Photochemical Reactions of Contact Charge-Transfer Pairs of 1-Arylcyclohexenes and Oxygen

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Photoexcitation of contact charge-transfer (CCT) pairs of 1-arylcyclohexenes **1** (aryl: phenyl, 4-methylphenyl, and 4-methoxyphenyl) and oxygen in acetonitrile and benzene gave 1,2-epoxy-1-arylcyclohexanes **2** as major products together with 2-aryl-2-cyclohexen-1-ols and acetophenones **4**. Similar irradiation of the CCT pairs in methanol/acetonitrile afforded mainly 2-aryl-2-methoxycyclohexanols instead of **2** and small amounts of 1-aryl-1-methoxycyclohexanes, 2-aryl-2-cyclohexen-1-ones, and **4**. The formation of these products can be explained by photoinduced electron transfer in the excited CCT pairs generating radical cations of **1** and superoxide anions.

Dye-sensitized oxygenation of organic substrates has been extensively investigated.[1,2] However, photochemistry of contact charge-transfer (CCT) pairs of the organic substrates and oxygen has not been so well investigated,[3–5] though spectral evidence for the CCT pairs has been documented.[6–8] Recently, we have reported selective photoexcitation of the CCT pairs of some organic compounds and molecular oxygen leading to specific reactions, in which their radical cations and superoxide anions play important roles. These reactive intermediates, after generation through electron transfer in the excited CCT pairs, can produce other reactive intermediates, for example, a) neutral free radicals through deprotonation of the radical cations, b) carbocations through electron transfer of the free radicals, and c) singlet oxygen through back electron transfer between the radical cations and superoxide anions.[9–12] The CCT pairs of olefins, such as 4-methoxy- and 4-methylstyrene, and oxygen in acetonitrile afforded, on excitation, their dimers accompanied by small amounts of their oxygenated products.[10,12] The reaction proceeds through their radical cations, which undergo addition to the ground-state olefin to give dimeric radical cations followed by electron transfer probably from superoxide anions. We now report structure dependence of the reaction course of excited CCT pairs of aromatic olefins and oxygen; 1-arylcyclohexenes (aryl: phenyl, 4-methylphenyl, and 4-methoxyphenyl) give mainly the corresponding epoxides or their derivatives in contrast to the above styrene derivatives.

Experimental

^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer with TMS as an internal standard. Infrared and UV spectra were measured on a Hitachi 260-10 and a Shimadzu UV-300 spectrophotometer, respectively. Mass spectra were determined on a Shimadzu QP-1000 mass spectrometer.

Materials. 1-Phenylcyclohexene (**1a**),[13] 1-(4-methylphenyl)cyclohexene (**1b**),[13] and 1-(4-methoxyphenyl)cyclohexene (**1c**)[14] were prepared by the reaction of cyclohexanone with the corresponding 4-substituted phenylmagnesium bromide followed by treatment with 4-methylbenzenesulfonic acid in benzene.

1,2-Epoxy-1-phenylcyclohexane (**2a**)[15] was prepared from 2-bromo-1-phenylcyclohexanol by treatment with an aqueous potassium hydroxide solution;[16] bp 94 °C/5 Torr (1 Torr=133.322 Pa).

1-Methoxy-1-phenylcyclohexane (**6a**)[17] and 2-phenyl-2-cyclohexen-1-one (**7a**)[18] were prepared as previously described.

Acetonitrile, methanol, and benzene (guaranteed reagents) were purchased from Wako Pure Chemical Industries, and distilled before use.

Absorption Spectra of CCT Pairs. Samples of **1** (neat or 1 mol dm^{-3} in benzene) 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, and a stream of argon through the sample in the reference cell. Immediately after a spectrum was measured, argon was passed through the sample cell and a spectrum was again recorded. The band observed under oxygen atmosphere disappeared completely by argon bubbling.

