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

Tatsuya Kanno, Motoyuki Hisaoka, Hirochika Sakuragi,* and Katsumi Tokumaru
Department of Chemistry, The University of Tsukuba, Sakura-mura, Ibaraki 305

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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.

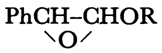
Results and Discussion

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-phenyloxirane (**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/dm^3), 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-phenyloxirane (**5a**, 9%). The epoxide was isolated by pre-

Table 1. Yield of autoxidation products of *cis*-β-alkoxystyrenes in the dark at room temperature$^{a)}$ (mol/mol olefin consumed)

Alkoxystyrene	Products		
	HCO_2R	PhCHO	 $\mathrm{PhCH{-}CHOR}$ (O)
PhCH=CHOMe	0.08$^{b)}$	0.47	0.28$^{b)}$
PhCH=CHOEt	0.35$^{c)}$	0.57	—
PhCH=CHO^{i}Pr	0.37$^{d)}$	0.50	—

a) No radical initiator was used. b) R=Me. c) R=Et. d) R=^{i}Pr.

Table 2. Yield of oxygenation products on irradiation of alkoxystyrenes and alkylstyrenes at room temperature (mol/mol olefin consumed)

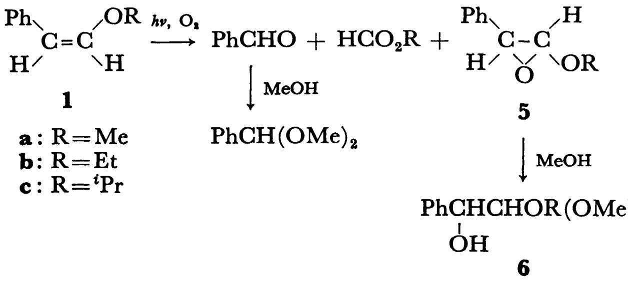
Substrate	Solvent	Products		
		PhCHO	$\underset{\diagdown O \diagup}{\mathrm{PhCH{-}CHOR}}$	$\mathrm{Ph\underset{OH}{CH}{-}\underset{OMe}{C}HOR}$
cis-PhCH=CHOMe	—	0.53[c)]	0.09[e)]	
	PhH	0.13[c)]		
	MeCN	0.20[c)]		
	MeOH	0.55[d)]		0.27[e)]
cis-PhCH=CHOEt	—	0.55[c)]		
	PhH	0.55[c)]		
	MeCN	0.55[c)]		
	MeOH	0.42[d)]		0.38[i)]
cis-PhCH=CHO^{i}Pr	—	0.87[c)]		
	PhH	0.74[c)]		
	MeCN	0.67[c)]		
	MeOH	0.51[d)]		0.38[j)]
		$\mathrm{Ph_2CO}$	$\underset{\diagdown O \diagup}{\mathrm{Ph_2C{-\!\!-}CHOMe}}$	$\mathrm{Ph_2\underset{OH}{C}{-}CH(OMe)_2}$
$\mathrm{Ph_2C{=}CHOMe}$	PhH	0.10	0.35	
	MeCN	0.10	0.36	
	MeOH	0.02		0.57
		PhRCO	$\underset{\diagdown O \diagup}{\mathrm{PhRC{-\!\!-}CR'_2}}$	
$\mathrm{PhMeC{=}CH_2}$[a)]	—	0.60[e)]	0.05[e,g)]	
$\mathrm{Ph_2C{=}CMe_2}$[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=^{i}Pr.

parative GLPC and its *trans*-configuration was confirmed by its NMR spectrum.[8)] 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).

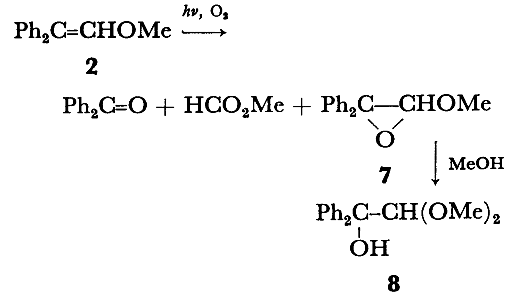
Irradiation of **1a**, **1b**, and **1c** as neat under oxygen at 0 °C also afforded benzaldehyde and the corresponding alkyl formates. Epoxide **5a** was also formed in the case of **1a**. The product distributions were very similar to those in the reaction at room temperature.



It is noticeable that the photooxidation of **1a**, **1b**, and **1c** in methanol gave 2-alkoxy-2-methoxy-1-phenylethanols (**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 alkoxyl substituents and the polarity of the solvents employed (Table 2).

