

Oxygenation of Aromatic Vinyl Ethers. A Noticeable Formation of Epoxides and Reaction Mechanism

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cis- β -Alkoxystyrenes such as *cis*- β -methoxy-, *cis*- β -ethoxy-, and *cis*- β -isopropoxystyrene were autoxidized as neat at room temperature in the dark even in the absence of any radical generator. UV-irradiation and the use of a radical generator facilitated the oxygenation of these olefins. These oxidations afforded the corresponding epoxides or their derivatives in considerable yields as well as carbonyl compounds resulting from oxidative cleavage of the double bonds. The mechanisms for these oxidations are proposed to involve free-radical chain pathways and charge-transfer complexes between the olefins and oxygen which play an important role in the initiation steps.

Autoxidation of olefins usually affords allylic hydroperoxides, carbonyl compounds formed by cleavage of the double bond, and the remaining polyperoxide residues, but scarcely gives epoxides.¹⁻⁴ Dye-sensitized photooxygenation of olefins affords, through singlet oxygen mechanism, hydroperoxides, endoperoxides, and dioxetanes which are often converted into carbonyl compounds, and the formation of epoxides is also only a minor path.⁵ However, Shimizu and Bartlett showed that epoxides arose efficiently when biacetyl or benzil was employed as a sensitizer on photooxidation of olefins.⁶ Previously we observed that direct irradiation of β -alkoxystyrenes under oxygen led to an oxidative cleavage of the double bond *via* a different pathway from singlet oxygen mechanism.⁷ During the course of the investigation, we have found the following noticeable facts: (1) *cis*- β -methoxystyrene (**1a**) as neat or in concentrated solution is sensitive to oxygen at room temperature in the dark even in the absence of any radical generator, while this olefin is not reactive with oxygen in dilute solution at room temperature or as neat at 0 °C in the dark; (2) UV-irradiation of the olefin without dye sensitizer accelerated the oxygenation in dilute solution at room temperature and also as neat at 0 °C; (3) a radical generator effected the autoxidation of the olefin at 50 °C; (4) all these ways of oxygenation of the olefin led to nearly the same distribution of the products, the corresponding epoxide and carbonyl compounds (benzaldehyde and methyl formate). This work was undertaken to investigate the nature of these oxygenations under photochemical and/or thermal conditions using alkoxystyrenes (**1**), 2-methoxy-1,1-diphenylethylene (**2**), 2-phenylpropene (**3**), and 2-methyl-1,1-diphenylpropene (**4**) as substrates. The results are described in detail and the possible reaction mechanism is discussed below.

Results and Discussion

Oxidation Products. 1) *Autoxidation in the Absence of Radical Generator in the Dark:* *cis*- β -Methoxy- (**1a**), *cis*- β -ethoxy- (**1b**), and *cis*- β -isopropoxy-styrene (**1c**) were found to be sensitive to molecular oxygen as neat and in concentrated solution (*ca.* 50 vol%) even in the absence of any radical generator at room temperature in the dark. Thus, a highly purified specimen of neat **1a** (432 mg, 3.16 mmol) was stirred overnight under

oxygen atmosphere at room temperature in the dark until **1a** was almost consumed. The NMR, GLPC, and chemical examination of the reaction mixture showed the formation of *trans*-2-methoxy-3-phenyl-oxirane (**5a**, 28%), benzaldehyde (47%), and methyl formate (8%). Likewise, **1b** and **1c** were autoxidized to benzaldehyde and alkyl formates; however, the corresponding epoxides and their isolable derivatives were not detected among the products. The results are summarized in Table 1. At 0 °C the olefins were not oxidized. When dissolved in solvents such as benzene, acetonitrile, and methanol (*ca.* 0.5 mol/dm³), the olefins were scarcely consumed by stirring under oxygen at room temperature for several hours.

2) *Photooxidation:* To conduct oxygenation effectively, **1a**, **1b**, **1c**, 2-methoxy-1,1-diphenylethylene (**2**), 2-phenylpropene (**3**), and 2-methyl-1,1-diphenylpropene (**4**) were irradiated as neat or in solution under oxygen atmosphere with a high pressure mercury lamp, and the products were determined as summarized in Table 2.