Measurements of Oxidation Potentials. Oxidation potentials of olefins **1**'s were determined by cyclic voltammetry using a three-electrode cell with a Nikko Keisoku NPG-501 potentiogalvanostat and a Nikko Keisoku NFG-3 function generator. The working electrode was a platinum wire (diameter, 1 mm) sealed into glass and a counter electrode was a platinum gauze. A saturated caromel electrode (SCE) was used as a reference electrode and tetraethylammonium perchlorate (0.1 mol dm^{-3}) as a supporting electrolyte. The current-potential curves were recorded directly from the output of the potentiogalvanostat on a Watanabe WX-1000 X-Y recorder. The oxidation potentials were 1.59, 1.51, and 1.28 V (vs. SCE) for **1a**, **1b**, and **1c**, respectively.

Irradiations. Photochemical reactions were carried out with a 400 W high-pressure mercury lamp (Riko UVL-400HA) and a 160 W low-pressure mercury lamp (Riko UVL-160LA). The irradiation mixtures were analyzed on a Shimadzu GC-8A gas chromatograph equipped with a flame ionization detector using 3.2 mm×2 m glass columns packed with Silicone OV-17 (2%, Chromosorb W AW-DCMS, 60—80 mesh) and FON (10%, Chromosorb W AW-DCMS, 80—100 mesh). An internal standard (1,2-diphenylethane) was used to determine composition of the reaction mixtures.

Irradiation of 1-Arylcyclohexenes (1). In Acetonitrile: A solution (3 cm^3) of **1a** (0.1 mol dm^{-3}) in acetonitrile was irradiated under oxygen atmosphere for 9 h at 20 °C in a Pyrex tube with a 400 W high-pressure mercury lamp. GLPC analysis of the sample revealed the formation of 1,2-epoxy-1-phenylcyclohexane (**2a**, 22%), 2-phenyl-2-cyclohexen-1-ol (**3a**, 6%), and acetophenone (**4a**, 4%) at 68% consumption of **1a**.

Cyclohexene **1a** (3.16 g, 20 mmol) was irradiated in acetonitrile (200 cm^3) under oxygen with the high-pressure mercury lamp for 3.5 h. The reaction mixture was concentrated and chromatographed on silica gel under pressure. Epoxide **2a** was isolated and the structure was determined by comparing its ^{13}C NMR spectra with those of an authentic sample.

In Benzene: A solution (3 cm^3) of **1a** (0.1 mol dm^{-3}) in benzene was irradiated for 9 h in a similar way to that in acetonitrile. The yields of **2a** (22%), **3a** (8%), and **4a** (3%) were determined by GLPC.

In Methanol/Acetonitrile: A solution (3 cm^3) of **1a** (0.1 mol dm^{-3}) in a mixture of methanol and acetonitrile (1:2 by volume) in a Pyrex tube was irradiated under oxygen atmosphere with a 400 W high-pressure mercury lamp for 20 h at 20 °C. GLPC analysis of the reaction mixture showed almost complete consumption of **1a** and the formation of **4a** (9%), 2-methoxy-2-phenylcyclohexanol (**5a**, 30%), 1-methoxy-1-phenylcyclohexane (**6a**, 2%), and 2-phenyl-2-cyclohexen-1-one (**7a**, 5%).

A solution of **1a** (0.1 mol dm^{-3}) was similarly irradiated in the mixed solvent under argon atmosphere. No reaction products were detected in the irradiation mixture by GLPC analysis.

Cyclohexene **1a** (3.96 g, 25 mmol) was irradiated under oxygen in a 1:2 methanol–acetonitrile mixture (250 cm^3) with the high-pressure mercury lamp for 21 h. The reaction mixture was concentrated and chromatographed on silica gel under pressure. Cyclohexanol **5a** was isolated together with **4a**, **6a**, and **7a**. GLPC and ^{13}C NMR spectra showed that **5a** consisted of two stereoisomers.