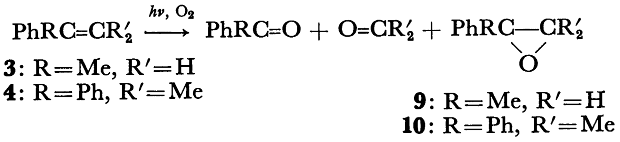
Likewise, photooxidation of **2** in benzene and acetonitrile gave the corresponding epoxide (**7**) together with the oxidative cleavage products, benzophenone and methyl formate. In methanol 2,2-dimethoxy-1,1-diphenylethanol (**8**) was obtained instead of the epoxide (Table 2). The epoxide (**7**) and alcohol (**8**) were isolated by preparative GLPC and characterized by comparison of their IR and NMR spectra with those of authentic specimens.



$$Ph_2C{=}CHOMe \xrightarrow{h\nu,\ O_2} Ph_2C{=}O + HCO_2Me + Ph_2C\overset{O}{-}CHOMe \xrightarrow{MeOH} Ph_2C(OH){-}CH(OMe)_2$$

2, 7, 8

Photooxidation of 2-phenylpropene (**3**)[9] and 2-methyl-1,1-diphenylpropene (**4**) led to the formation of the oxidative cleavage products and the corresponding epoxides (Table 2), although their oxidation proceeded much more slowly than that of **1**.



$$PhRC{=}CR'_2 \xrightarrow{h\nu,\ O_2} PhRC{=}O + O{=}CR'_2 + PhRC\overset{O}{-}CR'_2$$

3: R=Me, R'=H
4: R=Ph, R'=Me
9: R=Me, R'=H
10: R=Ph, R'=Me

3) Autoxidation in the Presence of Radical Generator: To investigate the mechanism for the oxygenation of these olefins their autoxidation with a radical initiator was carried out. Autoxidation of neat β-alkoxystyrenes (**1**) with azobisisobutyronitrile (AIBN) as an initiator at 50 °C afforded the same products as did the photooxidation; benzaldehyde and alkyl formates were produced along with epoxide **5a** from **1a**. To examine the effect of oxygen pressure on the product yields autoxidation of **1a** (1 mmol) containing AIBN (0.02 mmol) was carried out at 50 °C for 5.5 h under varying partial pressures of oxygen diluted with nitrogen in a total pressure of 760 Torr (1 Torr=133.322 Pa). The yields of benzaldehyde and the epoxide were determined by GLPC as depicted in Fig. 1, which shows that the yield of the epoxide increased with decreasing oxygen pressure and that the maximum yield (about 60%) was attained at nearly 40 Torr of the partial pressure of oxygen.

Mechanisms for Oxygenations. When **1**'s were stirred as neat under oxygen in the presence of hydroquinone, the well-known radical inhibitor, at room temperature, the olefins were recovered unchanged. Hydroquinone also inhibited the photooxygenation of **1**'s as neat or in benzene solution. Addition of 1,4-diazabicyclo[2.2.2]octane (DABCO) also inhibited autoxidation of **1a** at room temperature without a radical generator and at 50 °C in the presence of AIBN. Since it has been shown that oxidation by singlet oxygen is inhibited by DABCO but usually not by hydroquinone,[10] these results indicate that free singlet oxygen plays no role in the present oxygenation, and the production of the *trans*-epoxide from **1a** requires a stepwise mechanism by way of a freely rotating intermediate.

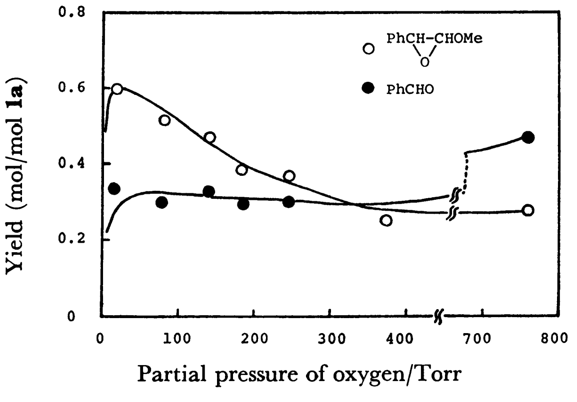
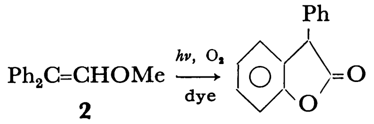


Fig. 1. Effect of oxygen pressure on the yield of autoxidation products of *cis*-β-methoxystyrene (**1a**).