Direct irradiation of **1a**, **1b**, and **1c** under oxygen afforded the corresponding epoxides or their derivatives depending upon the substituents and the solvents employed in addition to benzaldehyde and methyl, ethyl, and isopropyl formate, respectively. In a typical run employing a neat olefin, **1a** (100 mg, 0.75 mmol) was irradiated in a stream of oxygen for 4 h with a 400-W high pressure mercury lamp through a Pyrex wall at room temperature until **1a** was almost completely consumed as revealed by NMR spectra. The NMR, GLPC, and chemical examination of the reaction mixture showed the formation of benzaldehyde (47%), benzoic acid (6%), and *trans*-2-methoxy-3-phenyl-oxirane (**5a**, 9%). The epoxide was isolated by pre-

TABLE 1. YIELD OF AUTOXIDATION PRODUCTS OF *cis*- β -ALKOXYSTYRENES IN THE DARK AT ROOM TEMPERATURE^{a,b} (mol/mol olefin consumed)

Alkoxystyrene	Products		
	HCO ₂ R	PhCHO	PhCH-CHOR \O/
PhCH=CHOMe	0.08 ^{b)}	0.47	0.28 ^{b)}
PhCH=CHOEt	0.35 ^{c)}	0.57	—
PhCH=CHO ^t Pr	0.37 ^{d)}	0.50	—

a) No radical initiator was used. b) R = Me. c) R = Et. d) R = ⁱPr.

TABLE 2. YIELD OF OXYGENATION PRODUCTS ON IRRADIATION OF ALKOXYSTYRENES AND ALKYLSTYRENES AT ROOM TEMPERATURE (mol/mol olefin consumed)

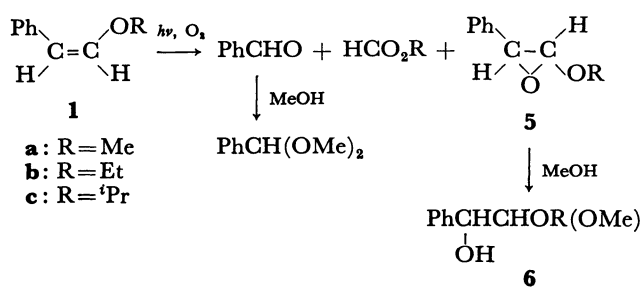
Substrate	Solvent	Products		
		PhCHO	PhCH-CHOR \O/	PhCH-CHOR OH OMe
<i>cis</i> -PhCH=CHOMe	—	0.53 ^{a)}	0.09 ^{a)}	
	PhH	0.13 ^{a)}		
	MeCN	0.20 ^{a)}		
	MeOH	0.55 ^{d)}		0.27 ^{a)}
<i>cis</i> -PhCH=CHOEt	—	0.55 ^{a)}		
	PhH	0.55 ^{a)}		
	MeCN	0.55 ^{a)}		
	MeOH	0.42 ^{d)}		0.38 ^{b)}
<i>cis</i> -PhCH=CHO ⁱ Pr	—	0.87 ^{a)}		
	PhH	0.74 ^{a)}		
	MeCN	0.67 ^{a)}		
	MeOH	0.51 ^{d)}		0.38 ^{b)}
Ph ₂ C=CHOMe	—	Ph ₂ CO	Ph ₂ C-CHOMe \O/	Ph ₂ C-CH(OMe) ₂ OH
	PhH	0.10	0.35	
	MeCN	0.10	0.36	
	MeOH	0.02		0.57
PhMeC=CH ₂ ^{a)}	—	PhRCO	PhRC-CR' ₂ \O/	
	—	0.60 ^{a)}	0.05 ^{a,e)}	
Ph ₂ C=CMe ₂ ^{b)}	—	0.36 ^{f)}	0.15 ^{f,h)}	

a) Conversion, 18%. b) Conversion, 29%. c) A sum of benzaldehyde and benzoic acid. d) A sum of benzaldehyde and its dimethyl acetal. e) R=Me. f) R=Ph. g) R'=H. h) R'=Me. i) R=Et. j) R=ⁱPr.

parative GLPC and its *trans*-configuration was confirmed by its NMR spectrum.⁹⁾ On treatment of the reaction mixture with deuterated water, NMR signals due to the epoxide instantaneously disappeared because of its high sensitivity to moisture.

