

Photochemical Transformations of Small Ring Carbonyl Compounds. X. Photodesulfurization of Dibenzoylstilbene Episulfide¹⁻³

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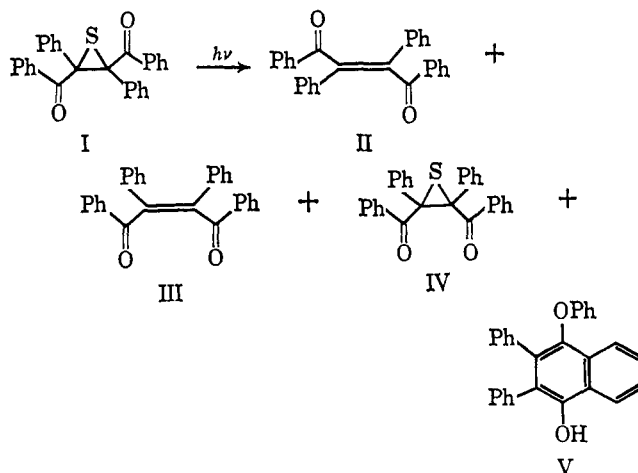
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Abstract: The photolysis in benzene of *trans*-dibenzoylstilbene episulfide has been found to afford four products. The structures have been assigned as *cis*- and *trans*-dibenzoylstilbene, *cis*-dibenzoylstilbene episulfide, and 1-hydroxy-2,3-diphenyl-4-phenoxynaphthalene. The formation of the naphthol has been rationalized by an intramolecular migration of phenyl to oxygen producing an ene-ketene which undergoes subsequent cyclization and aromatization. The photodesulfurization of the *trans* and *cis* episulfide was shown to be stereoselective. A two-step photoextrusion of sulfur from the excited $n-\pi^*$ state accommodates the stereoselectivity observed.

Past investigations⁶ have established that under appropriate reaction conditions, olefins may be formed by the removal of sulfur from episulfides. Reagents which are known to be effective for this are the organolithium compounds,⁷ Grignard reagents,⁸ and tervalent phosphorus compounds.^{9,10} Certain episulfides have also been thermally degraded to an olefin and sulfur.¹¹ In view of the structural relationship between benzoyl episulfides and ethylenimine ketones and as a logical extension of our photochemical studies of small ring carbonyl compounds,¹² it became of interest to determine if benzoyl episulfides would parallel the photoextrusion of the heteroatom recently observed with the ethylenimine ketones.¹³ With these ideas in mind, we set out to explore the photochemistry of dibenzoylstilbene episulfide (I). In this paper we describe the photoextrusion of sulfur from I by ultraviolet light and the subsequent rearrangement of the primary photoproducts.

Photolysis of *trans*-dibenzoylstilbene episulfide (I) in benzene with a Pyrex filter gave a mixture of products which were separated using scanning liquid-liquid partition chromatography.¹⁴ In addition to unreacted *trans*-dibenzoylstilbene episulfide (I), four new compounds were obtained. The two major products were identified as *trans*-dibenzoylstilbene (II), mp 230–231°, and *cis*-dibenzoylstilbene (III), mp 208–210°. The two

minor components were shown to be *cis*-dibenzoylstilbene episulfide (IV) and 1-hydroxy-2,3-diphenyl-4-phenoxynaphthalene (V). In a typical run the irradiation of 1.19 g of *trans*-dibenzoylstilbene episulfide (I) afforded 0.56 g of II, 0.12 g of III, 0.04 g of IV, and 0.05 g of V. Furthermore, the two olefins were photochemically interconvertible under the reaction conditions employed. Numerous attempts to identify the



sulfur portion produced from the photolysis of I failed. Careful chromatography on a silica gel column afforded only brown, tarry materials which defied all attempts at characterization. Attempts to trap any volatile components also failed to produce characterizable products. Since a well-defined sulfur compound could not be isolated, it must be concluded that the active sulfur formed reacted with solvent to form high molecular weight tars.

The structure of the *cis* episulfide IV is inferred from its composition and molecular weight, spectral data, its mode of preparation, and chemical behavior. Its ultraviolet absorption spectrum is similar to that of the *trans* isomer, and its proton magnetic resonance spectrum is identical with that of the *trans* episulfide. Treatment of IV with triphenylphosphine in refluxing xylene afforded exclusively *trans*-dibenzoylstilbene. It is interesting to note that the *cis* episulfide gave essentially pure *trans* olefin. In every case previously studied, the *cis* episulfide gave pure *cis* olefin, and the *trans* episulfide gave pure *trans* olefin.¹⁵ The stereospecific

(1) Support of this work by the Air Force Office of Scientific Research (Grant No. AF-AFOSR-820-65) is gratefully acknowledged.

(2) For a preliminary report of this work see A. Padwa and D. Crumrine, *Chem. Commun.*, 506 (1965).

(3) For part IX, see A. Padwa, L. Hamilton, and L. Norling, *J. Org. Chem.*, **31**, 1244 (1966).

(4) To whom inquiries should be directed at the Department of Chemistry, State University of New York at Buffalo, Buffalo, N. Y.

(5) National Science Foundation Undergraduate Research Participant, Summer, 1965.

(6) For a recent compilation of references, see the review of D. D. Reynolds and D. L. Fields, "Heterocyclic Compounds with Three and Four Membered Rings," Part I, A. Weissberger, Ed., John Wiley and Sons, Inc., New York, N. Y., 1964, p 576.

