

## Photolysis and Pyrolysis of the Episulfoxide of Dibenzoylstilbene<sup>1-3</sup>

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Photolysis or pyrolysis of the episulfoxide of dibenzoylstilbene (2,3-dibenzoyl-2,3-diphenylthiirane 1-oxide) yields monothioibenzil and benzil. Triplet sensitizers have no effect on the products of photolysis except as internal filters. A mechanism which involves ring expansion of the sulfoxide is suggested for the formation of the products.

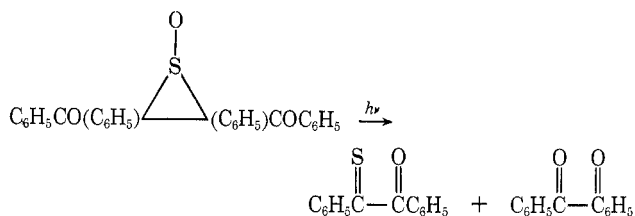
Oxidation of the yellow episulfide of dibenzoylstilbene (believed to be the *cis* isomer) by hydrogen peroxide in acetic acid yields two episulfoxides.<sup>4</sup> Oxidation of a *cis* isomer would yield two meso episulfoxides, a *trans* and a pair of enantiomorphs. The low melting episulfoxide (mp 165–167°) shows in the mass spectrum much more intense fragments formed by loss of SO<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub> than the high melting isomer (mp 184–186°). This indicates that in the low melting isomer the sulfoxide oxygen may be *cis* to the two benzoyl groups, there being more opportunity for the loss of an oxygen from a benzoyl group to the sulfoxide group or *vice versa* in this configuration. The relative integrated intensity of the carbonyl absorption to the phenyl absorption in the infrared is less for the low melting isomer. This favors a *cis* configuration for the low melting isomer in accord with the effect of nearby polar substituents on the stretching frequency of carbonyl groups.<sup>5</sup> The episulfoxides form unstable complexes with anhydrous cobalt(II) bromide and nitrate. The bromide forms a complex with 4 mol of episulfoxide and the nitrate with 2. The complexes appear to be too unstable for use in characterization.

Oxidation of an episulfide to an episulfoxide in an acidic medium is rare and until 1965 only a patent claimed such a synthesis.<sup>6</sup> Several examples of the oxidation of episulfides to episulfoxides have been reported since, but these episulfoxides are unstable in acid.<sup>7</sup> This paper reports on the photolysis and pyrolysis of the episulfoxide of dibenzoylstilbene. Some of the results of photolysis experiments were reported in preliminary form.<sup>8</sup>

**Photolysis.**—Previous investigations of the photochemistry of sulfoxides have been limited to the photosensitized oxidation of sulfoxides to sulfones,<sup>9</sup> the photochemical rearrangement of 2,2-dimethylthiachromane 1-oxide,<sup>10</sup> the photochemical racemization of optically

active sulfoxides,<sup>11</sup> and the photodesulfurization of a thiaphenylene sulfoxide.<sup>12</sup>

Solutions of the episulfoxides<sup>13</sup> were irradiated in benzene at 6–11° with a water-cooled, internal mercury arc lamp (wavelength at maximum output was 366 nm) through filters of quartz, Vycor, or Pyrex. The products were monothioibenzil and benzil, obtained in comparable amounts.



Although there are carbonyl groups in the episulfoxides no carbonyl  $n \rightarrow \pi^*$  absorption band is discernible in the ultraviolet spectrum. The tail of the  $\pi \rightarrow \pi^*$  absorption obscures the  $n \rightarrow \pi^*$  band in *cis*-dibenzoylstilbene,<sup>14</sup> and the  $n \rightarrow \pi^*$  absorption in the episulfoxides likewise may be obscured.