Actually, the products from the oxygenations of **1**'s are different from those resulting from their dye-sensitized photooxygenation, which gave neither epoxides nor their derivatives. Thus, Methylene Blue-sensitized photooxygenation of *trans*-β-ethoxystyrene in dichloromethane was reported to give benzaldehyde and ethyl formate,[11] and recently it was demonstrated that the use of diacenaphtho[1,2-*b* : 1′,2′-*d*]thiophene as sensitizer on photooxygenation of *cis*- and *trans*-β-methoxystyrene at −78 °C led to 1,4-cycloaddition of singlet oxygen across the side chain β-carbon and the *ortho*-carbon of the aromatic ring, and that the *cis*-isomer reacted much more rapidly than the *trans*-isomer under the same conditions.[12] Also, the direct photooxygenation of **2** gave the completely different products from 3-phenyl-2,3-dihydrobenzofuran-2-one (**11**) which was reported to arise on dye-sensitized photooxygenation of **2** through 1,4-cycloaddition of singlet oxygen.[13]



2, 11

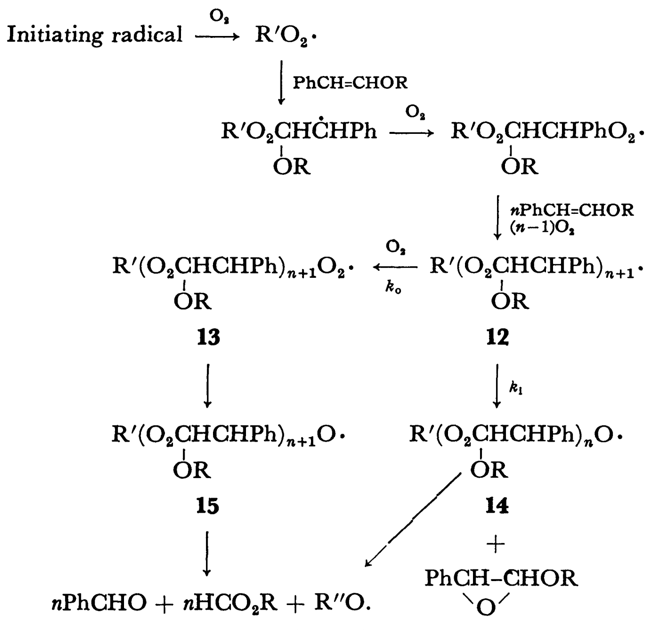
Furthermore, treatment of a mixture of **1a** and 1-methylcyclohexene or 2,3-dimethyl-2-butene, which is known to be highly susceptible to singlet oxygen, with oxygen in the absence of an initiator in the dark at room temperature resulted in exclusive oxidation of **1a** accompanied by nearly quantitative recovery of the added olefin.

These findings, therefore, strongly indicate that the direct photooxygenation of **1**'s as well as their autoxidation in the presence and absence of an initiator involves triplet molecular oxygen without intervention of singlet oxygen.

The effect of oxygen pressure on the yield of the epoxide, combined with the product distribution and the effects of the additives, strongly suggests that the autoxidation of the present olefins in the dark proceeds through a mechanism similar to that proposed previously by Mayo for autoxidation of styrene and related olefins.[1] In Mayo's mechanism, alternating addition of styrene molecules and molecular oxygen results in copolymeric radicals, which finally either afford polymeric peroxides or undergo scission to benzaldehyde, formaldehyde, and phenyloxirane (*cf.* Scheme 1); the yields of these products are changed with the partial pressure of oxygen.

In the present work, however, it is remarkable that epoxide **5a** was produced in a moderate yield, for example, *ca.* 30%, even at 760 Torr oxygen pressure, and the maximum yield, *ca.* 60%, was attained at a lower oxygen pressure, *ca.* 40 Torr. This is in contrast to the autoxidation of styrene which afforded phenyloxirane in a very low yield (1%) at 760 Torr oxygen pressure and increased its yield to the maximum value (27%) at a very low partial pressure of oxygen (1 Torr).[14)]

Comparison of the present photooxygenation with the autoxidation in the product distribution and the behavior toward inhibitors mentioned above indicates that the photooxygenation mechanism is quite similar to that of the autoxidation except for the initiation steps. According to Scheme 1 described below, the intermediate benzylic radicals (**12**) will add to oxygen to give peroxyl radicals (**13**) (rate constant: k_o) or undergo intramolecular substitution on the peroxide linkage to afford the epoxide and alkoxyl radicals (**14**) (rate constant: k_i). Peroxyl radicals **13** give, through bimolecular interaction, alkoxyl radicals (**15**). Alkoxyl radicals **14** and **15** undergo scission into carbonyl compounds or again react with the olefin to give the benzylic radicals.