2-Methoxy-2-phenylcyclohexanol (**5a**).[19] Isomer **5a**-A: ^{13}C NMR(CDCl$_3$) δ=141.0 (s), 127.3 (d), 126.5 (d), 126.3 (d), 79.6 (s), 74.8 (d), 48.9 (q), 29.6 (t), 23.0 (t), and 20.6 (t); MS (70 eV) *m/z* (rel intensity) 206 (M$^+$, 34), 147 (100), 121 (75), 105 (44), 91 (49), and 77 (40); isomer **5a**-B: ^{13}C NMR(CDCl$_3$) δ=142.6 (s), 128.0 (d), 127.2 (d), 127.0 (d), 79.5 (s), 73.2 (d), 49.0 (q), 28.1 (t), 24.0 (t), 20.5 (t), and 18.9 (t); MS (70 eV) *m/z* (rel intensity) 206 (M$^+$, 29), 147 (100), 121 (51), 105 (40), 91 (37), and 77 (32).

A solution (3 cm^3) of epoxide **2a** (0.069 mol dm^{-3}) in a 1:2 methanol–acetonitrile mixture was irradiated in a Pyrex tube with a 400 W high-pressure mercury lamp for 9 h. GLPC analysis showed that **5a** was produced in 65% yield at 24% conversion of **2a**.

Cyclohexene **1b** (3.5 g, 20 mmol) was irradiated in a 1:2 methanol–acetonitrile mixture (200 cm^3) under oxygen with a 400 W high-pressure mercury lamp for 16 h. The reaction mixture was concentrated and chromatographed on silica gel under pressure. 2-Methoxy-2-(4-methylphenyl)cyclohexanol (**5b**), 1-methoxy-1-(4-methylphenyl)cyclohexane (**6b**), and 2-(4-methylphenyl)-2-cyclohexen-1-one (**7b**) were isolated (Table 1).

Similarly, when **1c** (0.1 mol dm^{-3}) was irradiated in a 2:3 methanol–acetonitrile mixture (50 cm^3) under oxygen in a uranium glass tube with a 400 W high-pressure mercury lamp for 39 h. 2-Methoxy-2-(4-methoxyphenyl)cyclohexanol (**5c**) and 1-methoxy-1-(4-methoxyphenyl)cyclohexane (**6c**) were isolated from the irradiation mixture (Table 1).

2-Methoxy-2-(4-methylphenyl)cyclohexanol (**5b**). Isomer **5b**-A: ^{13}C NMR (CDCl$_3$) δ=138.0 (s), 135.9 (s), 128.2 (d), 126.6 (d), 79.6 (s), 74.9 (d), 48.9 (q), 29.6 (t), 23.1 (t), 20.9 (t), and 20.3 (q); MS (70 eV) *m/z* (rel intensity) 220 (M$^+$, 30), 161 (100), 135 (74), 105 (43), and 91 (36); isomer **5b**-**B**: ^{13}C NMR(CDCl$_3$) δ=139.6 (s), 136.4 (s), 128.6 (d), 126.8 (d), 79.2 (s), 72.9 (d), 48.7 (q), 28.0 (t), 23.8 (t), 20.4 (t and q), and 18.8 (t); MS (70 eV) *m/z* (rel intensity) 220 (M$^+$, 28), 161 (100), 159 (43), 135 (74), 105 (72), and 91 (49). Found (for mixture of the isomers): C, 76.09; H, 8.85%. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15%.

1-Methoxy-1-(4-methylphenyl)cyclohexane (**6b**): bp 102—103 °C/5 Torr; ^{13}C NMR(CDCl$_3$) δ=142.8 (s), 136.0 (s), 128.7 (d), 125.9 (d), 76.9 (s), 49.1 (q), 35.4 (t), 25.6 (t), 21.9 (t), and 20.8 (q); MS (70 eV) *m/z* (rel intensity) 204 (M$^+$, 33), 161 (100), 129 (17), and 105 (27). Found: C, 82.57; H, 10.06%. Calcd for $C_{14}H_{20}O$: C, 82.30, H, 9.87%.

2-(4-Methylphenyl)-2-cyclohexen-1-one (**7b**):[20] ^{13}C NMR (CDCl$_3$) δ=197.9 (s), 147.2 (d), 140.1 (s), 137.0 (s), 133.5 (s), 128.5 (d), 128.3 (d), 38.9 (t), 26.4 (t), 22.8 (t), and 20.9 (q); MS (70 eV) *m/z* (rel intensity) 186 (M$^+$, 100), 130 (51), 129 (43), and 115 (49).