The photochemical decomposition of the episulfoxide mixture may proceed through either a singlet or triplet state. Triplet sensitizers or quenchers had no effect on the photolysis except that occasionally a decrease in the yield of products was observed, caused by internal filtering of light by the added compound. The results are given in Table I. Relatively small amounts of anthracene noticeably decrease the yield of monothioibenzil. Anthracene, which absorbs strongly around 366 nm, may be acting as an internal filter.

An excited triplet state probably is not involved in the rearrangement unless the rearrangement through this state occurs faster than its quenching. The greater than normal yield of benzil obtained when piperylene was present in the reaction mixture may be caused by removal of the monothioibenzil by a diene addition or by a photochemical 2 + 2 addition.<sup>15</sup> Re-

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(1) This work was aided by National Science Foundation Grant GP-5513 for which we are grateful.

(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 complete details, see G. E. Kuhlmann, Ph.D. Thesis, Syracuse University, 1968.

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

(5) R. N. Jones, D. A. Ramsay, F. Herling, and K. Dobriner, *J. Amer. Chem. Soc.*, **74**, 2828 (1952).

(6) S. B. Soloway, U. S. Patent 2,694,073; *Chem. Abstr.*, **49**, 3465 (1955). However, a rearrangement to a four-membered thietane sulfoxide may have occurred: F. K. Lautenschlaeger, *J. Org. Chem.*, **34**, 3998 (1969). The structure proof for the compound claimed in the patent was not given.

(7) G. E. Hartzell and J. N. Paige, *J. Amer. Chem. Soc.*, **88**, 2616 (1966); K. Kondo, A. Negishi, and M. Fukuyama, *Tetrahedron Lett.*, 2461 (1969); K. Kondo, A. Negishi, and G. Tsuchihashi, *ibid.*, 3173 (1969); G. E. Manser, A. D. Mesure, and J. G. Tillet, *ibid.*, 3153 (1968).

(8) D. C. Dittmer, G. C. Levy, and G. E. Kuhlmann, *J. Amer. Chem. Soc.*, **89**, 2793 (1967).

(9) G. O. Schenck and H. Krauch, *Chem. Ber.*, **96**, 517 (1963).

(10) R. A. Archer and B. S. Kitchell, *J. Amer. Chem. Soc.*, **88**, 3462 (1966).

(11) G. S. Hammond, H. Gotthardt, L. M. Coyne, M. Axelrod, D. R. Rayner, and K. Mislow, *ibid.*, **87**, 4959 (1965); K. Mislow, M. Axelrod, D. R. Rayner, H. Gotthardt, L. M. Coyne, and G. S. Hammond, *ibid.*, 4958 (1965); R. S. Cooke and G. S. Hammond, *ibid.*, **90**, 2958 (1968); R. A. Archer and P. V. DeMarco, *ibid.*, **91**, 1530 (1969).

(12) A. G. Schultz, C. D. DeBoer, and R. H. Schlessinger, *ibid.*, **90**, 5314 (1968).

(13) Mixtures of the two isomeric sulfoxides were used since the results are the same with either isomer alone (Pyrex filter). The proportion of each isomer in the mixtures was not determined for all experiments. In several experiments with approximately equimolar amounts of the two isomers the results were the same within experimental error as the results from the mixtures used in the runs in Table I.

(14) H. E. Zimmerman, H. G. Dürr, R. S. Givens, and R. G. Lewis, *J. Amer. Chem. Soc.*, **89**, 1863 (1967).

(15) Both types of addition are known: A. Schönberg and B. König, *Chem. Ber.*, **101**, 725 (1968); K. Yamada, M. Yoshioka, and N. Sugiyama, *J. Org. Chem.*, **33**, 1240 (1968); Y. Omote, M. Yoshioka, K. Yamada, and N. Sugiyama, *ibid.*, **32**, 3676 (1967).

