stripped down to yield a pale yellow residue, which was flash chromatographed (hexane). There was obtained 0.436 g (78%) of 8 as an oil, which was chromatographically and spectroscopically identical with the sample prepared as described earlier.

Acknowledgment. We thank the Swedish Natural Science Research Council and Engineering Research Council of the Swedish National Board for Technical Development for financial support, and Dr. Arnold Brossi (NIH) for kindly providing an authentic sample of compound **3**.

Registry No. (±)-**3**, 55228-77-8; **4**, 120883-52-5; (±)-**5**, 120883-53-6; (±)-**6**, 120883-54-7; (±)-**7**, 120883-55-8; (±)-**8**, 120883-56-9; (±)-**9**, 120883-57-0; (±)-**9** (tosylate), 120883-58-1; (±)-**10**, 120883-59-2; (±)-**11**, 120883-60-5; (±)-**12**, 98672-93-6; (±)-**13**, 120883-61-6; (±)-**14**, 120883-62-7; (±)-**15**, 120883-63-8; 2-$CH_3OC_6H_4CO_2H$, 579-75-9; BnO$(CH_2)_4$Br, 60789-54-0; BnO$(CH_2)_4$Li, 64740-31-4; 2-[4-(phenylmethoxy)butyl]-2-cyclohexen-1-one, 120883-49-0; (±)-2-[4-(phenylmethoxy)butyl]-2-cyclohexen-1-ol, 120883-50-3; (±)-2-[4-(phenylmethoxy)butyl]-2-cyclohexen-1-yl acetate, 120883-51-4; 2-butyl-2-cyclohexenone, 34737-39-8.

Chemistry of Singlet Oxygen. 52. Reaction with *trans*-Stilbene

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Substituted *trans*-stilbenes react with singlet oxygen to give substituted diendoperoxides along with corresponding epoxides, *cis*-stilbenes, and benzaldehydes. The diendoperoxides rearrange readily to keto compounds on treatment with base. In methyl alcohol, solvent adducts are isolated. Monoendoperoxides are the primary products isolated from the photooxygenation of mono- and dimethoxystilbenes. Structures of several products were confirmed by NMR and X-ray crystallography. The results suggest that endoperoxide formation occurs via a polar intermediate such as a perepoxide or zwitterion.

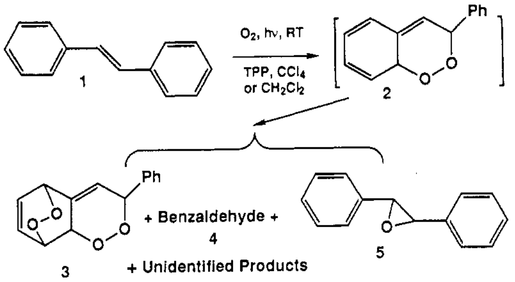
Introduction

Singlet oxygen usually reacts with conjugated dienes via [2 + 4] cycloaddition to give endoperoxides.[1] The reaction has been extensively studied since Schenck first used the term *endoperoxide* to describe bicyclic peroxides related to ascaridole[2] obtained by dye-sensitized photooxygenation of cyclohexa-1,3-dienes.[1]

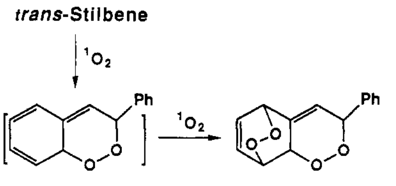
The mechanism of [2 + 4] cycloaddition of singlet oxygen to conjugated olefins has received relatively little attention because endoperoxidation resembles the well-known thermal Diels–Alder reaction. It is generally accepted that the cycloaddition of singlet oxygen to 1,3-dienes is concerted and proceeds through a six-membered transition state.[3] Recently, however, it has been suggested that polar intermediates (perepoxides or zwitterions) that rearrange to the endoperoxide are formed from acyclic dienes.[4] Zwitterionic intermediates have been proposed in the reactions of many dienes with electron-poor dienophiles; recent examples include hexadienes with singlet oxygen[5a] and triazolinediones.[5b–d]

Photosensitized oxygenation of vinyl aromatic compounds has been a recent area of investigation. Many groups have reported that stilbenes[6] and styrenes[7] react with singlet oxygen to give mono- or diendoperoxides. Singlet oxygen reacts initially at the β-position of the side chain and the ortho position of the aromatic ring to give a monoendoperoxide and, in some cases, goes on to form a diendoperoxide by further reaction with singlet oxygen.[6,7]

Scheme I



The photooxygenation of stilbene was first reported by Rio et al.[6a] to yield benzaldehyde as the final product. In 1977, Matsumoto et al.[6b] reinvestigated the photooxygenation of stilbenes and reported the formation of diendoperoxides. Foote and Boyd reported that the photooxygenation of stilbene depended on the reaction conditions.[6d] However, the structure of the initial monoendoperoxide and the mechanism of its formation are still unclear.