2-Methoxy-2-(4-methoxyphenyl)cyclohexanol (**5c**). Isomer **5c**-A: ^{13}C NMR (CDCl$_3$) δ=158.6 (s), 133.3 (s), 128.2 (d), 113.5 (d), 79.7 (s), 75.4 (d), 55.1 (q), 49.4 (q), 30.0 (t), 23.3 (t), and 21.4 (t); MS (70 eV) *m/z* (rel intensity) 236 (M$^+$, 39), 177 (100), 151 (90), and 121 (30); isomer **5c**-**B**: ^{13}C NMR(CDCl$_3$) δ=159.2 (s), 134.6 (s), 128.6 (d), 114.0 (d), 79.5 (s), 73.7 (d), 55.3 (q), 49.3 (q), 28.2 (t), 24.4 (t), 20.9 (t), and 19.3 (t); MS (70 eV) *m/z* (rel intensity) 236 (M$^+$, 36), 177 (100), 151 (84), and 121 (30). Found (for mixture of the isomers): C, 70.89; H, 8.73%. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53%.

1-Methoxy-1-(4-methoxyphenyl)cyclohexane (**6c**): bp 123 °C/6 Torr; ^{13}C NMR (CDCl$_3$) δ=158.5 (s), 137.9 (s), 127.3 (d), 113.6 (d), 55.1 (q), 49.3 (q), 35.5 (t), 25.7 (t), and 22.1 (t); MS (70 eV) *m/z* (rel intensity) 220 (M$^+$, 72), 189 (62), 177 (100), and 121 (73). Found: C, 76.53; H, 9.30%. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15%.

Dye-Sensitized Oxygenation of 1a. A solution (50 cm^3) of **1a** (1g, 6.32 mmol) in a 1:2 methanol–acetonitrile mixture containing Methylene Blue (50 mg, 0.134 mmol) was put in five uranium glass tubes (10 cm^3 each), and irradiated for 40 h under oxygen atmosphere through a filter solution of K_2CrO_4 (0.27 g dm^{-3}) and Na_2CO_3 (1 g dm^{-3}). The combined reaction mixture was evaporated in vacuo and 2-phenyl-2-cyclohexenyl hydroperoxide was isolated from the residue by flash-column chromatography[21] using a 1:3 hexane–benzene as an eluent. This compound was decomposed into cyclohexenol **3a** and cyclohexenone **7a** (**3a**/**7a**=1/1) in the GLPC column (240 °C). Reduction of the hydroperoxide by $NaBH_4$ gave cyclohexenol **3a** as a sole product. The yield of the peroxide was determined by

GLPC analysis after treatment with NaBH$_4$.

2-Phenyl-2-cyclohexenyl hydroperoxide (**8a**):[22] ^{13}C NMR (CDCl$_3$) δ=140.3 (s), 133.5 (s), 132.3 (d), 127.9 (d), 126.5 (d), 125.4 (d), 78.6 (d), 25.9 (t), 25.8 (t), and 16.2 (t).

2-Phenyl-2-cyclohexen-1-ol (**3a**):[23] ^{13}C NMR(CDCl$_3$) δ=140.3 (s), 139.1 (s), 128.2 (d), 126.8 (d), 125.9 (d), 65.2 (d), 31.6 (t), 26.0 (t), and 17.2 (t); MS (70 eV) *m/z* (rel intensity) 174 (M$^+$, 68), 117 (53), 115 (56), and 91 (100).

Photooxidation of 1a in the Presence of 2,3-Dimethyl-2-butene (TME) and 1,4-Diazabicyclo[2.2.2]octane (DABCO). A solution (3 cm^3) of **1a** (0.1 mol dm^{-3}) in a 1:2 methanol–acetonitrile mixture containing TME (0.1 mol dm^{-3}) in a Pyrex tube was irradiated under oxygen atmosphere with a 400 W high-pressure mercury lamp for 20 h at 20 °C. GLPC analysis of the irradiation mixture showed that the yields and distribution of the products are quite similar to those in the photooxidation of **1a** in the absence of TME. The results are shown in Table 2.

