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Electron Transfer Resulting from Excitation of Contact Charge Transfer Complexes of Some Styrene Derivatives and Oxygen. The Role of Oxygen as an Electron Acceptor

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Irradiation of contact charge transfer (CCT) bands (320—370 nm) of 4-methoxystyrene (**1a**) and 4-methylstyrene (**1b**) with molecular oxygen in acetonitrile and benzene resulted in the formation of the corresponding *cis*- and *trans*-1,2-diarylcyclobutanes (**2** and **3**) as well as benzaldehydes (**4**), oxidative cleavage products. In the case of **1b**, 7-methyl-1-(4-tolyl)-1,2,3,4-tetrahydronaphthalene (**5**) and 6-methyl-4-(4-tolyl)-1,2,3,4-tetrahydronaphthalen-1-one (**6**) were also afforded. The formation of these products is reasonably explained by electron transfer in the excited CCT pair followed by addition of the resulting **1** cation radical to ground-state **1** to form a dimer cation radical; its cyclization leads to the dimeric products and trapping of a cyclic dimer cation radical by oxygen affords ketone **6**.

In photochemical reactions, oxygen has often been investigated only as an oxidant. It is well-known that singlet oxygen generated by dye sensitization oxidizes olefins to afford hydroperoxides, endoperoxides, and dioxetanes.[1)] In contrast to active studies on singlet oxygen, another role of oxygen as an electron acceptor has attracted little attention.[2)]

The formation of contact charge transfer (CCT) complexes between organic compounds and oxygen has been observed.[3)] However, their roles in photochemical reactions had not been recognized until a few years ago. Recently, the copolymerization of styrene and its derivatives with oxygen was reported to be initiated by irradiation of the CCT bands between the olefins and oxygen.[4)] Also, the excitation of the CCT band between hexamethylbenzene and oxygen in methanol-benzene was shown to produce 2,3,4,5,6-pentamethylbenzyl cations followed by their reaction with methanol to give 1-methoxy-2,3,4,5,6-pentamethylbenzene.[2b)] Furthermore, in dye-sensitized photooxygenation of *trans*-stilbene, oxygen was reported to serve as an electron acceptor.[5)]

In a previous communication,[6)] we demonstrated that the photoexcitation of CCT complexes of 4-methoxy- and 4-methylstyrene with oxygen in acetonitrile induces electron transfer from the styrenes to oxygen to generate cation radicals of the styrenes followed by their addition to the styrenes finally affording dimers of the styrenes.[7)] The present paper describes a full account of our work on the photochemical reactions of the olefins resulting from their CCT band excitation.

Results

Formation of CCT Complexes of 4-Methoxy- and 4-Methylstyrene with Oxygen. The longest wavelength end of the absorption band of 4-methoxystyrene (**1a**) lies at 325 nm under argon in acetonitrile or benzene (Fig. 1a). On saturation with oxygen a new absorption band appeared in the range of 320—370 nm in both solvents. Figure 1c shows a difference spectrum of **1a** under argon and oxygen. This band disappeared reversibly on introduction of argon to exclude oxygen, and therefore, is reasonably assigned to a CCT pair of **1a** and oxygen. 4-Methylstyrene (**1b**) exhibited a similar absorption due to its CCT pair with oxygen in the region of 310—370 nm in acetonitrile (Fig. 1e).

On addition of 1,4-dicyanobenzene (DCNB) under nitrogen in acetonitrile, **1a** exhibited a new absorption band in the region of 320—390 nm (Fig. 1f). This band can be assigned to a charge transfer (CT) complex.