TABLE I

EFFECT OF SENSITIZERS AND QUENCHERS ON THE PHOTOLYSIS OF THE MIXTURE OF EPISULFOXIDES OF DIBENZOYLSTILBENE (PYREX FILTER)<sup>a</sup>

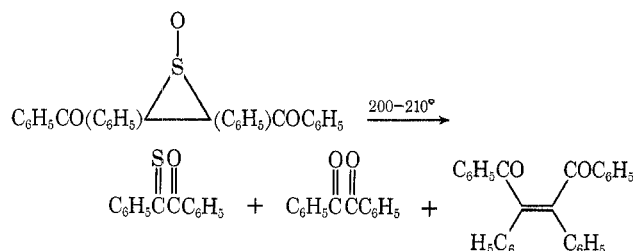
Compound added, 10 <sup>2</sup> mol	E <sub>T</sub> <sup>b</sup> , kcal mol <sup>-1</sup>	Episulfoxide, 10 <sup>4</sup> mol	Product	Mol % <sup>c</sup>
		8.30	Monothiobenzil	62.8 <sup>d</sup>
		5.65	Monothiobenzil	69.3 <sup>d</sup>
		3.27	Monothiobenzil	74.7 <sup>d</sup>
		5.60	Monothiobenzil	54.3
Acetophenone, 1.02	74	6.88	Monothiobenzil	51.8
Benzophenone, 13.8	69	11.6	Monothiobenzil	49.2 <sup>e</sup>
Biphenyl, 0.507	65	5.40	Monothiobenzil	54.8
Phenanthrene, 0.142	62	7.57	Monothiobenzil	54.4
Naphthalene, 10.5	61	10.4	Benzil	42.4
			Monothiobenzil	40.8
Piperylene, 100 <sup>f</sup>	55-60	9.57	Benzil	64
Biacetyl, 96.8 <sup>g</sup>	55	8.35	Monothiobenzil	34.2
Anthracene, 0.0102	42	7.94	Monothiobenzil	51.8
Anthracene, 0.0484	42	5.71	Monothiobenzil	43.0
Anthracene, 0.100	42	6.00	Monothiobenzil	33.3

<sup>a</sup> Solvent benzene, 500 ml; irradiation time 60 min unless otherwise noted; temperature between 6.3 and 10.7°. <sup>b</sup> N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, p 132. <sup>c</sup> Yield of deep blue monothiobenzil determined spectrophotometrically. <sup>d</sup> Irradiation time, 90 min. <sup>e</sup> By difference from the amount of starting material recovered. <sup>f</sup> In 400 ml of benzene. <sup>g</sup> In 350 ml of benzene.

moving the monothiobenzil removes an internal quencher which retards the reaction.<sup>16</sup>

When relatively large amounts of biacetyl or naphthalene are added, efficient sensitization or quenching of singlet states is not apparent. The somewhat lower yields that are observed may be caused by internal filtering or by incomplete quenching of excited singlets.

**Pyrolysis.**—Pyrolysis of a mixture of the two isomeric episulfoxides in a vacuum at 200–210° for 90 min gives a green sublimate and a brown residue. The sublimate consists of benzil (51%) and monothiobenzil (11%), and the residue contains *cis*-dibenzoylstilbene (3%), a trace of *trans*-dibenzoylstilbene, and three other unknown compounds detected by thin layer chromatography. The yield of monothiobenzil represents a lower limit because the compound is susceptible to conversion to benzil either by hydrolysis or oxidation.



This pyrolysis of an episulfoxide differs from that investigated by Hartzell and Paige who observed the loss of sulfur monoxide with the formation of 89% *cis*-2-butene and 11% *trans*-2-butene when the episulfoxide of *cis*-2-butene was pyrolyzed at 150°. <sup>17</sup>