Under similar conditions, **1a** (0.1 mol dm^{-3}) was irradiated with DABCO (0.1 mol dm^{-3}) for 20 h. The olefin was recovered almost quantitatively and trace amounts of **2a** and **4a** were detected by GLPC analysis.

Autoxidation of 1a. A solution (10 cm^3) of **1a** (0.1 mol dm^{-3}) in a 1:2 methanol–acetonitrile mixture containing AIBN (30 mg, 0.22 mmol) was heated at 65 °C for 20 h in an oxygen stream in the dark. The yields of the products, **2a**, **3a**, and **5a**, were determined by GLPC, and are shown in Table 1. **4a** and **6a** were not detected at all.

Results and Discussion

Absorption Spectra of the CCT Pairs of 1-Arylcyclohexenes and Oxygen. Under oxygen atmosphere, 1-phenylcyclohexene (**1a**) (neat or in benzene solution) exhibited a new weak absorption in the range of 320—400 nm. 1-(4-Methylphenyl)- (**1b**) and 1-(4-methoxyphenyl)cyclohexene (**1c**) also showed new absorptions at 320—410 and 325—450 nm, respectively, under similar conditions. These bands disappeared reversibly on introduction of argon to their solutions to exclude oxygen. These bands can be reasonably assigned to the CCT pairs of **1** and oxygen.[10,12]

Irradiation of the CCT Pairs of 1-Arylcyclohexenes and Oxygen. Selective irradiation into the CCT band of **1a** and oxygen in acetonitrile (effective wavelength of light: 313 nm) afforded 1,2-epoxy-1-phenylcyclohexane (**2a**, 22% based on **1a** consumed) together with 2-phenyl-2-cyclohexen-1-ol (**3a**, 6%), and acetophenone (**4a**, 4%). Similar irradiation of **1a** in benzene gave nearly the same distribution of the products (Table 1). However, in a mixture of methanol and acetonitrile (1:2 by volume) 2-methoxy-2-phenylcyclohexanol (**5a**, 30%) instead of epoxide **2a** was a main product, accompanying 1-methoxy-1-phenylcyclohexane (**6a**, 2%), 2-phenyl-2-cyclohexen-1-one (**7a**, 5%), and **4a** (9%). The formation of **5a** is assumed to be due to (photochemical) methanolysis of **2a** as a primary product since, in a control experiment, irradiation of **2a** with 313 nm light gave **5a** (a mixture of the cis- and trans-isomers) in a methanol–acetonitrile mixture.

However, on irradiation of **1a** under argon with 313 nm light in a methanol–acetonitrile mixture, no reaction products were detected by GLPC analyses. Also, on direct excitation of **1a** with 254 nm light, no products were obtained and the starting **1a** was recovered quantitatively both under argon and under oxygen. From these results it is reasonably concluded that all the products result from a sequence of reaction of the excited CCT pairs.

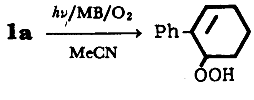
Table 1. Yields of Products on Irradiation and Autoxidation of 1-Arylcyclohexenes 1 under Oxygen in Solvents

Substrate	Additive	Solvent	Atmosphere	Irrad. wavelength /nm[b)]	React. time /h	Conv. /%	Yield[a)]/%				
							2	**3**[c)]	**4**	**5**	**6**
1a	—	MeCN	O$_2$	313	9	68	22	6	4	—	—
	—	PhH	O$_2$	313	9	38	22	8	3	—	—
	—	PhH	O$_2$	313	20	66	28	6	4	—	—
	—	MeOH/MeCN	O$_2$	254	15	0	—	—	—	—	—
	—	MeOH/MeCN	Ar	254	15	0	—	—	—	—	—
	—	MeOH/MeCN	O$_2$	313	20	95	Trace	6	9	30	2
	—	MeOH/MeCN	Ar	313	20	0	—	—	—	—	—
	AIBN/65 °C[d)]	MeOH/MeCN	O$_2$	—	20	53	8	4	—	46	—
	AIBN/65 °C	PhH	O$_2$	—	20	60	43	6	—	—	—
1b	—	MeOH/MeCN	O$_2$	313	15	96	—	3[e)]	2	23	8
	—	MeOH/MeCN	Ar	313	15	0	—	—	—	—	—
1c	—	MeOH/MeCN	O$_2$	366	20	98	—	—	Trace	59	13
	—	MeOH/MeCN	Ar	366	20	6	—	—	—	—	Trace