Irradiation of 4-Methoxystyrene (1a). Direct irradiation of **1a** under nitrogen in acetonitrile with 254- or 313-nm light afforded head-to-head cycloadducts, *cis*- and *trans*-1,2-bis(4-methoxyphenyl)cyclobutane

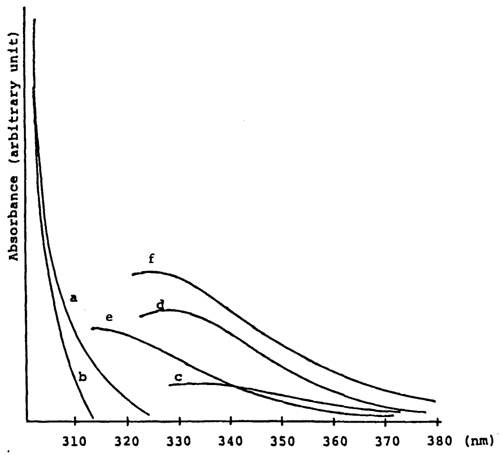
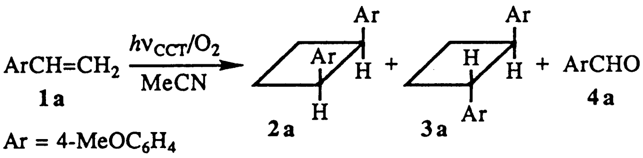


Fig. 1. UV spectra of CCT pairs.
a: **1a** under argon in MeCN. b: **1b** under argon in MeCN. c: **1a** under oxygen in MeCN. d: **1a** under oxygen in PhH. e: **1b** under oxygen in MeCN. f: **1a** in the presence of DCNB in MeCN.

(**2a** and **3a**, respectively, 63—65% yield) in a ratio of ca. 90/10.

Irradiation of **1a** under oxygen in acetonitrile with 366-nm light gave **2a** and **3a** (31%, **2a**/**3a**=5/95) together with 4-methoxybenzaldehyde (**4a**, 32%), an oxidative cleavage product (Scheme 1). However, no reaction products were essentially detected on irradiation under nitrogen. The results on irradiation of **1a** under various conditions are summarized in Table 1.

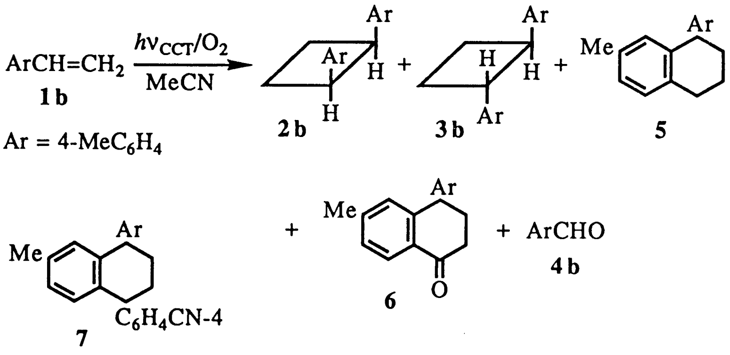
Irradiation of **1a** at 313 or 366 nm in the presence of DCNB under nitrogen in acetonitrile afforded **3a** predominantly with a small amount of **2a** (**2a**/**3a**=2/98, Runs 11 and 12 in Table 1). On benzophenone-sensitized irradiation (366 nm) under otherwise similar conditions, **1a** gave the dimers in an isomer ratio of **2a**/**3a**=13/87 (Run 10). 4-Methoxybenzaldehyde (**4a**) hardly sensitized the dimerization under 366-nm illumination; however, with 313-nm light **4a** sensitized the dimerization to produce **2a** and **3a** in a ratio of 22/78 (Run 9).



Scheme 1.

Irradiation of 4-Methylstyrene (1b). Irradiation of **1b** in acetonitrile under oxygen with 313-nm light led to the formation of three cyclodimers (20%), *cis*- and *trans*-1,2-bis(4-tolyl)cyclobutane (**2b** and **3b**, respectively, head-to-head cycloadducts) and a tetralin derivative, 7-methyl-1-(4-tolyl)-1,2,3,4-tetrahydronaphthalene (**5**) (isomer ratio, **2b**:**3b**:**5**=58:33:9), and a dimeric ketone, 6-methyl-4-(4-tolyl)-1,2,3,4-tetrahydronaphthalen-1-one (**6**, 20%) together with 4-methylbenzaldehyde (**4b**, 8%) (Scheme 2). On the other hand, the irradiation of **1b** under nitrogen gave cyclodimers **2b**, **3b**, and **5** in a ratio of 83:10:7, but no dimeric ketone **6**.