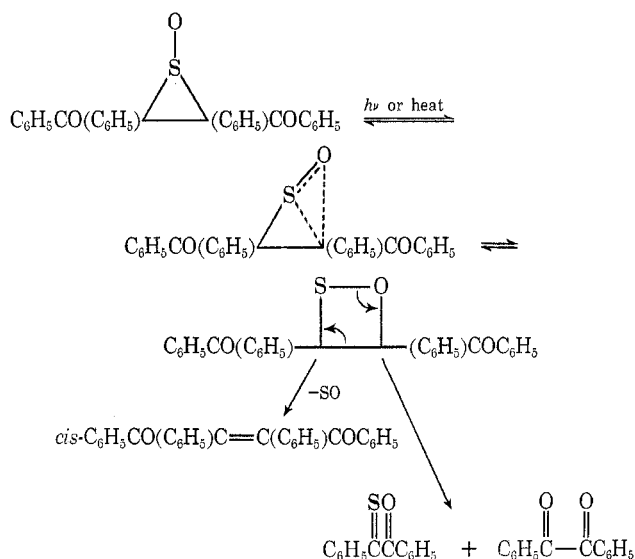
**Discussion.**—Because the pyrolysis of the episulfoxide of dibenzoylstilbene yields essentially the same products as the photochemical decomposition, a common

(16) For examples of self-quenching of photochemical reactions by products, see H. D. Becker, *J. Org. Chem.*, **32**, 2124 (1967); F. D. Lewis and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **90**, 3828 (1968).

(17) G. E. Hartzell and J. N. Paige, *J. Org. Chem.*, **32**, 459 (1967).

intermediate may be involved. The products may arise by way of a 1,2-oxathietane (cyclic sulfenate or monothiaperoxide),<sup>18</sup> which was suggested previously to account for the products from photolysis.<sup>8</sup> The oxathietane may decompose analogously to 1,2-dioxetanes (oxaoxetanes, cyclic four-membered peroxides).<sup>19</sup> Strain in the three-membered ring will dispose it to opening, but the electrophilic benzoyl and phenyl groups may require the opening to occur in such a way that some residual bonding (*i.e.*, electron density) remains at the site of bond breaking. This requirement can lead to the formation of the four-membered ring which is less strained than its precursor.

The role of the carbonyl groups in the episulfoxides in possible photochemical sensitization is unclear. They certainly play no unique photochemical role because the thermal decomposition leads to the same products. No dramatic effect is observed for relatively large amounts of added acetophenone or benzophenone but these external sensitizers may be of greatly decreased efficiency relative to the internal benzoyl groups.



Sulfenates are probable intermediates in the pyrolytic decomposition of dibenzyl sulfoxide or benzyl methyl sulfoxide.<sup>20</sup> The reverse reaction, the rearrangement of sulfenates to sulfoxides, is known.<sup>21</sup>

Absorption of light by the mixture of episulfoxides probably is followed quickly by decay of the initially formed electronically excited state to a vibrationally excited ground state from which rearrangement occurs. This excited ground state also may be attained by heating the episulfoxides. The recent discovery of the transfer of energy from a 1,2-dioxetane to organic mole-

(18) Expansions of cyclic sulfones to cyclic sulfenates (sultines) are known: D. C. Dittmer, R. S. Henion, and N. Takashina, *J. Org. Chem.*, **34**, 1310 (1969), and references cited therein; J. F. King, K. Piers, D. J. H. Smith, C. L. McIntosh, and P. deMayo, *Chem. Commun.*, 31 (1969).

(19) For recent examples, see K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969); C. S. Foote and J. Lin, *Tetrahedron Lett.*, 3267 (1968); J. E. Huber, *ibid.*, 3271 (1968); H. H. Wasserman, K. Stiller, and M. B. Floyd, *ibid.*, 3277 (1968). A 1,2-oxathiolane intermediate is alleged to decompose in a somewhat similar manner: Q. E. Thompson, *J. Org. Chem.*, **30**, 2703 (1965).

(20) E. Fromm and O. Achert, *Ber.*, **36**, 534 (1903); W. Carruthers, I. D. Entwistle, R. A. W. Johnstone, and B. J. Millard, *Chem. Ind. (London)*, 342 (1966).