We report here a study of the photooxygenation of stilbenes in which careful characterization of products,

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(1) For a general review of the reactions of singlet oxygen, see: (a) *Singlet Oxygen*; Frimer, A. A., Ed.; CRC Press: Boca Raton, FL, 1985. (b) Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359. (c) *Singlet Oxygen*; Wasserman, H, H., Murray, R. W., Eds.; Academic Press: New York, 1979.

(2) Schenck, G. O. *Angew. Chem.* **1949**, *61*, 434.

(3) (a) Gollnick, K.; Haisch, D.; Schade, G. *J. Am. Chem. Soc.* **1972**, *94*, 1747. (b) Machin, P. J.; Porter, A. E.; Sammes, P. G. *J. Chem. Soc., Perkin Trans. 1* **1973**, 404, 407.

(4) (a) Fenical, W.; Kearns, D. R.; Radlick, P. *J. Am. Chem. Soc.* **1969**, *91*, 3396. (b) Rio, G.; Berthelot, J. *Bull. Soc. Chim. Fr.* **1970**, 1509; **1971**, 2938. (c) Hasty, N. W.; Kearns, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 3380. (d) Manring, L. E.; Foote, C. S. *Ibid.* **1983**, *105*, 4710. (e) Ashford, R. D.; Ogryzlo, E. A. *J. Am. Chem. Soc.* **1975**, *97*, 3604.

(5) (a) O'Shea, K. E.; Foote, C. S. *J. Am. Chem. Soc.* **1988**, *110*, 7167. (b) Jensen, F.; Foote, C. S. *Ibid.* **1987**, *109*, 6376. (c) Clennan, E. L.; Earlywine, A. D. *Ibid.* **1987**, *109*, 7104. (d) Nelsen, S. F.; Kapp, D. L. *Ibid.* **1985**, *107*, 5548.

(6) (a) Rio, G.; Berthelot, J. *Bull. Soc. Chim. Fr.* **1969**, 3609. (b) Matsumoto, M.; Dobashi, S.; Kondo, K. *Tetrahedron Lett.* **1977**, 2329. (c) Manring, L. E.; Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 4275. (d) Boyd, J. D.; Foote, C. S. *Ibid.* **1979**, *101*, 6758.

(7) (a) Foote, C. S.; Mazur, S.; Burns, P. A.; Lerdal, D. *J. Am. Chem. Soc.* **1973**, *95*, 586. (b) Matsumoto, M.; Kuroda, K. *Tetrahedron Lett.* **1979**, 1607. (c) Foote, C. S.; Lerdal, D. *Ibid.* **1978**, 3227. (d) Burns, P. A.; Foote, C. S. *J. Org. Chem.* **1976**, *41*, 908.

Table I. ^1H NMR Chemical Shifts of the Photooxygenation Products of *trans*-Stilbene[a,b]

δ (ppm)	6	8	9	10
H_a	5.42	–	–	5.75
H_b	4.51	4.48	5.03	5.08
H_c	5.05	5.01	4.92	3.63
H_d	6.80	6.78	6.75	4.81
H_e	6.80	6.78	6.86	5.52
H_f	5.05	5.01	4.92	6.22
H_g	6.31	7.05	7.12	5.97

[a] Chemical shifts were measured on Bruker AF 200 (200 MHz) and AM 360 instruments (360 MHz) with TMS internal standard in $CDCl_3$. [b] The assignment of peaks was based on 2-D NMR.

Table II. ^1H NMR Chemical Shifts of Endoperoxides[a]

δ (ppm)	12	16	19	24
H_a	5.39	–	5.51	5.60
H_b	4.85	4.67	5.17	5.21
H_c	4.97	4.98	2.42 2.89	2.41 2.90
H_d	6.69	6.63	6.09	6.21
H_e	5.17	5.12	7.21	7.19
H_f	6.27	7.06	6.47	6.52

[a] Chemical shifts were determined on Bruker AF 200 or AM 360 (200 or 360 MHz) spectrometers with TMS internal standard in $CDCl_3$.