A control experiment showed that an authentic specimen of the *trans*-epoxide was recovered unchanged after being left under the reaction conditions, which rules out the possibility that benzaldehyde and the formate ester would be produced through decomposition of the epoxide formed as an intermediate. Photooxidation of **1b** and **1c** likewise afforded the corresponding oxidative cleavage products; however, the corresponding epoxides and their isolable derivatives were not detected among the reaction products (Table 2).

Irradiation of **1a**, **1b**, and **1c** as neat under oxygen at 0 °C also afforded benzaldehyde and the corresponding alkyl formates. Epoxide **5a** was also formed in the case of **1a**. The product distributions were very similar to those in the reaction at room temperature.



It is noticeable that the photooxidation of **1a**, **1b**, and **1c** in methanol gave 2-alkoxy-2-methoxy-1-phenylethanol (**6**) in considerable yields in addition to the cleavage products, benzaldehyde and its dimethyl acetal (Table 2). The resulting 2,2-dimethoxy- (**6a**), 2-ethoxy-2-methoxy- (**6b**), and 2-isopropoxy-2-methoxy-1-phenylethanol (**6c**) were isolated from the reaction mixtures by preparative GLPC and identified by NMR spectra. Formation of these products is reasonably accounted for by polar addition of the solvent methanol to the epoxides once formed as intermediates under the reaction conditions as confirmed by irradiation of **5a** in methanol under oxygen atmosphere yielding **6a**. These results indicate that the photooxidation of **1b** and **1c** also gives the corresponding epoxides which nevertheless seem too unstable to be isolated. Their instability is in keeping with the facts that these epoxides could not be prepared under similar conditions to those employed for the preparation of **5a**, and that **5a** was extremely sensitive to water.

The use of benzene and acetonitrile as solvent on photooxidation of **1a**, **1b**, and **1c** gave only the cleavage products regardless of the alkoxy substituents and the polarity of the solvents employed (Table 2).

Likewise, photooxidation of **2** in benzene and acetonitrile gave the corresponding epoxide (**7**) together with the oxidative cleavage products, benzophenone and methyl formate. In methanol 2,2-dimethoxy-1,1-diphenylethanol (**8**) was obtained instead of the epoxide (Table 2). The epoxide (**7**) and alcohol (**8**) were isolated

In the present work, however, it is remarkable that

a) Values evaluated from the equation by Farrell and Newton.²⁰⁾ b) Adiabatic values from photoelectron spectra of *cis*- β -methoxystyrene²¹⁾ and styrene.²²⁾

proposed by Farrel and Newton²⁰) for substituted benzene/TCNE complexes are used, the relationship is expressed by

$$h\nu_{CT} = 0.82I_D - 4.28 \text{ (eV)}.$$

This relationship leads to a much lower value of the ionization potential for **1a**, 7.70 eV, than for styrene, 8.34 eV,¹⁹) which are in reasonable agreement with the values observed by photoelectron spectroscopy, 7.54 for **1a**²¹) and 8.40 eV for styrene.²²) This result is in keeping with a fact that **1a** exhibits a much lower oxidation potential (1.00 V) than styrene (>1.95 V).^{21,23})

As described above, **1a** forms the charge-transfer complex with oxygen more efficiently than styrene. Therefore, it is not unreasonable to suppose that the charge-transfer complex plays an important role in generating free radicals both thermally and on ultraviolet irradiation to initiate the radical chain oxidation.²⁴)

Experimental

The IR and UV spectra were recorded on a Hitachi 215 infrared spectrometer and a JASCO UVIDEK-1 spectrophotometer, respectively. The NMR spectra were recorded on a Hitachi R-24 and a JEOL JNM-MH-100 spectrometer. Gas-liquid phase chromatographic analysis was performed on a Hitachi 163 and a Shimadzu GC-4CM-PF gas chromatograph equipped with a flame ionization detector, and a Hitachi 023 gas chromatograph was used for preparative purposes.