(21) D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *J. Amer. Chem. Soc.*, **88**, 3138 (1966); E. G. Miller, D. R. Rayner, and K. Mislow, *ibid.*, 3139 (1966).

cules (e.g., *trans*-stilbene)<sup>22</sup> suggests that the presence of the postulated 1,2-oxathietane intermediate might be revealed by observation of an energy transfer from excited molecules produced from the intermediate.

### 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 nm and the intensity ( $\epsilon$ ) of the absorptions in l./mol 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 cycles per second (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 with apparatus from Brinkman Instruments, Inc., Westbury, N. Y., and either Merck silica gel GF<sub>254</sub> or HF<sub>254</sub>. Visualization was effected by the use of ultraviolet light and the compounds were identified as dark spots over the silica gel.

**Dibenzoylstilbene Episulfoxides.**—A solution of the yellow episulfide<sup>4</sup> (13.8 g, 0.0326 mol) in 250 ml of ethyl ether was treated with 10.5 ml of peracetic acid (40% in acetic acid, FMC Corp.) to yield a mixture of episulfoxides (11.8 g, 0.0272 mol, 86%). The episulfoxide isomers (mp 165–167°, 184–186°) may be precipitated fractionally from ethyl acetate. The yield of each isomer is about 10% for each recrystallization; the major portion of product remains in solution as a mixture. The two isomers have a mixture melting point of about 145°, and a mixture apparently was obtained in an earlier investigation.<sup>4</sup>

The infrared spectrum of the lower melting episulfoxide isomer (KBr disk) exhibits bands at 3050 (w), 1680 (s), 1615 (m), 1595 (m), 1570 (m), 1485 (m), 1440 (s), 1315 (m), 1300 (m), 1260 (s), 1210 (s), 1175 (m), 1150 (w), 1110 (m), 1100 (m), 1055 (s), 1040 (m), 1020 (m), 1000 (m), 970 (w), 945 (w), 935 (w), 875 (w), 860 (m), 815 (w), 780 (m), 770 (s), 755 (s), 735 (s), and 690 cm<sup>-1</sup> (s). The infrared spectrum of the higher melting episulfoxide isomer (KBr disk) exhibits bands at 3050 (w), 1680 (s), 1615 (m), 1595 (m), 1570 (m), 1485 (m), 1440 (s), 1315 (m), 1300 (m), 1240 (s), 1205 (s), 1175 (m), 1160 (w), 1100 (m), 1055 (s), 1045 (s), 1020 (m), 1000 (s), 995 (m), 955 (m), 930 (m), 920 (m), 900 (m), 835 (w), 795 (w), 775 (m), 765 (s), 750 (s), 740 (s), and 685 cm<sup>-1</sup> (s).

The proton nmr spectrum (60 MHz in CDCl<sub>3</sub>) of each isomer was determined. The lower melting episulfoxide had two complex multiplets centered at 475 and 445 Hz relative to tetramethylsilane. The higher field multiplet had one strong peak at 438 Hz. The higher melting episulfoxide had two complex multiplets centered at 473 and 440 Hz. The higher field multiplet had three strong peaks at 447, 439, and 430 Hz.

Beer's Law is obeyed by the ultraviolet maxima of each episulfoxide.

Isomer mp, °C	Solvent	10 <sup>4</sup> $\epsilon$ , l./mol cm		10 <sup>4</sup> $\epsilon$ , l./mol cm	
		$\lambda_{\max}$ , nm	$\lambda_{\max}$ , nm	$\lambda_{\max}$ , nm	$\lambda_{\max}$ , nm
165–167	Acetonitrile	225	2.30	256	2.05
	95% ethanol	225	2.40	256	2.20
184–186	Acetonitrile	233	2.70	255 <sup>a</sup>	2.30
	95% ethanol	233	2.75	260 <sup>a</sup>	2.00

<sup>a</sup> Shoulder.