Scheme 1.

No production of polymeric peroxides together with efficient production of the epoxide in the oxidation of **1a** shows that benzylic radicals **12** resulting from **1a**, compared with the corresponding benzylic radicals arising from styrene, more facilely undergo the intramolecular substitution on the peroxide linkage in preference to growing up to polymeric matters.

Formation of Complexes between the Olefins and Oxygen. In order to get insight into the mechanism for the initiation of the free-radical chain oxidation of the alkoxystyrenes, particularly in the absence of any initiator, spectroscopic examination was carried out for the possible formation of charge-transfer complexes between these olefins and oxygen in view of the fact that several aromatic compounds form charge-transfer complexes with oxygen.[15–17)] When a stream of oxygen was passed into a cyclohexane solution of **1a** at 0 °C, a new broad band appeared at 305—400 nm with the maximum at 307 nm. When argon was bubbled through the solution, this new band completely disappeared. When the measurements were carried out at 23 °C, the new band decreased in intensity to one-fourth by bubbling with argon. These facts indicate reversible formation of a charge-transfer complex between **1a** and oxygen. Styrene was reported to develop a similar absorption band, when a neat sample was saturated with oxygen at atmospheric pressure, at 305—350 nm with the maximum at 310 nm, which was shifted to shorter wavelengths by dilution with a solvent.[15)]

In order to evaluate electron donating abilities of the olefins, their charge-transfer interaction with tetracyanoethylene (TCNE) was investigated. When **1a** or styrene was dissolved with TCNE in dichloromethane, charge-transfer bands appeared. The association constant, K, and extinction coefficient of the complex, ε_{CT}, were determined from concentration dependence of the optical density of the complex according to Benesi-Hildebrand's equation,[18)]

$$C_0/A = 1/K\varepsilon_{CT}D_0 + 1/\varepsilon_{CT},$$

where C_0 and D_0 are the initial concentrations of the acceptor and donor, respectively, and A is the absorbance for unit cell path length. The results for **1a**/TCNE and styrene/TCNE are listed in Table 3.

The results for styrene/TCNE accord with those reported by Cooper *et al.*[19)] Comparison of **1a** with styrene in the wavelength of the absorption maximum, λ_{CT}, and the association constant, K, shows that **1a** is a stronger donor to give a more stable charge-transfer complex than styrene.

The energy of the charge-transfer transition for the complexes formed by a series of donors with the same acceptor is related to the donor ionization potential, I_D:[19,20)]

$$h\nu_{CT} = aI_D + b,$$

where a and b are constant. When the values of a and b

TABLE 3. CHARACTERISTICS OF CHARGE-TRANSFER COMPLEXES BETWEEN TETRACYANOETHYLENE AND STYRENE DERIVATIVES IN DICHLOROMETHANE AT 23 °C

Donor	Absorption maximum			Association constant	Ionization potential	Free energy change
	λ_{CT}/nm	λ_{CT}/eV	ε_{CT}	K/mol^{-1} dm^3	I_D/eV	ΔG/kcal mol^{-1}
cis-PhCH=CHOMe	610	2.03	1250	1.38	7.70,[a)] 7.54[b)]	−0.19
PhCH=CH$_2$	480	2.56	1330	0.60	8.34,[a)] 8.40[b)]	0.30

a) Values evaluated from the equation by Farrell and Newton.[20)] b) Adiabatic values from photoelectron spectra of *cis*-β-methoxystyrene[21)] and styrene.[22)] proposed by Farrel and Newton[20] 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 UVIDEC-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 (CCl_4): 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 $C_{11}H_{14}O$: 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 (CCl_4): 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 (CCl_4): 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 $C_{16}H_{18}O_3$: 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 acid[30] or *N*-bromosuccinimide/sodium hydroxide[30] 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–H_3PO_4 (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 D_2O 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 (CCl_4): δ 2.50 (s, 1H, exchangeable with D_2O), 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(CCl_4): 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 $C_{11}H_{16}O_3$: C, 67.32; H, 8.21%.

2-Isopropoxy-2-methoxy-1-phenylethanol (**6c**), bp 84 °C/1 Torr; NMR(CCl_4): 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 $C_{12}H_{18}O_3$: 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-Alkoxystyrenes. 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 Sytrene Derivatives. C-T Spectra with Molecular Oxygen. Samples of **1a** (neat or 0.3 mol/dm^3 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/dm^3) with solutions of **1a** (0.23—0.34 mol/dm^3) or styrene (3.7—8.0 mol/dm^3) 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.

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