Irradiation of **1b** at 313 nm in the presence of DCNB under nitrogen in acetonitrile afforded 1-(4-cyanophenyl)-6-methyl-4-(4-tolyl)-1,2,3,4-tetrahydronaphthalene (**7**) as a main product (30%) together with the olefin dimers (5%, **2b**:**3b**:**5**=11:11:78). The results are summarized in Table 2.



Scheme 2.

Table 1. Photodimerization of 4-Methoxystyrene[a)]

Run	Conditions	$h\nu$[b)] nm	Conversion/%	Yield/% 2a+3a	Yield/% 4a	Isomer ratio 2a:3a
1)	MeCN, O_2	254	34	56	9	63:37
2)	MeCN, O_2	313	63	47	14	16:84
3)	MeCN, O_2	366	43	31	32	5:95
4)	MeCN, N_2	254	23	65	Trace	90:10
5)	MeCN, N_2	313	26	63	Trace	87:13
6)	MeCN, N_2	366	3	Trace	Trace	—
7)	PhH, O_2	313	37	18	11	80:20
8)	PhH, O_2	366	—	Trace	Trace	—
9)	MeCN, N_2 4-$MeOC_6H_4CHO$[c)]	313	28	75	Trace	22:78
10)	MeCN, N_2 Ph_2CO[d)]	366	12	50	Trace	13:87
11)	MeCN, N_2 DCNB[e)]	313	95	42	—	2:98
12)	MeCN,N_2 DCNB[f)]	366	77	68	—	2:98

a) Olefin concentration, 0.59 mol dm^{-3}. b) Effective excitation wavelength. c) 0.12 mol dm^{-3} d) 0.13 mol dm^{-3}. e) 0.13 mol dm^{-3}. f) 0.08 mol dm^{-3}.

Table 2. Photodimerization of 4-Methylstyrene[a)]

Run	Conditions	$h\nu$[b)]	Conversion/%	Yield/%				Isomer ratio
		nm		**2b**+**3b**+**5**	**4b**	**6**	**7**	**2b**:**3b**:**5**
1)	MeCN, O_2	313	45	14	8	20	—	58:33:9
2)	MeCN, N_2	313	15	42	—	—	—	83:10:7
3)	MeCN, N_2 DCNB[c)]	313	65	45	—	—	30	11:11:78

a) Olefin concentration, 0.63 mol dm^{-3} b) Effective excitation wavelength. c) 0.13 mol dm^{-3}.

Discussion

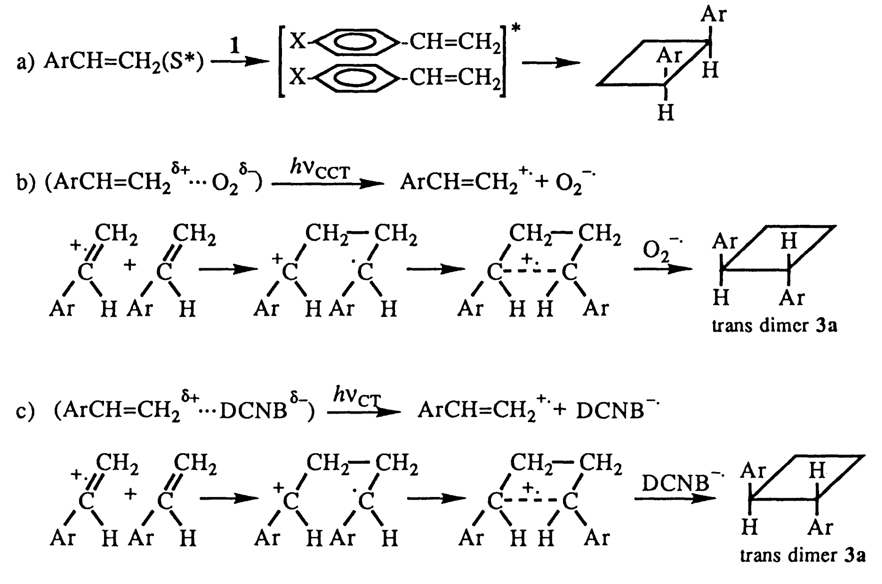
Photochemical Reactions of 4-Methoxystyrene on CCT Band Excitation. Direct irradiation of 4-methoxystyrene (**1a**) with 254- or 313-nm light in acetonitrile under nitrogen gave cis and trans cyclodimers **2a** and **3a** in a ratio of ca. 90/10. The predominant formation of **2a** indicates that the dimerization proceeds through an excimer with the geometry in which the aromatic rings are overlapped with each other, collapsing mainly into the cis dimer, as previously proposed for the dimerization of styrene[8)] (Scheme 3a).