The mass spectrum of the high melting isomer of the episulfoxide of dibenzoylstilbene showed no parent ion and ions at

TABLE II

YIELDS OF BENZIL OBTAINED BY PHOTOLYSIS OF MIXTURES OF EPISULFOXIDES OF DIBENZOYLSTILBENE

Filter	Time, min	Episulfoxides, 10 <sup>4</sup> mol,	Benzil	
			10 <sup>4</sup> Mol	Mol, %
Quartz	30	12.9	3.78	30.0 <sup>a</sup>
	45	15.2	6.51	42.8 <sup>a</sup>
	90	11.1	9.18	82.5 <sup>a</sup>
	105	8.39	7.16	85.4 <sup>a</sup>
Vycor	40	11.7	4.72	40.2 <sup>b</sup>
	90	11.1	8.78	70.0 <sup>a</sup>
Pyrex	60	5.60	2.94	52.5 <sup>a</sup>
	90	10.8	5.80	53.7 <sup>b</sup>
	120	10.0	5.19	51.9 <sup>a</sup>

<sup>a</sup> Determined spectrophotometrically at 258 nm,  $\epsilon$  (95% C<sub>2</sub>H<sub>5</sub>OH) 2.15 × 10<sup>4</sup>. <sup>b</sup> Determined by weight.

*m/e* (rel intensity) 388 [0.049, C<sub>6</sub>H<sub>5</sub>CO(C<sub>6</sub>H<sub>5</sub>)C=C(C<sub>6</sub>H<sub>5</sub>)COC<sub>6</sub>H<sub>5</sub>], 372 (0.016, tetraphenylfuran), 284 (0.019), 283 (0.052), 226 (6.31, C<sub>6</sub>H<sub>5</sub>CSCOC<sub>6</sub>H<sub>5</sub>), 210 (2.52, C<sub>6</sub>H<sub>5</sub>COCO-C<sub>6</sub>H<sub>5</sub>), 178 (0.040, C<sub>6</sub>H<sub>5</sub>C≡CC<sub>6</sub>H<sub>5</sub>), 165 (1.13), 152 (0.75), 123 (1.53), 122 (5.74), 121 (7.48, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>), 106 (11.4), 105 (100, C<sub>6</sub>H<sub>5</sub>CO). The mass spectrum of the low melting isomer also showed no parent ion and fragments at *m/e* 388 (1.56), 372 (1.32), 284 (4.09), 283 (1.51), 226 (5.88), 210 (2.78), 179 (2.94), 178 (3.32), 176 (2.30), 165 (3.12), 152 (2.74), 123 (2.33), 122 (12.4), 121 (27.4), 106 (8.46), 105 (100).

Complexes of the episulfoxides with anhydrous cobalt(II) bromide and cobalt(II) nitrate were obtained by treatment of the episulfoxide with the cobalt salt in dry dichloromethane. Analyses were not satisfactory but they indicated that cobalt(II) bromide complexes with four molecules of episulfoxide and that cobalt(II) nitrate complexes with two. In the complex with cobalt nitrate, the absorption in the infrared caused by the nitrate groups are at 1490 and 1275 cm<sup>-1</sup>, being shifted from 1380 and 1350 cm<sup>-1</sup>, the absorptions in cobalt(II) nitrate itself, and indicating that the nitrate ions are acting as ligands. The episulfoxide band was at 945 cm<sup>-1</sup> as compared with 1055 cm<sup>-1</sup> in the uncomplexed ligand. Because of the instability of these complexes to light and to moist air and because of their extreme insolubility, they were not investigated further.

**Pyrolysis of the Isomeric Episulfoxides of Dibenzoylstilbene.**—Pyrolysis of the mixed episulfoxides (0.643 g, 0.00147 mol) at 200–210° for 1.5 hr under vacuum (<1 mm) gave a green sublimate and a brown residue. The entire apparatus was wrapped in aluminum foil to keep out light. After the reaction mixture was cool, dry nitrogen was admitted and 15 ml of toluene was used to dissolve the green sublimate.