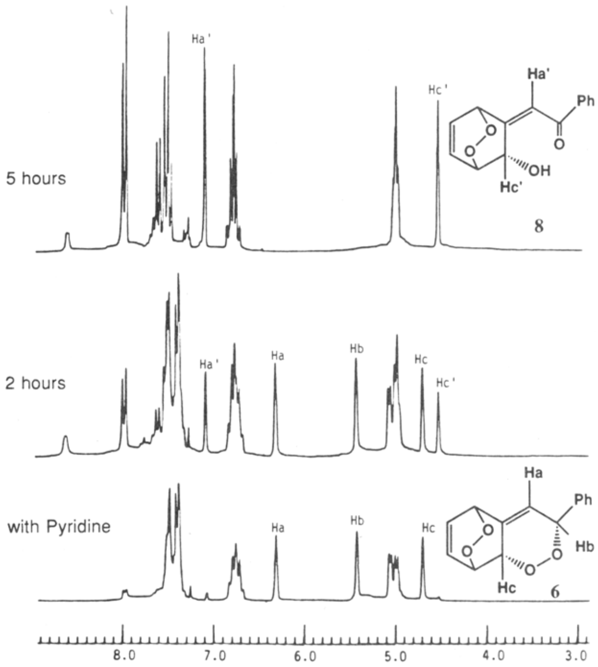


Figure 1. ^1H NMR spectra of the conversion of diendoperoxide **6** to **8**.

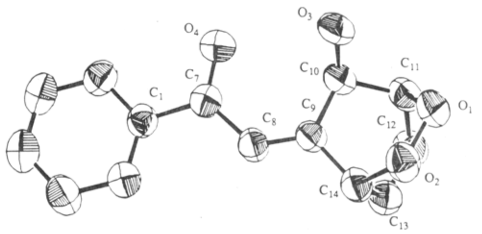


Figure 2. ORTEP view of compound **8**. Selected bond distances (Å) and angles (deg) (estimated standard deviations are in parentheses): distances, O1–O2 = 1.501 (4), O1–C11 = 1.449 (4), O2–C14 = 1.465 (5); angles, O1–C11–C12 = 107.7 (3), C10–C11–C12 = 110.3 (3), O2–C14–C13 = 108.1 (3), C9–C14–C13 = 109.0 (3).

including X-ray structures, allows exact assignment of endoperoxide structures and stereochemistry. Trapping experiments are used to study the mechanism of the 1,4-cycloaddition.

Results

Photooxygenation of *trans*-Stilbenes. *trans*-Stilbene (**1**) was photooxygenated at room temperature in CCl_4 or CH_2Cl_2 by using tetraphenylporphine (TPP) as sensitizer (Scheme I). The NMR spectrum of the reaction mixture showed the products to be mainly diendoperoxide **3** (about 80%), a small amount of benzaldehyde (**4**), *trans*-stilbene oxide (**5**), and a trace of unidentified products. Monoendoperoxide **2** was not detected in low-temperature experiments, suggesting that singlet oxygen reacts with **2** more rapidly than with the starting material.

Large-scale experiments at room temperature in CCl_4 or CH_2Cl_2 with a small amount of pyridine to prevent the bleaching of sensitizer allowed a diendoperoxide (shown to be the anti isomer **6**, see below), *trans*-stilbene oxide, *cis*-stilbene, and benzaldehyde to be separated by column chromatography. Two hydroxy ketone decomposition products, **8** and **9**, were also isolated. An epoxy endoperoxide, **10**, was also formed (<3% yield).

The structure of compound **8** was confirmed by X-ray crystallography (for further details, see Experimental Section and Figure 2). The structures of **9** and **10** were assigned by comparing their spectral data with those of **8** and **6**. The structure of **6** was further confirmed by comparison with reported spectral values[6b] and by NMR (COSY, DEPT, and ^1H–^{13}C-heterocorrelation 2-D NMR). The structure of epoxide **10** was assigned by a variety of NMR experiments, including homonuclear decoupling, COSY, heterocorrelation 2-D NMR, and NOE experiments. The coupling constants (J_{bc} = 2.47 and J_{dc} = 5.67 Hz) and the lack of an NOE between H_b and H_c suggest that the epoxide is anti to the endoperoxide (see Tables I–III for spectra of these and related compounds).

Compounds **8** and **9** are probably products of the well-known base-catalyzed rearrangement of diendoperoxides **6** and **7**.[7] This suggestion was confirmed by the reaction of pure **6** in $CDCl_3$ with a catalytic amount of pyridine to give **8** as the sole product by ^1H NMR (see Figure 1). *syn*-Diendoperoxide **7**, which was not detected