Materials. *cis*- β -Methoxystyrene (**1a**),²⁵) *cis*- β -ethoxystyrene (**1b**),²⁶) and *cis*- β -isopropoxystyrene (**1c**) were prepared by heating phenylacetylene with potassium hydroxide in the corresponding alcohols.

cis- β -Isopropoxystyrene (**1c**), bp 58 °C/2 Torr (1 Torr = 133.322 Pa); IR (liq): 2975, 1650 cm⁻¹; NMR (CCl₄): δ 1.31 (d, 6H), 3.94 (septet, 1H), 5.06 (d, J = 7.0 Hz, 1H), 6.04 (d, J = 7.0 Hz, 1H), and 6.9–7.5 (m, 5H); Found: C, 81.05; H, 8.64%. Calcd for C₁₁H₁₄O: C, 81.43; H, 8.69%.

2-Methoxy-1,1-diphenylethylene (**2**)²⁷) and 2-methyl-1,1-diphenylpropene (**4**)²⁸) were prepared by the Wittig reactions employing benzophenone. *trans*-2-Methoxy-3-phenyloxirane (**5a**)²⁹) and 3-methoxy-2,2-diphenyloxirane (**7**) were prepared from reactions of 2-chloro-2-phenylethanal and 2-chloro-2,2-diphenylethanal with sodium methoxide, respectively, according to the method reported by Kirrmann *et al.*²⁹) The latter epoxide was irradiated in methanol to give 2,2-dimethoxy-1,1-diphenylethanol (**8**).

3-Methoxy-2,2-diphenyloxirane (**7**), mp 49–51 °C; NMR (CCl₄): δ 3.30 (s, 3H), 4.55 (s, 1H), and 7.1–7.3 (m, 10H).

2,2-Dimethoxy-1,1-diphenylethanol (**8**), bp 140 °C/1 Torr; NMR (CCl₄): δ 2.91 (s, 1H), 3.25 (s, 6H), 4.48 (s, 1H), and 7.1–7.4 (m, 10H); Found: C, 74.56; H, 7.05%. Calcd for C₁₆H₁₈O₃: C, 74.39; H, 7.02%.

On treatment of 2-chloro-2-phenylethanal with sodium ethoxide and sodium isopropoxide, epoxides could not be isolated. Epoxidation of **1b** and **1c** with *m*-chloroperoxybenzoic acid³⁰) or *N*-bromosuccinimide/sodium hydroxide³⁰) was also unsuccessful. 2-Methyl-2-phenyloxirane (**9**)³¹) and 2,2-dimethyl-3,3-diphenyloxirane (**10**)³²) were prepared by epoxidation of 2-phenylpropene (**3**) and **4** with *m*-chloroperoxybenzoic acid, respectively.

Photooxidation of Olefins. Typical procedures are described below for *cis*- β -methoxystyrene (**1a**).

Without Solvent. Liquid **1a** (100 mg, 0.75 mmol) in a

Pyrex tube was irradiated in an oxygen stream with a 400-W high pressure mercury lamp for 4 h at room temperature. GLPC and NMR analyses of the reaction mixture showed almost complete consumption of **1a** and the formation of benzaldehyde (47%), benzoic acid (6%), methyl formate, and *trans*-2-methoxy-3-phenyloxirane (**5a**, 9%). The product distribution was determined by GLPC using internal standards and authentic reference materials on Polypropylene glycol 4025 (5%) and diethylene glycol succinate polyester-H₃PO₄ (5%) columns at 130 and 180 °C, respectively. The epoxide was isolated from the reaction mixture by preparative GLPC on polyethylene glycol (10%) at 150 °C and identified by comparing its IR and NMR spectra with those of an authentic sample. On addition of D₂O to the reaction mixture, signals due to the epoxide disappeared instantaneously in the NMR spectrum.

Liquid **1a** (134 mg, 1 mmol) was irradiated similarly under oxygen atmosphere at 0 °C for 4 h. GLPC and NMR analyses of the reaction mixture showed the formation of benzaldehyde, epoxide **5a**, and methyl formate. The product distribution was found to be very similar to that in the reaction at room temperature.

