene on heating or irradiation.[27] However, acyl radicals lose carbon monoxide especially at temperatures above 100° to give phenyl radicals.[28] No products such as biphenyl from this type of reaction were observed and formation of benzoyl radicals is not believed to occur unless dimerization of the benzoyl radicals is faster than loss of carbon monoxide.

The mass spectrum of the episulfone at 350° is not inconsistent with the thermal decomposition schemes. The parent ion is at *m/e* 452 with fragments observed at *m/e* 388, 242, 226, 210, and 178. The base peak is at *m/e* 105 (C_6H_5CO). A mass spectral decomposition scheme is shown (Scheme II) based on the 1,3,2-dioxathiolane **3** but one based on the cyclic sulfinate **2** can be written just as well.

As has been mentioned,[16] orbital correlation diagrams[29] indicate that a concerted loss of sulfur dioxide from episulfones may be a high-energy process involving strongly antibonding orbitals, but that its loss from the 1,3,2-dioxathiolane **3** is not. Perhaps all episulfones undergo ring expansion to a 1,3,2-dioxathiolane prior to the concerted loss of sulfur dioxide which preserves

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(23) D. Sommerfeld, Dissertation, Technische Hochschule München, 1966. Quoted by G. Kresze and W. Wucherpfennig, *Angew. Chem. Intern. Ed. Engl.*, **6**, 162 (1967).

(24) W. A. Sheppard and J. Diekmann, *J. Am. Chem. Soc.*, **86**, 1891 (1964).

(25) H. Staudinger and F. Pfenninger, *Ber.*, **49**, 1941 (1916).

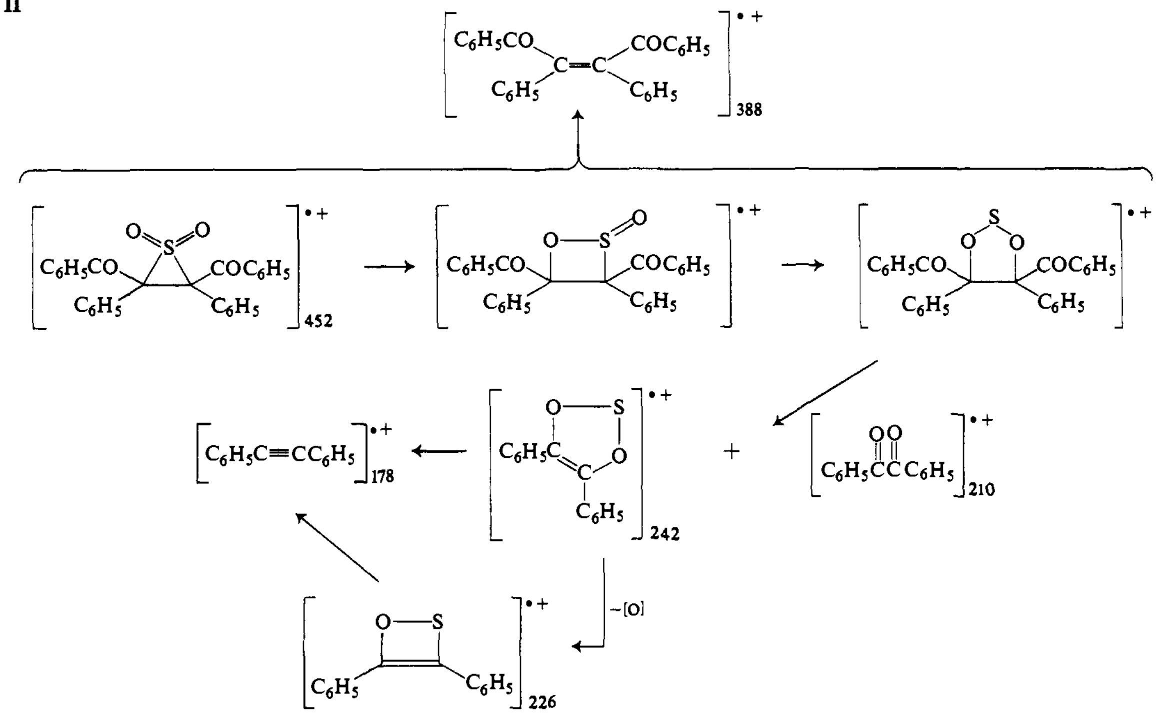
(26) H. Staudinger and R. Endle, *ibid.*, **50**, 1042 (1917).