Table III. ^{13}C NMR Chemical Shifts of Photooxygenation Products[a,b]

compd	C-1	C-2	C-3	C-4	C-5	C-6
6	80.58 (d)	77.68 (d)	72.89 (d)	129.91 (d)	131.64 (d)	74.78 (d)
8	192.36 (s)	65.15 (d)	76.11 (d)	131.56 (d)	133.85 (d)	76.62 (d)
9	192.28 (s)	65.75 (d)	73.84 (d)	129.851 (d)	133.64 (d)	76.39 (d)
10	80.49 (d)	78.66 (d)	56.55 (d)	80.44 (d)	110.26 (d)	141.66 (d)
19	80.02 (d)	74.21 (d)	40.16 (t)	191.99 (s)	128.98 (d)	113.91 (d)
24	80.38 (d)	74.27 (d)	40.40 (t)	195.34 (s)	129.79 (d)	128.61 (d)
25	80.99 (d)	82.32 (d)	100.29 (d)	95.42 (d)	132.78 (d)	129.92 (d)

[a] Chemical shifts were determined on a Bruker AF 200 (50 MHz) spectrometer in $CDCl_3$. [b] All peaks were assigned by ^1H–^{13}C-heterocorrelation 2-D NMR, and multiplicity was determined by DEPT; s = singlet, d = doublet, and t = triplet.

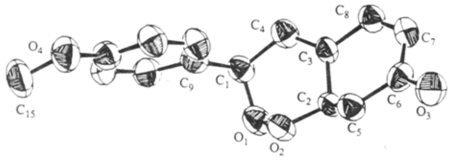


Figure 3. X-ray crystal structure of **19**. Selected bond distances (Å) and angles (deg) (estimated standard deviations are in parentheses): distances, O1–O2 = 1.457 (6), C1–O1 = 1.410 (6), C2–O2 = 1.419 (6); angles, C1–O1–O2 = 109.3 (4), O2–C2–C5 = 105.8 (4), O1–O2–C2 = 107.7 (4), C9–C1–O1 = 109.2 (4).

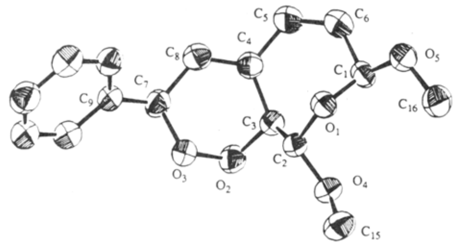
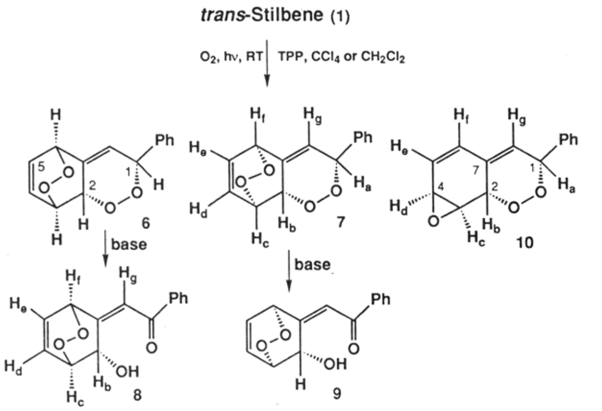


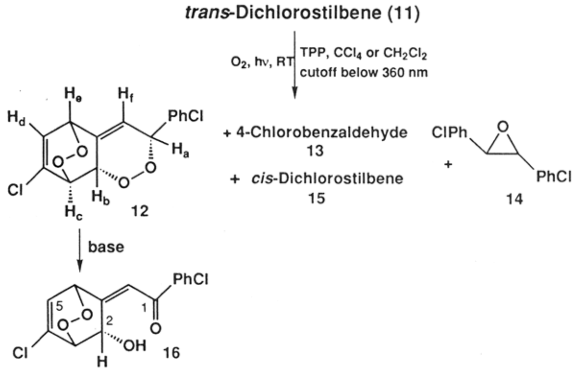
Figure 4. ORTEP drawing of the structure of **25**. Selected bond distances (Å) and angles (deg) (estimated standard deviations are in parentheses): distances, O2–O3 = 1.476 (2), C1–O1 = 1.434 (3), C2–O1 = 1.410 (3); angles, C2–O1–C1 = 115.6 (2), O1–C2–O4 = 112.3 (2), O2–C3–C2 = 110.5 (2), O1–C1–O5 = 107.9 (2).

directly and was probably formed in very small amounts, is presumably the precursor of **9**.