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

(8) F. G. Bordwell, H. M. Anderson, and B. M. Pitt, *ibid.*, **76**, 1082 (1954).

(9) M. J. Boskin and D. B. Denney, *Chem. Ind. (London)*, 330 (1959).

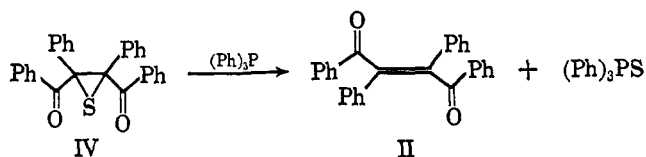
(10) R. E. Davis, *J. Org. Chem.*, **23**, 1767 (1958).

(11) C. O. Guss and D. L. Chamberlain, *J. Am. Chem. Soc.*, **74**, 1342 (1952).

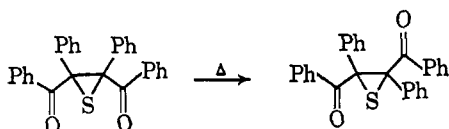
(12) A. Padwa in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., in press.

(13) A. Padwa and L. Hamilton, *J. Am. Chem. Soc.*, **87**, 1821 (1965).

(14) H. E. Zimmerman and D. Schuster, *ibid.*, **84**, 4527 (1962).



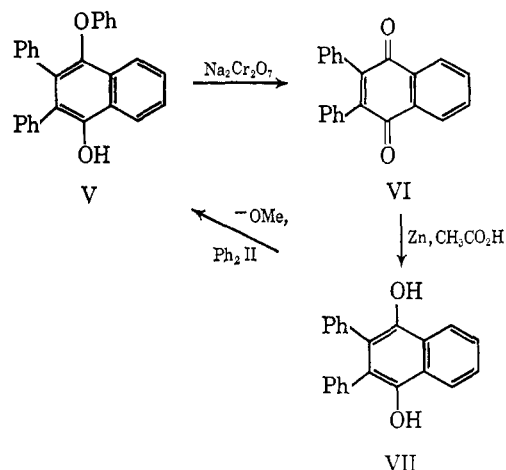
desulfurization of episulfides with tertiary phosphines has been rationalized by a mechanism which involved direct attack by the nucleophile on the sulfur atom of the episulfide ring.⁷ Such an attack gives rise to the products by proceeding through a transition state which yields the olefin and the phosphine sulfide in one step. Since the nonstereospecific desulfurization of IV is novel, it seemed of interest to investigate in more detail the exact nature of the desulfurization step. It seemed likely that the stereochemistry of the reaction was being influenced by factors other than the normal desulfurization path. Consequently, the stereochemical stability of *cis* episulfide IV was determined under the conditions of the ring desulfurization of the episulfides. *cis*-Dibenzoylstilbene episulfide (IV) was completely isomerized to the thermodynamically more stable *trans*-dibenzoylstilbene episulfide (I) after 30 min. This



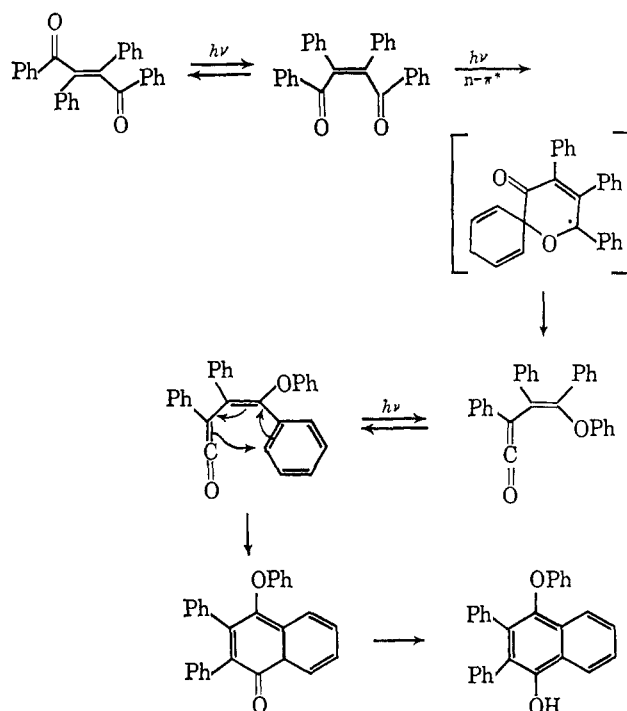
finding indicates that there has been no mechanistic change in the desulfurization of IV with triphenylphosphine. The apparent nonstereospecificity observed is controlled primarily by the relative rates of isomerization and desulfurization of the episulfides.

The structure of V was elucidated by elemental analysis, infrared, ultraviolet, nmr, and degradation. The pure naphthol V was a solid (white needles from methanol), mp 157–158°. The infrared spectrum shows a hydroxyl band at 2.85 and a carbon-oxygen stretching band at 8.26 μ . The ultraviolet spectrum (λ_{\max} (95% alcohol) 245 $m\mu$ (ϵ 32,000) and 317 $m\mu$ (ϵ 6000)) of V shows marked similarity to the spectrum of 2,3-diphenyl-1,4-naphthalenediol (λ_{\max} (95% alcohol) 246 $m\mu$ (ϵ 32,000) and 325 $m\mu$ (ϵ 6200)). Chemical confirmation was obtained by sodium dichromate oxidation of V. The product obtained in better than 90% yield was identical with an authentic sample of 2,3-diphenyl-1,4-naphthoquinone (VI) synthesized by the method of Crawford.¹⁶ Structure V was further confirmed by its unequivocal synthesis from 2,3-diphenyl-1,4-naphthalenediol (VII) and diphenyliodonium iodide.