(27) (a) L. A. Carpino and L. V. McAdams, III, *J. Am. Chem. Soc.*, **87**, 5804 (1965); (b) F. G. Bordwell, J. M. Williams, Jr., and B. B. Jarvis, *J. Org. Chem.*, **33**, 2026 (1968).

(28) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, pp 277–279.

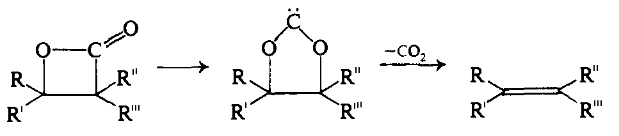
(29) The orbitals used for sulfur dioxide and sulfones were described previously: S. P. Ionov and M. A. Porai-Koshits, *J. Struct. Chem. USSR*, **7**, 245 (1966); R. S. Mulliken, *Can. J. Chem.*, **36**, 10 (1958); A. D. Walsh, *J. Chem. Soc.*, 2266 (1953); W. A. Moffitt, *Proc. Roy. Soc.* (London), **200**, 409 (1950).

Scheme II



the stereochemistry. When benzoyl groups are present in the episulfone an alternate more favorable pathway occurs for decomposition of the dioxathiolane.

Thermal decomposition of β-lactones to carbon dioxide and an alkene bears a resemblance to the thermal decomposition of episulfones in that stereochemistry is preserved.[16b] This preservation of the stereochemistry of the lactone in the alkene formed may be explained by a stereospecific ring expansion to a dialkoxycarbene which may concertedly decompose to alkene and carbon dioxide (nonlinear). Corey and Winter suggested such



a carbene as an intermediate in their stereospecific synthesis of olefins from cyclic thionocarbonates,[30] and Crank and Eastwood also considered a dialkoxycarbene as a possible intermediate in stereospecific thermal decompositions of 2-ethoxy-1,3-dioxolanes to olefin, ethanol, and carbon dioxide.[31] Lemal, Gosselink, and Ault observed the possible fragmentation of ethylenedioxycarbene to ethylene and carbon dioxide.[32]

Although some sulfones decompose photochemically with loss of sulfur dioxide,[12,27b,33] the episulfone of dibenzoylstilbene is inert.

Tracer experiments with oxygen-18 and the investigation of other substrates would provide more information about the mechanism of the thermal decompositions of episulfones, and work is in progress to obtain this information.

Experimental Section

Melting points were obtained on a Fisher-Johns melting point apparatus (corrected). Microanalyses were performed at Galbraith Laboratories, Knoxville, Tenn., or at the Scandinavian Microanalytical Laboratory, Herlev, Denmark. All chemicals were either "Chromatoquality" or reagent grade.

Infrared spectra were taken on either a Perkin-Elmer Model 137 infrared spectrophotometer or on a Perkin-Elmer Model 521 grating spectrophotometer. The infrared absorptions are reported as weak (0–20%, w), medium (20–80%, m), and strong (80–100%, s). Ultraviolet spectra were obtained on a Perkin-Elmer Model 202 ultraviolet spectrophotometer. The absorptions are reported in mμ and the intensity (ε) of the absorptions in liters/(mole cm). Proton nuclear magnetic resonance (nmr) spectra were obtained on a Varian Model A-60 nuclear magnetic resonance spectrometer. The nmr absorptions are reported as hertz (Hz) and tetramethylsilane was used as an internal standard. Molecular weight determinations were done by vapor pressure osmometry in an appropriate solvent or by mass spectrometry. Mass spectra were obtained on a Perkin-Elmer-Hitachi Model RMU-6E single focusing spectrometer. Thin layer chromatography (tlc) was performed according to standard methods[34] using apparatus from Brinkmann Instruments, Inc., Westbury, N. Y., and either Merck silica gel GF_{254} or HF_{254}. Visualization was effected by the use of ultraviolet light and the compounds were identified as dark spots over the silica gel.

Dibenzoylstilbene Episulfide (Yellow Isomer). The procedure described earlier was followed.[4] The episulfide may be purified by column chromatography on silicic acid with benzene to yield yellow crystals, mp 110–111°. The proton nmr spectrum (60 MHz in $CDCl_3$) of the episulfide had complex multiplets centered at 440 Hz (16 H) and 470 Hz (4 H, *ortho* protons of benzoyl groups).