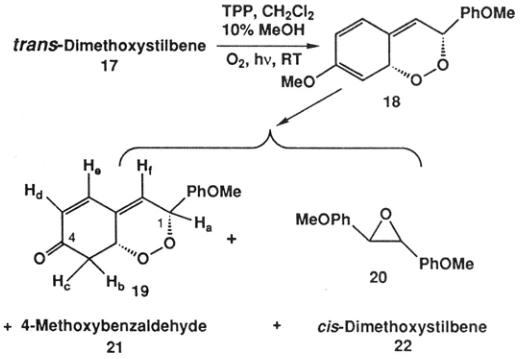


Photooxygenation of *trans*-4,4′-dichlorostilbene (**11**)[8] gave rise to an analogous series of compounds, *anti*-diendoperoxide **12**, benzaldehyde **13**, and epoxide **14** (Scheme II). With no filter solution (cutoff below 360 nm), *trans*-dichlorostilbene was converted readily to the cis isomer **15** in addition to undergoing oxygenation; however, with a filter solution (cutoff < 360 nm), a small amount of the cis isomer was detected. (Photooxygenation of **15** has not yet been investigated.) Diendoperoxide **12** also decomposed to alcohol **16** under the basic conditions.

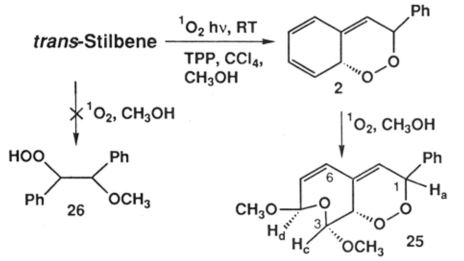
Scheme II



Scheme III

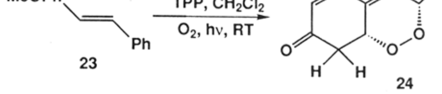


Scheme IV



Formation of Monoendoperoxide. *trans*-4,4′-Dimethoxystilbene (**17**) was photooxygenated in dichloromethane with and without $\sim$10% methyl alcohol with TPP as sensitizer and a tungsten–halogen lamp as light source with a water filter. Since enol ethers are very labile under mildly acidic conditions, we expected that the oxygenation might terminate at the monoendoperoxide stage by reaction of the product enol ether. After 2 h, only one product and a trace of starting material were detected by TLC. NMR of the reaction mixture showed multiplets near δ 2.4 and 2.9, assigned to protons α to a carbonyl. The product was isolated by silica gel column chromatography and the structure found by X-ray crystallography to be ketoendoperoxide **19** (Figure 3). Enol ether **18** is apparently hydrolyzed by acid from the solvent and adventitious water to **19**, stopping the oxygenation. Traces of epoxide **20**, 4-methoxybenzaldehyde (**21**) and *cis*-4,4′-dimethoxystilbene (**22**) were also formed. The reactions are shown in Scheme III.

Epoxide **20** is probably formed directly from **17** rather than from **18**, because epoxides were not detected from the similar endoperoxide **19**, and compound **18** is rapidly converted to **19** under the conditions. The analogous ketoendoperoxide **24** was produced from methoxystilbene **23** under the same conditions.



Trapping with CH$_3$OH. If a perepoxide or zwitterion is on the reaction pathway for the formation of endoperoxide, as frequently proposed,[9] it should react with solvents such as CH$_3$OH to give addition products. Methoxy ketal **25** (about 10%) was isolated from photooxygenation of

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(8) Nakayama, J.; Tanuma, M.; Honda, Y.; Hoshirio, M. *Tetrahedron Lett.* **1984**, *25*, 4553.

(9) (a) Jefford, C. W.; Rimbault, C. G. *Tetrahedron Lett.* **1976**, 2479. (b) Jefford, C. W.; Boschung, A. F.; Rimbault, C. G. *Helv. Chim. Acta* **1976**, *59*, 2542.

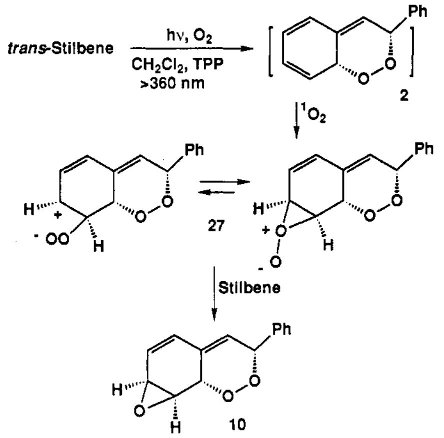
trans-stilbene in 20% CH_3OH/CCl_4 (Scheme IV). However, hydroperoxide **26**, which might have been formed from addition to the stilbene, was not detected. The structure of **25** was confirmed by X-ray crystallography (Figure 4).

Discussion

Singlet oxygen reacts with the β-position of the side chain and the ortho position of the aromatic ring of *trans*-stilbenes to give a monoendoperoxide as the initial product.[6] This mechanism was confirmed by the isolation of ketoendoperoxides **19** and **24** from **17** and **23**, respectively. The methoxy group of initial endoperoxide **18** from dimethoxystilbene is very labile and was hydrolyzed to give **19** during the photolysis (presumably by water unavoidably present and acid from the halogenated solvents). No diendoperoxide was detected under the conditions used with mono- or dimethoxystilbene, presumably because of the rapid reaction of the initial monoendoperoxide. Reaction of the initial endoperoxide is apparently so much faster than that of the stilbene in the other cases that the initial monoendoperoxide could not be detected.