Suspicion that naphthol V was a secondary photo-product was confirmed by the finding that the photolysis of *trans*-dibenzoylstilbene (II) in benzene afforded *cis*-dibenzoylstilbene (III) and naphthol V. An attractive mechanism for the photoconversion of II to V involves initial photoisomerization of II to III followed by intramolecular attack of the $n-\pi^*$ excited carbonyl group on the aromatic ring of the second benzoyl group.^{17–19} Subsequent collapse of the spiro Ar_1-6 diradical species affords a *cis*-ene-ketene. Photo-



isomerization of the *cis*-ene-ketene to the *trans*-ene-ketene and cyclization in the manner described below readily accounts for the final product. The rearrange-



ment of dibenzoylstilbene to a ketene by means of a 1,5-phenyl migration to oxygen is not without analogy. The related photochemical rearrangements of dibenzoyl-ethylene,¹⁷ 1,2-dibenzoylstyrene,¹⁸ and tetrabenzoyl-ethylene²⁰ all proceed with phenyl migration to oxygen, the former two cases proceeding *via* a 1,5-phenyl shift. The cyclization of the ketene intermediate is related to the reaction by which diphenylketene and diphenylacetylene form triphenylnaphthol,²¹ as well as by the formation of 1-phenyl-2-ethoxy-4-hydroxynaphthalene from diphenylketene and ethoxyacetylene,²² and by the large number of known photocyclization reactions of cyclohexadienes.²³

From the formation of the naphthol, it appears that an initial intramolecular migration of phenyl to oxygen

(15) D. B. Denney and M. J. Boskin, *J. Am. Chem. Soc.*, **82**, 4736 (1960).

(16) H. M. Crawford and H. B. Nelson, *ibid.*, **68**, 134 (1946).

(17) G. W. Griffin and E. J. O'Connell, *ibid.*, **84**, 4148 (1962).

(18) H. E. Zimmerman, H. G. C. Durr, R. G. Lewis, and S. Braun, *ibid.*, **84**, 4149 (1962).

(19) W. A. Henderson and E. F. Ullman, *ibid.*, **87**, 5424 (1965).

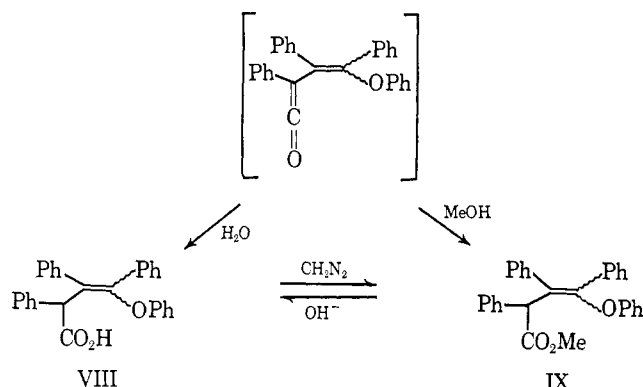
(20) H. Schmid, M. Hochweber, and H. von Halban, *Helv. Chim. Acta*, **30**, 1513 (1947).

(21) L. I. Smith and H. H. Hoehn, *J. Am. Chem. Soc.*, **63**, 1181 (1941).

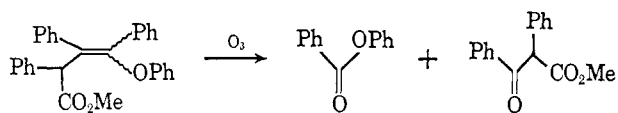
(22) J. Druey, E. F. Jenny, K. Schenker, and R. B. Woodward, *Helv. Chim. Acta*, **45**, 600 (1962).

(23) O. L. Chapman, *Advan. Photochem.*, **1**, 345 (1963).

takes place to give an ene-ketene as a transient intermediate. This suggestion is supported from infrared spectra of samples taken from the reaction mixture intermittently. Photolyzed solutions developed a strong infrared band at $4.79\ \mu$, which was immediately discharged by the addition of a few drops of alcohol. The photoreaction of II with aqueous dioxane takes an alternate course. Under these conditions, the naphthol V was not formed and the major product (85%) was 2,3,4-triphenyl-4-phenoxy-3-butenic acid (VIII), mp $197-198^\circ$. Irradiation of I in anhydrous methanol afforded methyl 2,3,4-triphenyl-4-phenoxy-3-butenate (IX), mp $124-125^\circ$ (62%). The stereochemistry of the acid and ester obtained has not been determined. The structure of IX was assigned on the basis of the chemical and physical data cited below. The elemental analysis of this component (*Anal.* Calcd for $C_{29}H_{24}O_3$: C, 82.83; H, 5.75. Found: C, 82.57; H, 5.74) indicates that it is a 1:1 adduct



of starting material and solvent. Spectral peaks appeared as follows: (ultraviolet spectrum) λ_{max} (95% ethanol) $252\ \text{m}\mu$ (ϵ 14,500) and $277\ \text{m}\mu$ (ϵ 8500); (infrared spectrum) λ_{max} (KBr) $5.75\ \mu$; (60-Mc nmr) (deuteriochloroform) multiplet at τ 3.05, singlet at 4.84, singlet at 6.35. The peak areas are in the ratio of 20:1:3. Treatment of VIII with diazomethane in ether gave an ester whose infrared spectrum is identical in every detail with pure IX. Corroborative evidence for structure IX was obtained by acid hydrolysis to phenol and by ozonolysis to phenyl benzoate and methyl phenylbenzoylacetate.