a) Yields of products: [(moles of products)/(moles of **1** consumed)] × 100. The conversions of olefins **1** and the yields of the products were determined by GLPC analyses. b) Effective excitation wavelength. c) The sum of cyclohexenol **3** and cyclohexenone **7**. d) AIBN: azobisisobutyronitrile. e) The yield of cyclohexenone **7b**.

Irradiation into the CCT bands of 1-(4-methylphenyl)- (**1b**) and 1-(4-methoxyphenyl)cyclohexene (**1c**) under oxygen in a methanol–acetonitrile mixture led to similar results to the case of **1a** as shown in Table 1; **1b** afforded 2-methoxy-2-(4-methylphenyl)cyclohexanol (**5b**), 1-methoxy-1-(4-methylphenyl)cyclohexane (**6b**), 2-(4-methylphenyl)-2-cyclohexen-1-one (**7b**), and 1-(4-methylphenyl)ethanone (**4b**), and **1c** gave 2-methoxy-2-(4-methoxyphenyl)cyclohexanol (**5c**), 1-methoxy-1-(4-methoxyphenyl)cyclohexane (**6c**), and 1-(4-methoxyphenyl)ethanone (**4c**).

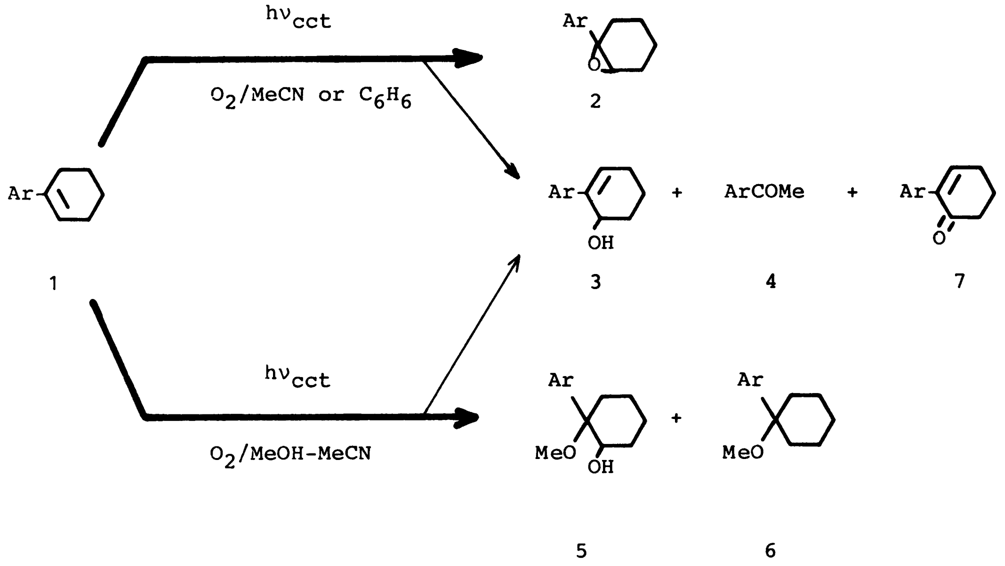
Some control experiments were carried out to examine oxygen species involved in the present oxygenation. In Methylene Blue(MB)-sensitized photooxygenation of **1a**, 2-phenyl-2-cyclohexenyl hydroperoxide (**8a**), which is known as a product in singlet oxygen oxygenation of **1a**,[22] was solely isolated (45%), but none of the products obtained from the CCT pair excitation was detected. Accordingly, it can be concluded that singlet oxygen is not associated with the reactions induced by CCT pair excitation of **1**.[10,11]



8a

Furthermore, addition of 2,3-dimethyl-2-butene (TME), a highly reactive singlet oxygen trap, brought about no effects on the product distribution in the CCT pair excitation of **1a** in a methanol–acetonitrile mixture (Table 2).