The solution was chromatographed on silicic acid under nitrogen with chloroform to give monothiobenzil<sup>8,23</sup> (0.000161 mol, 11% calculated from the visible spectrum) and 0.156 g (0.000744 mol, 51%) of benzil, mp 92–93°, mmp 92–94°. The visible and ultraviolet spectrum of monothiobenzil in chloroform was identical with that of the monothiobenzil produced in the photolysis of the episulfoxides.

The addition of 10 ml of toluene to the brown residue afforded a yellow solution and *cis*-dibenzoylstilbene, mp 209–211° (0.0184 g, 0.0000473 mol, 3%). An infrared spectrum of the *cis*-dibenzoylstilbene was the same as that of an authentic sample.<sup>24</sup> Analysis by tlc showed the yellow solution contained benzil, a trace of *trans*-dibenzoylstilbene, *cis*-dibenzoylstilbene, and at least three other compounds.

**Photolysis of Dibenzoylstilbene Episulfoxide.**—An internal mercury arc lamp (Hanovia Type L, 450 W) which emits light with a maximum at 366 nm was used in a water-cooled quartz immersion well. The benzene solvent (Baker and Adamson) was dried with sodium ribbon and distilled. The silicic acid (Baker and Adamson) used for chromatography was dried overnight at 115°. All solvents and flasks used with monothiobenzil were flushed with Linde high purity dry nitrogen and the flasks were wrapped in aluminum foil to keep out light.

The benzene solutions of mixtures of the two episulfoxides were photolyzed at 6–11°. The deep blue-green solutions obtained after irradiation were chromatographed on silicic acid as de-

(22) E. H. White, J. Wiecko, and D. F. Roswell, *J. Amer. Chem. Soc.*, **91**, 5194 (1969); E. H. White, J. Wiecko, and C. C. Wei, *ibid.*, **92**, 2167 (1970).

(23) D. C. Dittmer and G. E. Kuhlmann, *J. Org. Chem.*, in press.

(24) N. M. Bikales and E. I. Becker, *ibid.*, **21**, 1405 (1956).

scribed in the section on the pyrolysis. The chromatography column was wrapped in aluminum foil to keep out light.

The course of the reaction usually was followed by the production of benzil, and the concentration of monothiobenzil can be determined spectrophotometrically. Benzil was recovered by the flash evaporation of the chloroform at room temperature followed by extraction with hot 95% ethanol and filtration.

The benzil yield was determined either by weight or by ultraviolet spectroscopy. Data on yields are given in Table I and Table II and results with various quenchers and sensitizers are summarized in Table I.

**Registry No.**—2,3-Dibenzoyl-2,3-diphenylthiirane 1-oxide, 988-04-5.

## Photolysis of Bis[*p*-(1,1,3,3-tetramethylbutyl)phenyl] Terephthalate

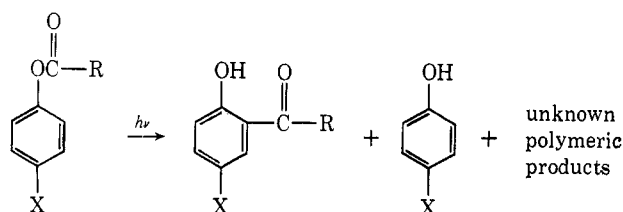
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The photolysis of bis[*p*-(1,1,3,3-tetramethylbutyl)phenyl] terephthalate in various solvents resulted in two consecutive photo-Fries rearrangements, whose quantum efficiencies were much lower than for simple aryl esters. Changes in solvent polarity and moderate changes in viscosity had little effect on the photolysis, but the efficiency in a rigid matrix was lowered considerably. In aqueous dioxane, the chief reaction was a photohydrolysis to give *p*-(1,1,3,3-tetramethylbutyl)phenol and terephthalic acid.