The formation of VIII and IX upon irradiation of II in hydroxylic solvents is reasonably formulated as proceeding *via* a ketene precursor, which then reacts with ethanol and water to form the observed ester and acid. The failure to isolate V suggests that either nucleophilic attack on the ketene proceeds at a faster rate than cyclization or that the rate of cyclization may actually be controlled by the light intensity through its effect on the rate of *cis-trans* ketene isomerization.

The photodesulfurization of I was examined as a function of exposure duration. The data is summarized in Table I. Consideration of the product distribution as a function of time in a number of photolyses showed that as II decreased, III appeared and more slowly V was formed. This contrasted with a steady amount

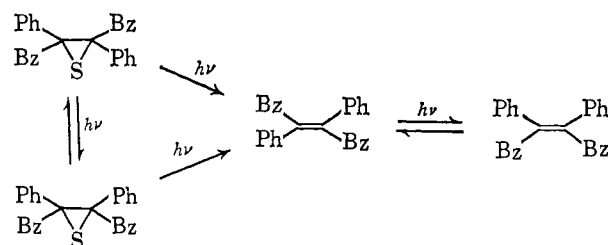
of IV. With short exposures *trans*-dibenzoylstilbene (II) accounts for nearly all of the products produced. At longer exposures, owing to secondary reactions, the yield of *trans* olefin gradually decreases. From the time studies, it is clear that the desulfurization of *trans* episulfide I is 97% stereospecific and that *trans*-dibenzoylstilbene is a primary reaction product. It is also evident from Table I that III and V are secondary photoproducts. The increase in amount of *cis* isomer is due to *in situ* photoisomerization. This was demonstrated by irradiation of *trans*-dibenzoylstilbene in benzene under comparable conditions. Photolysis of a solution of II for 4 hr afforded both III and V. A photostationary state between II and III was never established because of the competing cyclization of III.

Table I. Product Distribution *vs.* Extent Conversion from the Photolysis of *trans*-Dibenzoylstilbene Episulfide (I)

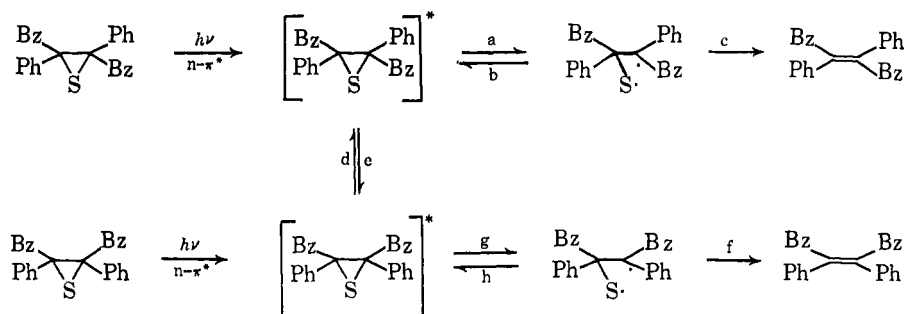
Run no.	Time, hr	Products, % yield ^a			
		II	III	IV	V
1	0.5	74	2	1	...
2	1	68	11	1	1
3	1.5	62	14	2	2
4	3	62	14	3	5
5	6	35	40	2	11
6	18	19	40	..	19

^a For details, see the Experimental Section.

The yield of the minor product, *cis*-dibenzoylstilbene episulfide (IV) is independent of time, indicating that IV is formed as a primary photoproduct. To determine whether the small amount of III isolated from low conversions of I is derived from IV or whether it arises from *in situ* photoisomerization, the irradiation of IV was performed. In this irradiation, no III could be detected, and instead only *trans* olefin II (80%) and *trans* episulfide I (20%) were isolated. While the photodesulfurization of I led to product of the same configuration, the loss of sulfur from *cis* episulfide IV afforded product with the reverse configuration. Both isomers of dibenzoylstilbene episulfide afforded one stereoisomeric olefin. We may therefore conclude that the reaction stereochemistry is controlled by factors other than retention of the original configuration.



The loss of sulfur from the episulfide upon photolysis is most simply explained by assuming a cleavage of the $\text{C}_\alpha\text{-S}$ bond of the three-membered ring followed by loss of atomic sulfur. The low-energy $n\text{-}\pi^*$ band is undoubtedly the significant absorption band, since light above $280\ \text{m}\mu$ was employed. The light absorbed by I and IV possesses sufficient energy to effect a bond cleavage. The energy corresponding to $316\text{-m}\mu$ radiation (90.8 kcal/mole) is substantially greater than the maximum energy required for bond dissociation in ethylene sulfide itself, which in turn is higher than that