When **1a** was irradiated under oxygen in a methanol–acetonitrile mixture in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO), only trace amounts of **2a** and **6a** were formed (Table 2). DABCO works not only as a singlet oxygen quencher but also



Scheme 1. **1a**: Ar=Ph; **1b**: Ar=4-MeC_6H_4; **1c**: Ar=4-MeOC_6H_4.

Table 2. Effects of 2,3-Dimethyl-2-butene (TME) and 1,4-Diazabicyclo[2.2.2]octane (DABCO) on Irradiation of 1-Arylcyclohexenes (**1**) under Oxygen in MeOH/MeCN

Substrate	Additive	Irrad. wavelength /nm[b]	Conversion /%	Yield[a]/%				
				2	**3**[c]	**4**	**5**	**6**
1a	—	313	95	Trace	6	9	30	2
	TME	313	83	Trace	5	9	34	4
	DABCO	313	12	Trace	—	—	—	—
	MB[d]	>400	97	—	45[e]	—	—	—
1c	—	366	98	—	—	Trace	59	13
	TME	366	94	—	—	Trace	62	25
	DABCO	366	8	—	—	—	—	—

a) Yields of products: [(moles of products)/(moles of **1** consumed)]×100. b) Effective excitation wavelength. c) The sum of cyclohexenol **3** and cyclohexenone **7**. d) Methylene Blue(MB)-sensitized oxygenation. e) The yield of hydroperoxide **8a**, which was determined by GLPC analysis after treatment with sodium borohydride.

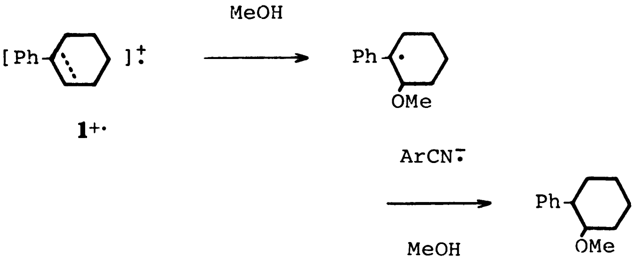
as an electron-donating quencher. Since the oxidation potential of DABCO (E_{ox}: 0.68 V vs. SCE) is by ca. 0.9 V lower than that of **1a** (1.59 V) and, as mentioned above, TME does not affect the photoreaction of the CCT pairs of **1a**, it is reasonably supposed that **1a** radical cations generated from the excited CCT pairs were reduced by DABCO, thus recovering **1a**.

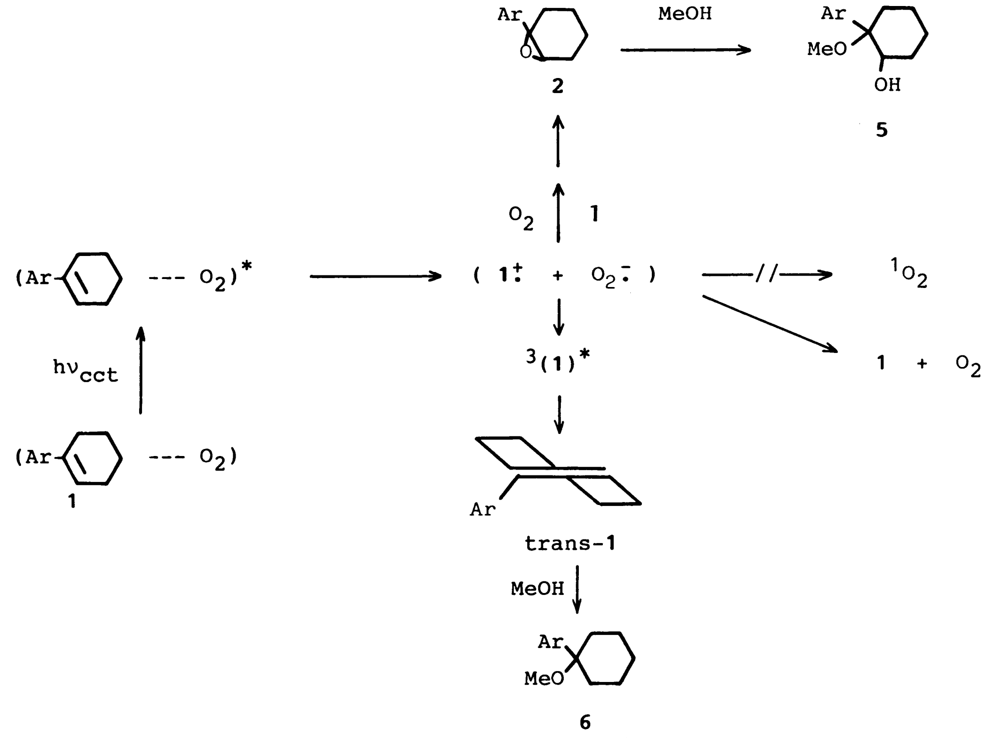
Reaction Course of Excited CCT Pairs. The above product study shows that the photochemical reactions take place only when the CCT pairs of **1** and oxygen were excited. The main product is epoxide **2** in acetonitrile and benzene; however, in the presence of methanol **2** is converted into methoxyalcohol **5**.