In Methanol. A solution of **1a** (56 mg, 0.42 mmol) in methanol (1 ml) was irradiated in a Pyrex tube under oxygen atmosphere with a 400-W high pressure mercury lamp for 4 h at room temperature. After almost all the solvent was removed by rotary evaporation, the reaction mixture was subjected to GLPC analysis, which revealed the formation of benzaldehyde (trace), dimethoxyphenylmethane (51%), benzoic acid (5%), and 2,2-dimethoxy-1-phenylethanol (**6a**, 27%). The product **6a** was isolated from the reaction mixture by preparative GLPC, and identified by comparing its IR and NMR spectra with those of an authentic sample,³³) which was prepared by irradiation of **5a** in methanol; NMR (CCl₄): δ 2.50 (s, 1H, exchangeable with D₂O), 3.15 (s, 3H), 4.05 (d, J = 6 Hz, 1H), 4.60 (d, J = 6 Hz, 1H), and 7.0–7.2 (m, 5H).

2-Ethoxy-2-methoxy-1-phenylethanol (**6b**) and 2-isopropoxy-2-methoxy-1-phenylethanol (**6c**) were similarly isolated from the photooxidation mixtures of *cis*- β -ethoxystyrene (**1b**) and *cis*- β -isopropoxystyrene (**1c**) in methanol, respectively. The structures were determined by comparing their NMR spectra with that of **6a**. The NMR spectra showed that each of the ethanols consisted of two stereoisomers.

2-Ethoxy-2-methoxy-1-phenylethanol (**6b**), bp 76 °C/1 Torr; NMR (CCl₄): δ 0.92 and 1.13 (t, J = 6 Hz, 3H), 3.29 and 3.09 (s, 3H), 3.3–3.8 (m, 2H), 4.09 (broad s, 1H), 4.18 (d, J = 6.5 Hz, 1H), 4.47 (d, J = 6.5 Hz, 1H), and 7.0–7.4 (m, 5H); Found: C, 67.00; H, 7.88%. Calcd for C₁₁H₁₆O₃: C, 67.32; H, 8.21%.

2-Isopropoxy-2-methoxy-1-phenylethanol (**6c**), bp 84 °C/1 Torr; NMR (CCl₄): δ 0.65–1.25 (m, 6H), 3.0 (broad s, 1H), 3.11 and 3.36 (s, 3H), 3.50 and 3.82 (m, 1H), 4.25 (d, J = 6 Hz, 1H), 4.43 (d, J = 6 Hz, 1H), and 7.0–7.4 (m, 5H); Found: C, 68.41; H, 8.61%. Calcd for C₁₂H₁₈O₃: C, 68.54; H, 8.62%.

2,2-Dimethoxy-1,1-diphenylethanol (**8**) was isolated similarly from the reaction mixture of 2-methoxy-1,1-diphenylethylene (**2**) in methanol. The structure was determined by comparing its NMR spectrum with that of an authentic sample.

In Benzene and Acetonitrile. Photooxidation was performed in a similar way to that in methanol. The reaction mixtures were, after rotary evaporation, analyzed quantitatively by GLPC.

3-Methoxy-2,2-diphenyloxirane (**7**) was isolated from the reaction mixture in benzene by preparative GLPC and

identified by comparison of its IR and NMR spectra with those of an authentic sample.

Autoxidation of cis- β -Methoxystyrene (1a) in the Dark without Initiator. Neat **1a** (432 mg, 3.16 mmol) was stirred overnight at room temperature under oxygen atmosphere in the dark. GLPC analysis of the reaction mixture revealed almost complete consumption of **1a** and the formation of benzaldehyde (47%), benzoic acid, methyl formate (8%), and **5a** (28%).

A solution of **1a** (134 mg, 1.0 mmol) in methanol (2 ml) was stirred for 10 h under oxygen at room temperature in the dark. GLPC analysis of the reaction mixture showed a quite low consumption of **1a** and the formation of trace amounts of benzaldehyde and **6a**.

Effect of Oxygen Pressure on the Product Yields in Autoxidation of 1a. Neat **1a** (134 mg, 1.0 mmol) containing azobisisobutyronitrile (6.8 mg, 0.04 mmol) was stirred at 50 °C for 5.5 h in the dark under an atmosphere of varying partial pressures of oxygen (760–40 Torr) diluted with nitrogen (760 Torr in the total pressure). The yields of benzaldehyde and **5a** were determined by GLPC as shown in Fig. 1.