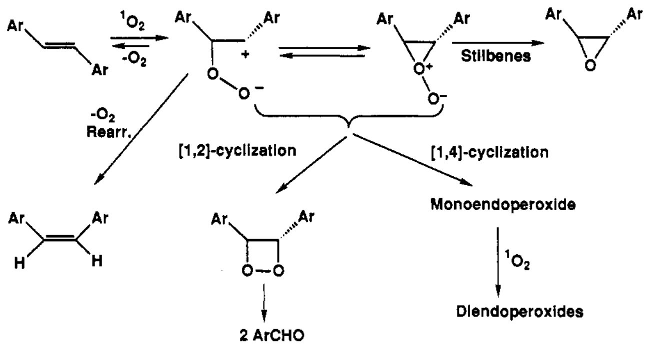
The formation of benzaldehydes, epoxides, and cis isomers from the photooxygenations, even when a filter was used to remove wavelengths below 360 nm, is not clearly understood.[10] The benzaldehydes are probably produced from dioxetanes, formed either directly or by rearrangement of monoendoperoxides. The formation of *cis*-stilbene suggests the intermediacy of a zwitterion, analogous to those responsible for the singlet-oxygen-catalyzed isomerization of dienes recently reported.[5a] A perepoxide could also be on the reaction coordinate, but is not required by the evidence. The results and proposed mechanisms are summarized in Scheme V.

Epoxide **10** is probably derived from *trans*-stilbene as shown below. Although only a small amount of this compound was produced, it also implies that polar intermediates such as perepoxide or zwitterion **27** are formed in $CDCl_3$. This reaction presumably occurs through the same pathway as the formation of stilbene oxides.

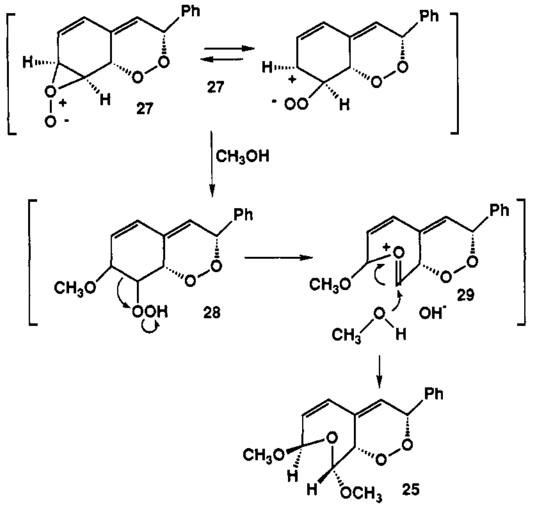


In the recent literature, a loose complex has been proposed as an intermediate in the formation of ene products and endoperoxides from cyclic dienes[11] and formation of an initial exciplex has been demonstrated.[12] Solvent adducts from the photooxygenation of cyclic dienes and aromatics are believed to be formed from polar intermediates such as perepoxides or zwitterions.[4] The present results suggest that a polar intermediate of this type may be intermediate in the photooxygenation of stilbenes as well.

Scheme V



The formation of compound **25** is probably related to this process. Methyl alcohol probably attacks perepoxide or zwitterion **27** to give hydroperoxide **28**, analogous to the ring-opening of epoxides. Hydroperoxide **28** decomposes via Baeyer–Villiger-type reaction to give oxonium ion **29**, and a second methyl alcohol reacts to form **25**.



Experimental Section

General Procedure. Rose bengal and tetraphenylporphine were obtained from Aldrich. All commercially available reagents were used without further purification.

Photooxygenations were performed by using either a Varian-Eimac 300-W xenon lamp or a 650-W Sylvania tungsten–halogen lamp (DWY). The output of the lamp was filtered with a 0.1 M K_2CrO_4 solution (in NH_4OH/NH_4Cl at pH 10) to remove light below 460 nm or with $BiCl_3$ in HCl solution for a cutoff below 360 nm.[13] Photolyses were carried out in Pyrex or NMR tubes (5 and 10 mm) inside a temperature-controlled cell described previously.[14] Sometimes a small amount of pyridine was used to prevent bleaching of sensitizer. Oxygen was passed through a drying tube containing anhydrous $CaCl_2$ and molecular sieves and was bubbled through the solution being photooxygenated via a Teflon tube.