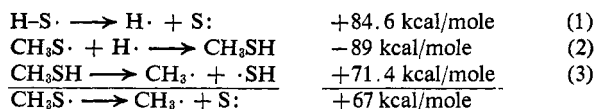


required for bond rupture in I and IV. The driving force for the fission of the episulfide ring can be attributed to the tendency of the excited $n-\pi^*$ state to eliminate α substituents as odd-electron species. The formal first step of the reaction is reminiscent of light-induced fission processes which result in the loss of electronegative substituents from a position α to the carbonyl group.²⁴⁻²⁸ As Zimmerman recently noted during a discussion on the reactivities of the $n-\pi^*$ excited states of carbonyl groups, such fissions may be traced to the tendency of the excited chromophore to eliminate α substituents as odd electron or anionic species according to the reaction medium.²⁹

The detailed mechanism of the desulfurization appears to be consistent with the above sequence of elementary steps.³⁰ To obtain a high degree of stereoselectivity, k_e and k_a must be large compared to k_c and k_f . If the rotation (k_e) of the diradical is given by $k_e = 10^{13}e^{-E_r/RT}$ and E_r , the activation energy for bond rotation, is taken as 3 kcal,³¹ k_e then has the value $10^{10.8} \text{ sec}^{-1}$. From the Rice-Ramsperger-Kassel relation³²

$$k = A \left[\frac{E - E_a}{E} \right]^{S-1}$$

we may then estimate the rates k_c and k_f . In the case of *trans* episulfide I the 0-0 energy of the first excited singlet can be estimated as 81 kcal/mole. Assuming adiabatic conversion of electronic to vibrational energy, we can estimate the energy of the vibrationally excited molecules reacting (E) as 81 kcal/mole. The energetics of sulfur extrusion from the diradical requires knowledge of $D(\text{R-S}\cdot)$ which may be estimated from the thermochemical cycle eq 1-3. From the appearance



potentials the bond dissociation energy ($\text{H-S}\cdot$) of the $\text{HS}\cdot$ radical has been estimated to be 84 kcal/mole.³³

(24) A. N. Strachan and F. E. Blacet, *J. Am. Chem. Soc.*, **77**, 5254 (1954).

(25) C. Weizmann, Y. Hirschberg, and E. Bergmann, *ibid.*, **60**, 1799 (1938).

(26) I. Mandel and A. D. McLaren, *ibid.*, **73**, 1826 (1951).

(27) C. K. Johnson, B. Dominy, and W. Reusch, *ibid.*, **85**, 3894 (1963).

(28) H. E. Zimmerman, B. R. Cowley, C. Y. Tseng, and J. W. Wilson, *ibid.*, **86**, 947 (1964).

(29) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963).

(30) The excited-state formulation presented above is applicable to both singlet and triplet species. Experiments designed to distinguish between the two possibilities have not yet been performed.

(31) W. B. DeMore and S. W. Benson, *Advan. Photochem.*, **2**, 219, 219 (1964).

(32) N. B. Slater, "Theory of Unimolecular Reactions," Cornell University Press, Ithaca, N. Y., 1959, p 125.

The values for eq 2 and 3 are available from the literature.³⁴ The energetics of sulfur extrusion from the thio diradical will undoubtedly be less than this upper limit since the loss of sulfur leaves a radical which can be stabilized by both phenyl and benzoyl groups.³⁵ Assuming the same differential in bond dissociation energy holds between ethane and ethylbenzene ($\Delta DE = 21 \text{ kcal/mole}$)³⁶ as in methyl sulfide and benzyl sulfide radicals, we can estimate the activation energy for sulfur extrusion as lying between 30 and 40 kcal/mole. Using the lower figure as the activation energy required for loss of sulfur and additionally assuming that S is 73 or one-half the $3n - 6$ vibrational modes of I³⁷ and taking $A = 10^{13} \text{ sec}^{-1}$, we find k_c about 10^{-1} sec^{-1} . Thus rotation about the carbon-carbon bond is expected to be faster than elimination of sulfur, in agreement with experimental observations which show that the reaction stereochemistry is controlled by factors other than retention of the original configuration.

The high stereoselectivity observed in the reaction demands that rotational isomerization be a relatively efficient process compared to sulfur extrusion. In addition, the diradical formed must possess a relatively long lifetime for efficient loss of sulfur to occur. In an elegant investigation of the reaction of $\text{S}(^1\text{D})$ atoms with simple olefins, Gunning has amply demonstrated the stability and long lifetime of thiodimethylene diradicals.³⁸ The observed stereospecificity was rationalized by a slow rate of rotation compared to ring closure. However, it should be pointed out here that it is quite reasonable to expect that the rate of ring closure and bond rotation in that case to be comparable, but certainly larger than extrusion of the heteroatom.

Since *trans*-dibenzoylstilbene (II) is formed to the exclusion of its stereoisomer (III), it may be concluded that the over-all rate of formation of II is greater than the over-all rate of III and that the free energy of the sulfur extrusion transition state from II is lower than that of III. Since the stereoselectivity derives from the lower free energy of transition state II relative to III, it is instructive to examine the factors which may influence the free energy of the transition states and lead to the lower energy of II. These transition states differ by a 180° rotation about the carbon-carbon single bond of the diradical. Inspection of models

(33) T. F. Palmer and F. P. Lossing, *J. Am. Chem. Soc.*, **84**, 4661 (1962).

(34) J. L. Franklin and H. E. Lumpkin, *ibid.*, **74**, 1023 (1952).

(35) The odd electron residing on the β carbon should also be capable of lowering the bond dissociation energy for the diradical.