Dibenzoylstilbene Episulfone. The episulfone was prepared as described previously.[4] A better yield, however, is obtained

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(30) E. J. Corey and R. A. E. Winter, *J. Am. Chem. Soc.*, **85**, 2677 (1963).

(31) G. Crank and F. W. Eastwood, *Australian J. Chem.*, **17**, 1392 (1964).

(32) D. M. Lemal, E. P. Gosselink, and A. Ault, *Tetrahedron Letters*, 579 (1964).

(33) M. P. Cava, R. H. Schlessinger, and J. P. Van Meter, *J. Am. Chem. Soc.*, **86**, 3173 (1964); J. Saltiel and L. Metts, *ibid.*, **89**, 2232 (1967); Y. Odaira, K. Yamaji, and S. Tsutsumi, *Bull. Chem. Soc. Japan*, **37**, 1410 (1964); N. Kharasch and A. I. A. Khodair, *Chem. Commun.*, 98 (1967).

(34) J. Bobbitt, "Thin-Layer Chromatography," Reinhold Publishing Corp., New York, N. Y., 1963.

when the oxidation is done in refluxing benzene. A solution of yellow episulfide (2.17 g, 0.00515 mol) in benzene (100 ml) was refluxed with peracetic acid (3.0 ml of 40%) for 7.5 hr. The apparatus was wrapped in aluminum foil to keep out light and additional peracetic acid (6.0 ml of 40%) was added slowly. The solution was allowed to cool overnight. The benzene solution was washed with two 50-ml portions of 10% potassium hydroxide solution and one 50-ml portion of water and dried over anhydrous magnesium sulfate. Distillation of the benzene under reduced pressure and recrystallization from ethanol gave the episulfone, mp 145–148° (1.54 g, 0.00341 mol, 66%). Recrystallization from benzene–pentane gives the episulfone in a different crystalline modification, mp range 87–97°. Recrystallization of the low-melting form from ethanol gave material which melted at 145–148°. The infrared spectra of each form are identical in carbon disulfide. The ultraviolet spectrum and the proton nmr spectrum of each form are also identical.

When crystals of the higher melting form are dropped into a melt of the lower melting form at 100°, the liquid solidifies and remelts at 145–148°.

The episulfone also could be prepared by oxidation of the episulfoxides. A mixture of the isomeric episulfoxides (3.060 g, 0.00699 mol) was dissolved in warm glacial acetic acid (35 ml). After the solution had cooled, hydrogen peroxide (2 ml, 30%) was added, and the mixture heated at 70–90° for 3 hr and cooled overnight. Recrystallization of the precipitate from benzene–pentane gave the low-melting form of the episulfone, mp 90–93° (1.521 g, 0.00336 mol, 48%).

The episulfone had the following properties: infrared (low-melting form, KBr), 3040 (w), 1675 (s), 1640 (s), 1595 (m), 1575 (w), 1480 (m), 1440 (m), 1315 (s), 1260 (s), 1200 (m), 1180 (m), 1160 (m), 1140 (s), 1110 (m), 1095 (m), 1065 (m), 1040 (m), 1025 (m), 1000 (m), 965 (m), 940 (w), 920 (w), 885 (m), 850 (m), 830 (m), 776 (s), 750 (s), 710 (m), and 690 (s) cm^{-1}; infrared spectrum (high-melting form, KBr), 3040 (w), 1680 (m), 1650 (s), 1595 (m), 1570 (w), 1480 (m), 1440 (m), 1310 (s), 1240 (s), 1200 (m), 1180 (m), 1140 (s), 1095 (s), 1070 (m), 1060 (m), 1040 (m), 1025 (m), 1020 (m), 1000 (m), 965 (m), 920 (w), 870 (w), 845 (m), 830 (w), 770 (s), 760 (m), 745 (s), and 690 (s) cm^{-1}; infrared (either form, CS_2), 3050 (w), 1680 (m), 1650 (m), 1320 (s), 1255 (m), 1205 (m), 1180 (m), 1145 (s), 1105 (m), 1095 (m), 1070 (m), 1040 (w), 1015 (m), 1000 (w), 965 (m), 920 (w), 770 (m), 745 (s), and 690 (s) cm^{-1}; ultraviolet (CH_3CN), 232 sh (ε 21,500) 254 (ε 20,000); (95% C_2H_5OH), 233 sh (ε 21,500), 254 mμ (ε 19,500); nmr ($CDCl_3$), 475 (multiplet, 4 H) and 445 Hz (multiplet, 16 H); mass spectrum (350°, indirect inlet, 70 eV), *m/e* 454 (0.42), 453 (1.15), 452 (3.56, parent), 388 (0.57), 372 (0.91), 347 (0.40), 315 (1.52), 242 (0.75), 288 (0.17), 227 (0.33), 226 (1.46), 210 (0.82), 180 (1.06), 179 (13.7), 178 (77.5), 105 (100), and 64 (3.59) (percentage of base peak given in parentheses).