Effects of Hydroquinone, Diazabicyclo[2.2.2]octane (DABCO), and Olefins on the Oxygenations of β -Alkoxytyrenes. As an example, a solution of **1a** (134 mg, 1.0 mmol) and hydroquinone (11 mg, 0.1 mmol) in benzene (2 ml) was irradiated under oxygen atmosphere for 6 h at room temperature in a Pyrex tube with a 400-W high pressure mercury lamp. No consumption of **1a** was confirmed by GLPC analysis.

Neat **1a** (134 mg, 1.0 mmol) was stirred overnight with hydroquinone (11 mg, 0.1 mmol) at room temperature under oxygen atmosphere in the dark. GLPC analysis of the sample revealed almost no consumption of **1a** and the formation of no oxidation products. Neat **1b** and **1c** were also not consumed under similar conditions.

Neat **1a** (134 mg, 1.0 mmol) was similarly stirred with DABCO (11 mg, 0.1 mmol) instead of hydroquinone under oxygen. The olefin was almost completely recovered as revealed by GLPC analysis.

Neat **1a** (134 mg, 1.0 mmol) was stirred overnight with azobisisobutyronitrile (16 mg, 0.1 mmol) and DABCO (11 mg, 0.1 mmol) under oxygen at 50 °C. GLPC analysis of the sample showed almost no consumption of **1a**.

Neat **1a** (134 mg, 1.0 mmol) was stirred for 6 h with 2,3-dimethyl-2-butene or 1-methylcyclohexene (0.5 mmol) under oxygen at room temperature in the dark. NMR and GLPC analyses of the reaction mixture showed the formation of benzaldehyde, methyl formate, and **5a** and almost no consumption of the butene or the cyclohexene.

Charge-Transfer (C-T) Absorption Spectra of Styrene Derivatives. C-T Spectra with Molecular Oxygen. Samples of **1a** (neat or 0.3 mol/dm³ in cyclohexane) were placed in a sample cell and a reference cell, and a stream of oxygen was passed for several minutes through the sample in the sample cell. Spectra were measured at 0 and 23 °C. Immediately after a spectrum was recorded, argon was passed through the sample and a spectrum was again measured. The band observed under oxygen atmosphere completely disappeared at 0 °C by argon bubbling; however, at 23 °C the band remained at one-fourth of the intensity under oxygen atmosphere.

C-T Spectra with Tetracyanoethylene (TCNE). Solutions of the C-T complexes were prepared immediately before measurements by mixing dichloromethane solutions of TCNE (0.01 mol/dm³) with solutions of **1a** (0.23–0.34 mol/dm³) or styrene (3.7–8.0 mol/dm³) in the same solvent. The spectra were measured at 23 °C by a conventional method using a Hitachi 200-20 spectrophotometer. In a reference cell was

placed a dichloromethane solution of a donor at the same concentration as in a sample cell.