(36) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 50.

(37) H. E. Zimmerman and J. W. Wilson, *J. Am. Chem. Soc.*, **86**, 4036 (1964).

(38) K. S. Sidhu, E. M. Lown, O. P. Strausz, and H. E. Gunning, *ibid.*, **88**, 254 (1966).

suggests that the isomer with the phenyl groups *cis* should exhibit slightly greater steric interaction than the isomer with phenyl and benzoyl groups *cis*. Since phenyl is a more bulky group than benzoyl it is tempting to suggest that transition state II, in which the phenyl and benzoyl groups are *cisoid*, would be of lower energy than the transition state in which the two phenyl groups are *cisoid*. Hence, the van der Waals repulsive forces between two large groups may be the decisive factor for the exclusive formation of the *trans* olefin.

Experimental Section³⁹

Irradiation of *trans*-Dibenzoylstilbene Episulfide (I). *trans*-Dibenzoylstilbene episulfide was prepared according to the procedure of Dittmer and Levy.⁴⁰ The product, mp 109–111°, was recrystallized several times from methanol prior to irradiation. A solution of 1.19 g of I in 200 ml of benzene was irradiated with an internal cooled mercury arc lamp (Hanovia, Type L, 450 w) with a Pyrex filter to eliminate wavelengths below 280 m μ . Aliquots were removed and analyzed by thin layer chromatography. After 6 hr, the spot on a thin layer plate due to I had almost disappeared and several new spots had appeared in its place. Concentration of the solution left an oil which was subjected to liquid–liquid partition chromatography. The separation was carried out in a water-jacketed column (150 \times 3.5 cm) which was kept at a constant temperature of 29.0 \pm 0.05°. The two-phase system (prepared from 1000 ml of cyclohexane, 400 ml of dimethylformamide, 250 ml of ethyl acetate, and 30 ml of water) was allowed to equilibrate for at least 30 min before use. The liquid–liquid apparatus used in these experiments and the processing of the fraction has been described in detail elsewhere.¹⁴ The chromatogram showed five peaks with retention volume of 1600, 1830, 1920, 2250, and 3100 ml of mobile phase. The first peak (230 mg) was identified as recovered starting material. The third and fourth peaks were assigned structures II (*trans*-dibenzoylstilbene), mp 230° (560 mg), and III (*cis*-dibenzoylstilbene), mp 208–210° (120 mg); *cis*- and *trans*-dibenzoylstilbene were identified by comparison of infrared and mixture melting point with that of an authentic sample.

***cis*-Dibenzoylstilbene Episulfide.** The second fraction from the liquid–liquid partition chromatogram contained 40 mg of a white solid, mp 164–173°. Recrystallization from 95% ethanol afforded a crystalline solid, mp 174–175°. The structure of this material is assigned as *cis*-dibenzoylstilbene episulfide (IV) on the basis of the following observations.

Anal. Calcd for C₂₈H₂₀O₂S: C, 79.97; H, 4.80; S, 7.63. Found: C, 79.52; H, 4.83; S, 7.89.

The infrared spectrum shows a strong carbonyl band at 5.96 μ and strong bands at 8.0, 8.5, 9.4, 9.8, 11.8, 12.6, and 13.0 μ . The ultraviolet spectrum in 95% ethanol has maxima at 247 m μ (ϵ 33,000) and 345 m μ (ϵ 900). The nmr (deuteriochloroform) showed a complex multiplet for the aromatic protons centered at τ 2.34.

***cis*-Dibenzoylstilbene episulfide (100 mg) and triphenylphosphine (10 mg)** were dissolved in 5 ml of xylene and the solution was refluxed for 24 hr. Water was added and the white solid (85 mg) which appeared at the water–xylene interface was removed by filtration. Recrystallization from glacial acetic acid gave *trans*-dibenzoylstilbene, mp 230–231° (lit.⁴¹ mp 230.3–230.6°). Triphenylphosphine sulfide, mp 154–155° (lit.⁴² mp 157°), was also isolated from the reaction mixture. Its infrared spectrum was identical in every detail with that of an authentic sample.

A sample of the *cis* episulfide IV (100 mg) was heated for 30 min in refluxing xylene. Removal of the solvent *in vacuo* left 98

mg of a white solid. Recrystallization from glacial acetic acid gave pure *trans*-dibenzoylstilbene.

1-Hydroxy-2,3-diphenyl-4-phenoxy-naphthalene (V). The last fraction from the liquid–liquid partition chromatogram contained 50 mg of a solid, mp 143–154°. Recrystallization from methanol gave white needles, mp 157–158°.

Anal. Calcd for C₂₈H₂₀O₂: C, 86.57; H, 5.19. Found: C, 86.33; H, 5.17.

The infrared spectrum of this material showed a hydroxyl band at 2.85 and a carbon–oxygen stretching band at 8.26 μ ; the ultraviolet spectrum (λ_{max}) (95% ethanol) 246 m μ (ϵ 32,000) and 325 m μ (ϵ 6200).