Analytical gas chromatography was done by using a Hewlett-Packard Model 5800 instrument equipped with a 25-m 50% phenyl/50% methyl silicone capillary column and an FID detector. IR spectra were obtained on a Perkin-Elmer Model 137 instrument and mass spectra on an AEI MS-902 instrument. Low-temper-

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[10] The mechanisms of these reactions are under current investigation.

[11] Matusch, R.; Schmidt, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 718.

[12] (a) Gorman, A. A.; Gould, I. R.; Hamblett, T. *J. Am. Chem. Soc.* **1982**, *104*, 7098. (b) Hurst, J. R.; Schuster, G. B. *Ibid.* **1982**, *104*, 6854. (c) Yamaguchi, K.; Ikeda, Y.; Fueno, T. *Tetrahedron* **1985**, *41*, 2099. (d) Gorman, A. A.; Hamblett, I.; Lambert, C.; Spencer, B.; Standen, M. C. *J. Am. Chem. Soc.* **1988**, *110*, 8053–8059.

[13] *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum Press: New York, 1984; p 493.

[14] Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3424.

ature ^{1}H and ^{13}C NMR data were obtained on a Bruker AM 360 instrument operating at 360 MHz for ^{1}H NMR and 90 MHz for ^{13}C NMR. Chemical shift values are reported in δ (parts per million) relative to an internal TMS standard. 2-D NMR (COSY), DEPT (for ^{13}C NMR), and ^{1}H–^{13}C-heterocorrelation 2-D spectra were obtained by using Bruker AF-200 or Bruker AM-500 instruments.[15]

Preparation of *trans*-4,4′-Dichlorostilbene (11).[8] To a solution of (4-chlorophenyl)methanesulfonyl chloride in THF was added excess triethylamine (3 equiv) at −50 °C. After 1 h, the mixture was warmed to room temperature and stirred overnight. The residue after evaporation was dissolved in water and the resulting solid collected by filtration. *trans*-Dichlorostilbene (11) was obtained by recrystallization from acetone and hexane: mp 176–177 °C (lit.[16] mp 176 °C); ^{1}H NMR ($CDCl_3$, TMS, δ) 6.98 (s, 2 H), 7.4 (m, 8 H).

Photooxygenation of *trans*-Stilbene (1). Typical procedure: 2 mmol of 1 in dichloromethane or carbon tetrachloride (5 mL) containing methylene blue or TPP ($3–5 \times 10^{-4}$ M) as sensitizer was photolyzed at 25–50 °C with the Varian-Eimac lamp and K_2CrO_4 or $BiCl_3$ filter solution until no more substrate was detected by TLC. Sometimes a small amount of pyridine was used to prevent bleaching of sensitizers. Large-scale reactions were carried out without filter solution with a 650- or 1000-W tungsten–halogen lamp. The reaction mixture was concentrated under vacuum at room temperature, and the products were purified by column chromatography (CH_2Cl_2 and hexane eluent). *trans*-Stilbene oxide (5): mp 65–66 °C (lit.[17] mp 65–67 °C); ^{1}H NMR ($CDCl_3$, TMS, δ) 7.37 (aromatic, 10 H), 3.88 (s, 2 H). *cis*-Stilbene:[18] ^{1}H NMR ($CDCl_3$, TMS, δ) 7.20 (aromatic, 10 H), 6.57 (s, 2 H). Compound 6: mp 103–104 °C; coupling constants J_{ag} = 2.6 Hz, J_{cd}, J_{ef} = 13.1 Hz; IR (KBr) 1680, 1460, 1380, 1160, 1090, 1040 cm^{-1}; high-resolution ms calcd for $C_{14}H_{12}O_4$ *m/z* 244.0735, found 244.0733. Compound 8: mp 165–166 °C; coupling constants J_{ef} = 13.1 Hz; IR (KBr) 1660, 1615, 1465, 1270, 1245, 1225, 1180, 1090, 1025 cm^{-1}; high-resolution ms calcd for $C_{14}H_{12}O_4$ *m/z* 244.0736, found 244.0758. Compound 9: mp 162–164 °C; coupling constants J_{bc} = 8.3 Hz, J_{cd}, J_{ef} = 13.1 Hz; IR (KBr) 1660, 1615, 1465, 1270, 1240, 1225, 1180, 1100, 1020 cm^{-1}; high-resolution ms calcd for $C_{14}H_{12}O_4$ *m/z* 244.0736, found 244.0738. Compound 10: mp 91–92 °C; coupling constants J_{ag} = 2.6 Hz, J_{bc} = 2.5 Hz, J_{cd} = 5.7 Hz, J_{de} = 6.9 Hz; IR (KBr) 3008, 2874, 1611, 1428, 1294, 1260, 1245, 1176, 1103, 1085, 1074 cm^{-1}; high-resolution ms calcd for $C_{14}H_{12}O_3$ *m/z* 228.0786, found 228.0790.