The isotope peaks at *m/e* 453 and 454 were used to check the empirical formula: calcd for $C_{28}H_{20}O_4S$, $100(P + 1)/P$, 31.5; $100(P + 2)/P$, 9.8; found, $100(P + 1)/P$, 32.3; $100(P + 2)/P$, 11.8.

A probable side reaction in the synthesis of the episulfone is a Baeyer–Villiger reaction.[35] A small amount of white solid, mp 87–89° after recrystallization from benzene–pentane, was obtained by chromatography of part of a mixture obtained from oxidation of the episulfide in acetic acid; this white compound showed a strong ester carbonyl band at 1740 cm^{-1} in the infrared and sulfone bands at 1320 and 1150 cm^{-1}. Maxima at 233 and 278 mμ in the ultraviolet spectrum in 95% ethanol were observed. The residue obtained by evaporation of the benzene–pentane solvent used for recrystallization was treated with 10% aqueous potassium hydroxide. Acidification of the aqueous base gave a precipitate of benzoic acid, mp 121–122°, mmp 121–122°. The infrared spectrum was identical with that of an authentic sample of benzoic acid.

Pyrolysis of Dibenzoylstilbene Episulfone. The episulfone was pyrolyzed in a vacuum sublimator. The vacuum (about 25 mm) was provided by an aspirator. In the first run, the episulfone (1.48 g, 0.00328 mol) was heated by the flame of a burner (about 300°) for 60 min during which the liquid refluxed. After the mixture cooled, the products were washed out of the sublimator with 15 ml of toluene. The odor of sulfur dioxide was strong. A precipitate of episulfone (0.602 g, 0.00133 mol, 42%) was recovered and identified by infrared spectroscopy and thin layer chromatography.

Chromatography of the toluene solution on 50 g of silicic acid and elution with 600 ml of 4:1 toluene–pentane gave diphenylacetylene (0.131 g, 0.000733 mol, 31%) in the first 100 ml. Vacuum sublimation at 100° gave white crystals, mp 58–59° (lit.[36] mp 58–59°). Its infrared spectrum was identical with that of an authentic sample; a picrate was obtained, mp 110–112° (lit.[37] mp 111°).

The second compound, obtained in the next 200 ml, was identified as the lactone of 4-hydroxy-2,2,3,4-tetraphenyl-3-butenoic acid (0.0887 g, 0.000228 mol, 7%). Recrystallization from ethanol gave crystals melting at 132–133° (lit.[7] mp 136°). Its infrared spectrum was identical with that reported.[7]

The third compound, obtained in the next 300 ml, was benzil (0.155 g, 0.000736 mol, 31%), mp 94–95° (lit.[38] mp 94.4°). Its infrared spectrum was identical with that of an authentic sample.

A second pyrolysis of episulfone (1.058 g, 0.00234 mol) for only 15 min was treated as above to yield diphenylacetylene (0.110 g, 0.000617 mol, 26%), lactone (0.0315 g, 0.0000810 mol, 3%), and benzil (0.166 g, 0.000791 mol, 34%).

Both diphenylacetylene and the lactone exhibited a molecular ion in their mass spectra and correct isotope ratios were observed for the molecular ion.

Attempted Photolysis of Dibenzoylstilbene Episulfone. Irradiation of dibenzoylstilbene episulfone (1.078 g, 0.00238 mol) in 500 ml of benzene through a Pyrex filter for 120 min gave a slightly yellow solution. Analysis by tlc showed only the presence of unchanged episulfone. Recrystallization from benzene–pentane gave episulfone (0.900 g, 0.00109 mol, 84%), mp 92–94°.

Irradiation of episulfone (1.333 g, 0.00294 mol) through a Vycor filter as above gave a yellow solution. Analysis by tlc showed only the presence of unchanged episulfone. Recrystallization from benzene–pentane gave 0.804 g (0.00178 mol, 60%) of episulfone, mp 89–91°. During the recrystallization, a black tarry material was separated by filtration from the episulfone.

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