Azobisisobutyronitrile(AIBN)-initiated autoxidation of **1a** also gave **2a** as a main product (Table 1). As already reported, β-alkoxystyrenes give, on excitation of their CCT pairs with oxygen, the corresponding epoxides through an olefin–oxygen copolymerization process together with carbonyl compounds resulting from oxidative cleavage of the double bond.[24,25] Therefore, similar processes may be operative in the present oxygenation of **1** (Scheme 2).

More remarkable is the formation of 1-methoxy-1-arylcyclohexanes **6**, Markownikoff adducts of methanol to **1**. It is well-known that *trans*-cyclohexenes react with methanol to give addition products such as **6a**.[26–31] The adducts **6** were formed on excitation of the CCT pairs with oxygen, but not on direct excitation of the olefins under argon. Therefore, it is probable that excitation of the CCT pair leads to the formation of the triplet state of **1** [triplet energy (E_T) of **1a**: 56±3 kcal mol^{-1}],[32,33] which is deactivated from its twisted geometry to the *trans*-cyclohexene in the ground state. The cyclohexene triplets may be generated by back electron transfer between the olefin radical cations and superoxide anions, the energy of these pairs being 57 kcal mol^{-1} over the ground state as estimated from their electrochemical potentials.[34] The yields of ethers **6** were increased by introduction of an electron-donating group on the aromatic ring of **1a** (**6a**, 2%; **6b**, 8%; **6c**, 13%), probably because of increase in electron density on the double bond of *trans*-arylcyclohexene with increasing electron-donating ability of the substituent.[36]

Another possibility for **6** formation might be a reaction of the **1** radical cation with methanol followed by electron transfer and protonation. However, this possibility can be ruled out since addition of methanol to the **1** radical cation is assumed to take place at the 2-position of **1** on the basis of cyanoaromatics-sensitized addition of methanol to **1a**.[37] The present results indicate that the **1** radical





Scheme 2.

cations react probably with superoxide anions to give either some radical intermediates initiating autoxidation of **1** affording the epoxides or the triplet **1** decaying to *trans*-**1** (Scheme 2).

Photochemical behavior of CCT pairs of arylcyclohexenes **1** is in contrast with that of 4-methoxystyrene which gives a dimeric product as reported previously.10,12) The difference in the reaction course between these CCT pairs may be associated with reactivity of the olefins towards their radical cations. Generally, trisubstituted and 1,2-disubstituted olefins are less reactive than monosubstituted olefins in free radical addition reactions,38) whereas **1a** undergoes photodimerization in the excited state.31,39) Therefore, it is reasonably supposed that arylcyclohexenes **1** are not so reactive with their radical cations as 4-methoxystyrene with its radical cation. As a result, the radical cations of **1** react with superoxide anion or oxygen rather than with **1**.

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