Photooxygenation of 1 in Dichloromethane and Methyl Alcohol. Compound 1 (10 mmol) in dichloromethane (150 mL) and methyl alcohol (15 mL) containing TPP ($3–5 \times 10^{-4}$ M) as a sensitizer was photolyzed in a Pyrex tube with a water cooling jacket at room temperature and a 650-W Sylvania tungsten–halogen lamp (DWY). The reaction mixture was concentrated under vacuum at room temperature, and product 25 was purified by column chromatography (CH_2Cl_2 and hexane as eluent). Compound 25: mp 143–144 °C; coupling constants J_{ag} = 1.8 Hz, J_{cd} = 7.5 Hz, J_{ef} = 12.3 Hz; IR (KBr) 3060, 2980, 2860, 1605, 1430, 1050 cm^{-1}; high-resolution ms calcd for $C_{16}H_{18}O_5$ *m/z* 290.1152, found 290.1156.

Photooxygenation of *trans*-4,4′-Dichlorostilbene (11). Photooxygenation of 11 was carried out under the same conditions as that of *trans*-stilbene. *cis*-4,4′-Dichlorostilbene (15): ^{1}H NMR ($CDCl_3$, TMS, δ) 6.52 (s, 2 H), 7.21 (aromatic, 8 H). *trans*-4,4′-Dichlorostilbene oxide (14): mp 119–121 °C (lit.[16] mp 118–119 °C); ^{1}H NMR ($CDCl_3$, TMS, δ) 7.25 (aromatic, 8 H), 3.81 (s, 2 H). Compound 12: mp 124 °C; coupling constants J_{ag} = 2.7 Hz, J_{ab} = 1.8 Hz, J_{ef} = 6.2 Hz; IR (KBr) 2920, 1608, 1485, 1410, 1290, 1080 cm^{-1}; high-resolution ms calcd for $C_{14}H_{10}Cl_2O_4$ *m/z* 311.9956, found 311.9973. Compound 16: mp 145 °C; IR (KBr) 3500, 3100, 2910, 1675, 1610, 1595, 1410, 1205, 1095, 1010, 840 cm^{-1}; high-resolution ms calcd for $C_{14}H_{10}Cl_2O_4$ *m/z* 311.9956, found 311.9981.

Photooxygenation of *trans*-4,4′-Dimethoxystilbene (17) and *trans*-4-Methoxystilbene (23). Compound 17 or 23 (10 mmol) in dichloromethane (150 mL) with or without methyl alcohol (15 mL) and containing TPP ($3–5 \times 10^{-4}$ M) was photolyzed in a Pyrex tube under the same conditions as *trans*-stilbene. The reaction mixture was concentrated under vacuum at room temperature, and product 19 or 24 was purified by column chromatography (CH_2Cl_2/hexane eluent). Dimethoxystilbene oxide was also isolated.[19] Compound 19: mp 122–123 °C; coupling constants J_{ag} = 4.3 Hz, J_{cd} = 7.5 Hz, J_{ef} = 12.3 Hz; IR (KBr) 3050, 2980, 2860, 1675, 1655, 1502, 1240, 1080 cm^{-1}; high-resolution ms calcd for $C_{15}H_{14}O_4$ *m/z* 290.1152, found 290.1156. Compound 24: mp 96–98 °C; IR (KBr) 2980, 1685, 1564, 1460, 1265, 1255, 1202, 1180, 1040 cm^{-1}; high-resolution ms calcd for $C_{14}H_{12}O_3$ *m/z* 228.0786, found 228.0789.

X-ray Crystallographic Determination of 8, 19, and 25. Crystals of these compounds were grown from dichloromethane and hexane at −14 °C. A rectangular parallelepiped single crystal was mounted in a glass capillary. Diffraction data were collected at room temperature on a Picker or Syntex diffractometer equipped with graphite monochromator. Unit cell parameters were determined by a least-squares refinement of 31, 27, or 25 reflections ($20° < 2\theta < 10°$). The intensities were corrected for Lorentz and polarization effects but not for absorption. All atoms were located with the direct-methods program MULTAN.[20] Hydrogen positions were calculated and not refined. More detailed information on refinement and parameters is given in the supplementary material.

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Supplementary Material Available: Summary of crystal data, tables of bond lengths and angles, and a listing of positional and equivalent isotropic and anisotropic temperature factors derived from crystallographic analysis of 8, 19, and 25 (18 pages). Ordering information is given on any current masthead page.

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