References

- 1) F. R. Mayo, A. A. Miller, and G. A. Russell, *J. Am. Chem. Soc.*, **80**, 2500 (1958); F. R. Mayo, *Acc. Chem. Res.*, **1**, 193 (1968), and references cited therein. Some olefins such as cyclooctene²⁾ and 2,4,4-trimethyl-1-pentene^{3,4)} were reported to give the corresponding epoxides in exceptionally high yields.
- 2) D. E. Van Sickle, F. R. Mayo, and R. M. Arluck, *J. Am. Chem. Soc.*, **87**, 4824 (1965).
- 3) E. J. Gasson, A. F. Millidge, G. R. Primavesi, W. Webster, and D. P. Young, *J. Chem. Soc.*, **1954**, 2161.
- 4) F. R. Mayo, *J. Am. Chem. Soc.*, **80**, 2497 (1958).
- 5) "Singlet Oxygen," ed by H. H. Wasserman and R. W. Murray, Academic Press, New York, N. Y. (1979); M. Matsumoto and K. Kondo, *J. Synth. Org. Chem.*, **35**, 188 (1977); C. W. Jefford and A. F. Boschung, *Helv. Chim. Acta*, **57**, 2257 (1974).
- 6) N. Shimizu and P. D. Bartlett, *J. Am. Chem. Soc.*, **98**, 4193 (1976). Also see, P. D. Bartlett and M. E. Landis, *ibid.*, **99**, 3033 (1977).
- 7) H. Sakuragi, K. Tokumaru, and O. Simamura, Symposium on Photochemistry, Tokyo (1967). Abstracts of Papers, p. 83.
- 8) J. M. Lehn and J. J. Riehl, *Mol. Phys.*, **8**, 33 (1964).
- 9) Autoxidation of **3** was reported to afford acetophenone and an epoxide: H. Hock and M. Siebert, *Chem. Ber.*, **87**, 546 (1954); F. R. Mayo and A. A. Miller, *J. Am. Chem. Soc.*, **80**, 2480 (1958).
- 10) C. S. Foote, "Singlet Oxygen," ed by H. H. Wasserman and R. W. Murray, Academic Press, New York, N. Y. (1979), p. 139.
- 11) G. Rio and J. Berthelot, *Bull. Soc. Chim. Fr.*, **1969**, 3609.
- 12) D. Lerdal and C. S. Foote, *Tetrahedron Lett.*, **1978**, 3227. Also see, M. Matsumoto, S. Dobashi, and K. Kondo, *ibid.*, **1977**, 2329; **1977**, 3361.
- 13) C. S. Foote, S. Mazur, P. A. Burns, and D. Lerdal, *J. Am. Chem. Soc.*, **95**, 586 (1973).
- 14) F. R. Mayo, *J. Am. Chem. Soc.*, **80**, 2465 (1958).
- 15) D. F. Evans, *J. Chem. Soc.*, **1953**, 345.
- 16) H. Tsubomura and R. S. Mulliken, *J. Am. Chem. Soc.*, **82**, 5966 (1960).
- 17) V. I. Stenberg, R. D. Olson, C. T. Wang, and N. Kulevsky, *J. Org. Chem.*, **32**, 3227 (1967); V. I. Stenberg, C. T. Wang, and N. Kulevsky, *ibid.*, **35**, 1774 (1970).
- 18) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949); L. J. Andrews and R. M. Keefer, *ibid.*, **74**, 458 (1952); R. E. Merrifield and W. D. Phillips, *ibid.*, **80**, 2778 (1958).
- 19) A. R. Cooper, C. W. P. Crowne, and P. G. Farrell, *Trans. Faraday Soc.*, **62**, 18 (1966).
- 20) P. G. Farrell and J. Newton, *J. Phys. Chem.*, **69**, 3506 (1965).
- 21) T. Kanno, T. Oguchi, H. Sakuragi, K. Tokumaru, and T. Kobayashi, *Denki Kagaku*, **49**, 134 (1981).
- 22) J. P. Maier and D. W. Turner, *J. Chem. Soc., Faraday Trans. 2*, **69**, 196 (1973).
- 23) The oxidation potentials were determined by means of cyclic voltammetry in acetonitrile using a Ag/Ag⁺ (0.1 mol/dm³) electrode as a reference electrode and 0.1 mol/dm³ tetraethylammonium perchlorate as supporting electrolyte.
- 24) Participation of the charge-transfer complexes of ethers with oxygen was described to initiate their photochemical oxidation.¹⁷⁾

- 25) K. Auwers, *Chem. Ber.*, **44**, 3514 (1911).
26) J. U. Nef, *Justus Liebigs Ann. Chem.*, **308**, 264 (1899).
27) G. Wittig and M. Schlosser, *Chem. Ber.*, **94**, 1373 (1961).
28) A. Brodhag and C. R. Hauser, *J. Am. Chem. Soc.*, **77**, 3024 (1955).
29) A. Kirrmann, R. Muths, and J.-J. Riehl, *Bull. Soc. Chim. Fr.*, **1958**, 1469.
30) R. Filler, B. R. Camara, and S. M. Naqvi, *J. Am. Chem. Soc.*, **81**, 658 (1959).
31) S. Danilow and E. V. Danilowa, *Chem. Ber.*, **60**, 1050 (1927).
32) H. Böhme, *Org. Synth.*, Coll. Vol. III, 619 (1955).
33) S. H. Pine and J. Cheney, *J. Org. Chem.*, **40**, 870 (1975).
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