The photolysis of aryl esters has recently been reviewed.<sup>1</sup> The course of the reaction is well established, but whether the photo-Fries rearrangement involves a separated free-radical intermediate<sup>2</sup> or a 1,3-sigmatropic shift<sup>3</sup> is not known. The quantum efficiency for ketone formation,<sup>3,4</sup>  $\phi_k$ , is usually 0.15–0.20,

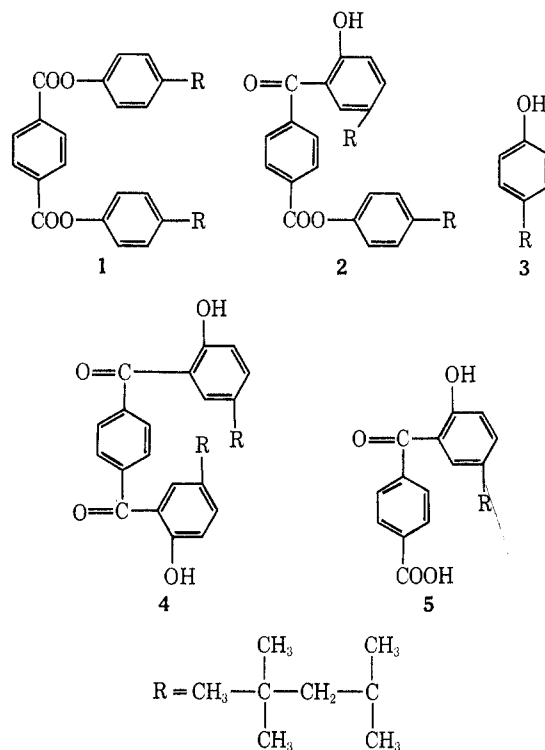


and the quantum efficiency,  $\phi_p$ , for phenol production, is about 0.05–0.15 in nonviscous, inert solvents.<sup>3</sup> The effect of solvents on this photolysis is poorly understood. An increase in solvent polarity was reported to be without effect on either  $\phi_k$  or  $\phi_p$  in the photolysis of *p*-tolyl acetate<sup>3</sup> but was reported to increase both  $\phi_k$  and  $\phi_p$  in the photolysis of 3,5-di-*tert*-butylphenyl benzoate.<sup>5</sup> Increased solvent viscosity reduced  $\phi_p$ .<sup>3</sup> In fluid solvents the yield of ketone is only 10–50%, and much of the ester is converted to unknown products; however, photolysis of aryl benzoates in a polymeric matrix has been reported to proceed without side reactions.<sup>6,7</sup> Many aryl esters of aromatic monocarboxylic acids have been studied; however, the photo-Fries rearrangement of nonpolymeric esters of aromatic dicarboxylic acids has not been reported. Photolysis of polymeric esters such as poly(isopropylidenedi-*p*-phenylene isophthalate) resulted in the formation of 2-hydroxybenzophenone moieties in the polymer.<sup>6</sup>

We report here the results of the photolysis of a nonpolymeric diester, bis[*p*-(1,1,3,3-tetramethylbutyl)phenyl] terephthalate (**1**), in a number of fluid solvents and in a rigid, polymeric matrix.

## Results and Discussion

Photolysis of **1** in anhydrous solvents gave four products which could be separated by glc: **2**, **3**, **4**, and **5**.



Each of these was also isolated and characterized by other means. In the presence of water, terephthalic acid was also a major product. Table I gives the product distribution, as determined by glc, for photolysis of **1** in various solvents.

Approximate quantum efficiencies for some of the reactions are given in Table II. These values were determined by using polychromatic light; loss of **1** was 10% or less. Because of the complexity of the mixture, the values are not corrected for absorption of light by the products.<sup>4</sup>

For further information on the effect of solvent polarity and viscosity, photolyses were carried out in mixtures of dioxane and acetonitrile. The results are shown in Table III.

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