Chemical confirmation was obtained by sodium dichromate oxidation of V. To 50 mg of the above 1-hydroxy-2,3-diphenyl-4-phenoxy-naphthalene (V) in 2 ml of glacial acetic acid, was added 150 mg of sodium dichromate and the mixture was heated to 80° for 30 min. After being cooled, the mixture was poured onto ice, and extracted with ether; drying and evaporating the solvent yielded a yellow solid, mp 134–138°. Recrystallization from 95% ethanol gave 38 mg (92%) of yellow crystals, mp 138–139° (lit.⁴³ mp 135–136°). The product obtained was identical with an authentic sample of 2,3-diphenyl-1,4-naphthoquinone synthesized by the method of Crawford.¹⁸

Structure V was further confirmed by its unequivocal synthesis from 2,3-diphenyl-1,4-naphthalenediol and diphenyliodonium iodide. 2,3-Diphenyl-1,4-naphthalenediol (VII) was prepared by the method of Weiss and Bloch.⁴⁴ To a solution of 46 mg of sodium in 5 ml of methanol there was added, under nitrogen, 312 mg of 2,3-diphenyl-1,4-naphthalenediol (VII). To this red solution at room temperature with stirring and under nitrogen 140 mg of diphenyliodonium iodide was added, and the mixture was heated to gentle reflux. Within 10 min, the red color was discharged, and the mixture turned light orange. The solvent was evaporated on a steam bath and the residue was chromatographed on a Florisil (50 g) column prepared in hexane. The column was eluted with 500 ml of 50% hexane–benzene. The eluent, in 50-ml fractions, was concentrated and dried *in vacuo*. Fractions 4–9 contained 212 mg of a yellow solid, mp 135–139°. Recrystallization from ethanol afforded pure 2,3-diphenyl-1,4-naphthoquinone, mp 138–139°. The benzene eluate, after removal of solvent, gave 106 mg of a white solid, mp 156–157°, whose infrared spectrum was identical with that of V, isolated from the irradiation of *trans* episulfide I.

Photolysis of *trans*-Dibenzoylstilbene (II). A solution of 1.0 g of II in 1 l. of anhydrous benzene was irradiated with an internal water-cooled mercury arc lamp (Hanovia, Type L, 450 w) with a Pyrex filter to eliminate wavelengths below 280 m μ . Aliquots were removed and analyzed by thin layer chromatography. After 4 hr, the spot on a plate due to II had diminished and two new spots had appeared. Concentration of the solution left an oil which was chromatographed by liquid–liquid partition chromatography. The chromatogram showed three peaks with retention volume of 1940, 2250, and 3100 ml. The first peak (240 mg) was identified as recovered starting material. The second peak (340 mg) was shown to be *cis*-dibenzoylstilbene (III). The final band contained 410 mg (41%) of 1-hydroxy-2,3-diphenyl-4-phenoxy-naphthalene (V).

The photoreaction of II with aqueous dioxane as solvent takes an alternate course. Ultraviolet irradiation of 1.0 g of II in 550 ml of dioxane and 150 ml of water followed by evaporation of the solvent under reduced pressure gave a yellow oil. This material was taken up in ether and the ether layer was extracted with 200 ml of 10% sodium carbonate. Acidification at 0° yielded a white precipitate which was taken up in ether. Drying and evaporation of the ether gave 890 mg (85%) of 2,3,4-triphenyl-4-phenoxy-3-butenic acid (VIII), mp 197–198°.

Anal. Calcd for C₂₈H₂₂O₃: C, 82.73; H, 5.45. Found: C, 82.37; H, 5.45.

The neutralization equivalent of the crystalline compound is in accord with its assignment as a carboxylic acid.

Anal. Calcd for C₂₈H₂₂O₃: neut equiv, 406. Found: neut equiv, 408.

The infrared spectrum of this acidic substance in a potassium bromide pellet had a broad band from 3.2 to 4.1 and a strong carbonyl band at 5.88 μ . The ultraviolet spectrum (95%) has a maximum at 252 m μ (ϵ 16,800) and a shoulder at 277 m μ (ϵ 8800).

Methyl 2,3,4-Triphenyl-4-phenoxy-3-butenate (SX). Diazo-methane was prepared from an excess of N-nitroso-N-methylurea

(39) All melting points are corrected and boiling points are uncorrected. Elemental analyses were performed by Scandinavian Micro-analytical Laboratory, Herlev, Denmark, and Alfred Bernhardt Laboratories, Hohenweg, Germany. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 60 Mc with the Varian Associates high-resolution spectrophotometer. Tetramethylsilane was used as an internal standard.

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Table II. Photolysis of *trans*-Dibenzoylstilbene Episulfide (I)^a

Run no.	Amount of episulfide photolyzed, mg	Time of photolysis, hr	Products, mg (%) ^b				
			I	II	III	IV	V
1	109 ³	0.5	731 (67)	246 (74)	8 (2)	12 (1)	... ^c
2	1132	1	530 (47)	381 (68)	61 (11)	16 (1)	18 (1)
3	1213	1.5	462 (38)	432 (62)	96 (14)	23 (2)	27 (2)
4	1194	3	230 (19)	560 (62)	120 (14)	40 (3)	50 (5)
5	1236	6	124 (10)	361 (35)	411 (30)	21 (2)	130 (11)
6	1175 ^d	18	... ^c	208 (19)	437 (40)	...	212 (19)

^a Material separated by liquid-liquid partition chromatography, figures present approximate yields. ^b Yields are based on reacted *trans* episulfide I. ^c Thin layer chromatography indicated the absence of these materials. ^d Material balance did not add up to 100% in the longer photolysis experiments due to the formation of other products which have not yet been identified.

by standard procedures. The yellow ethereal solution of diazomethane was added to a solution of 500 mg of 2,3,4-triphenyl-4-phenoxy-3-butenic acid (VIII) in 100 ml of ether cooled in an ice bath. When the yellow color persisted, addition was stopped and the mixture was allowed to stand for 2 hr. The bulk of the ether and excess diazomethane were distilled off on a steam bath. Hexane was added, the rest of the ether was boiled off, and the solution was concentrated to 8 ml. A crystalline precipitate soon settled, mp 120–124°. Recrystallization from hexane gave methyl 2,3,4-triphenyl-4-phenoxy-3-butenate (480 mg) as a colorless solid, mp 124–125°.

Anal. Calcd for C₂₉H₂₄O₃: C, 82.83; H, 5.75. Found: C, 82.57; H, 5.74.

The infrared spectrum shows a strong carbonyl band at 5.75 μ and a series of sharp bands at 8.15, 8.30, and 8.42 μ . The ultraviolet spectrum in 95% ethanol has maxima at 252 m μ (ϵ 14,500) and 277 m μ (ϵ 8500). The nmr spectrum is in excellent agreement with the structure. There is a multiplet centered at τ 3.05, a singlet at 4.84, and a singlet at 6.35. The peak areas are in the ratio of 20:1:3.

Photolysis of II in anhydrous methanol at 25° for 6 hr with ultraviolet light of wavelength above 280 m μ and concentration of the solution left an oil, which rapidly crystallized an addition of hexane-benzene to give IX, mp 124–125°. The infrared and nmr spectra of this material were identical in every detail with those of methyl 2,3,4-triphenyl-4-phenoxy-3-butenate prepared from the esterification of VIII. The mixture melting point of these two materials was undepressed at 123–124°. Saponification of the ester was carried out on 200 mg in 4 ml of methanol and 3 ml of 4 N sodium hydroxide at room temperature overnight. Acidification at 0° yielded a white precipitate which was filtered, dissolved in hot methanol, and precipitated slowly by addition of water to give 165 mg of VIII, mp 197–198°.

The identity of the photolysis ester as methyl 2,3,4-triphenyl-4-phenoxy-3-butenate (IX) was further confirmed by the ozonolysis of IX to phenyl benzoate and methyl phenylbenzoylacetate. A Welsbach ozonizer operating at 0.026 mmole of ozone/min and the ozonization procedure of Turner⁴⁵ were used. In 20 ml of ethyl acetate and 5 ml of glacial acetic acid was dissolved 420 mg (1.0 mmole) of unsaturated ester IX. Ozone was passed for 38 min (1.0 mmole) into the solution cooled to –20°. Then 10 ml of water and 5 ml of a 40% solution of peracetic acid in acetic acid were added and the mixture was allowed to stand at room temperature for 18 hr. The mixture was diluted with 200 ml of ether and washed successively with water. The ethereal solution was dried

over sodium sulfate and concentrated *in vacuo* leaving 340 mg of an oil. The products were separated on an Aerograph 350-B instrument with helium as the carrier gas on a column of diethylene glycol succinate (5% on Chromosorb P, 2 ft) at a flow rate of 60 cc/min. Analysis of the residue showed that the product was composed of two major components with retention times of 1.5 (79%) and 4.6 (28%) min on the Degs column. Comparison of retention times and infrared spectra with those of known samples of phenyl benzoate and methyl phenylbenzoylacetate⁴⁶ established the identity of the products.

Product Distribution vs. Time in the Photolysis of *trans*-Dibenzoylstilbene Episulfide. The yields of the four major products obtained from the irradiation of I are strongly affected by the length of the irradiation as shown in Table II. Consideration of the product distribution as a function of time in a number of photolyses showed that as II decreased, III appeared and more slowly V was formed. This contrasted with a steady amount of *cis*-dibenzoylstilbene episulfide (IV).

Ultraviolet irradiation of a solution of II (1.0 g) in benzene for 30 min utilizing a Pyrex filter affords 28 mg (2%) of *cis*-dibenzoylstilbene (III). Increasing the time of the photolysis (4 hr) gave a higher proportion of the *cis* olefin (III, 34%) but resulted in a diminished over-all yield of recovered starting material (24%). The lower yields can be attributed to the competing side reaction of *cis*-dibenzoylstilbene which begins to predominate at longer photolysis time. A photostationary state between the olefinic material was never established because of this side reaction.

Irradiation of *cis*-Dibenzoylstilbene Episulfide (IV). A solution of *cis*-dibenzoylstilbene episulfide (IV, 150 mg) in benzene (200 ml) was irradiated with a Hanovia 200-w mercury arc lamp using a Pyrex filter. The photolysis was followed by withdrawing small samples at fixed intervals without interrupting the system. The samples were analyzed by thin layer chromatography. After 1.5 hr, 98% of the starting material had disappeared and two spots had appeared in its place. After the irradiation was completed, the solution was evaporated to dryness and the residue was chromatographed using liquid-liquid partition chromatography. The chromatogram showed two peaks with retention volume of 1620 and 1930 ml of mobile phase. The infrared spectrum of the first band (20%) was identical in every detail with that of *trans*-dibenzoylstilbene episulfide (I). The second peak (80%) had an infrared spectrum identical in every detail with that of an authentic sample of *trans*-dibenzoylstilbene. The mixture melting point of these two materials was undepressed at 230–232°. There was no indication of any other component in the chromatogram.

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