Excitation of the CCT pair of **1a** and oxygen at 366 nm in the same solvent gave **2a** and **3a** in a contrasted ratio of 5/95 together with 4-methoxybenzaldehyde (**4a**); however, a similar irradiation in benzene gave no dimers. This remarkable solvent effect suggests that the excitation of CCT pair in polar solvents results in electron transfer from the olefin to molecular oxygen to afford the olefin cation radical and superoxide anion. The former either adds to **1a** in the ground state to form a dimer cation radical which is finally converted to the dimer (Scheme 3b) or accepts an electron from the latter to give the original olefin.

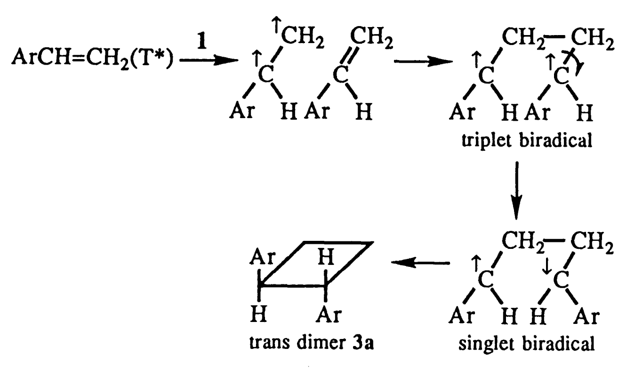
Irradiation under oxygen with light of wavelengths shorter than 366 nm tends to decrease the ratio of the trans isomer; 313-nm light resulted in a **2a**/**3a** isomer ratio of 16/84 and 254-nm light led to a ratio of 63/37. These results can be understood in terms of competitive excitation of the olefin and its CCT pair, leading to the formation of the excimer and cation radical, respectively.

Excitation of the CT band of **1a** and DCNB in acetonitrile also gave cis and trans dimer **2a** and **3a** in a ratio of 2/98 (Scheme 3c) as previously reported by Yamamoto et al.[7a)] This isomer ratio is very similar to that obtained in the CCT pair excitation. Yamamoto proposed a mechanism that excited **1a** interacts with DCNB to give the cation radical of **1a** finally resulting in dimerization of **1a**.[7a)] However, in the present case, the CT band excitation resulted in the dimerization of **1a**, indicating that the CT pair excitation also induces the electron transfer from **1a** to DCNB to generate **1a**$^{+\cdot}$ and DCNB$^{-\cdot}$.

On triplet sensitization with benzophenone under nitrogen in acetonitrile, **1a** gave the dimers in an isomer ratio (**2a**/**3a**=13/87) different from that in the above dimerization under oxygen (Scheme 4). 4-Methoxybenzaldehyde (**4a**) also sensitized (313 nm) the dimerization of **1a** to produce **2a** and **3a** (**2a**/**3a**=22/78); however, 366-nm irradiation of **4a** did not induce the dimerization. These results rule out a possibility that on irradiation of **1a** under oxygen with 366-nm



Scheme 3.



Scheme 4.

light the resulting **4a** would sensitize the reaction.

Photochemical Reaction of 4-Methylstyrene. Excitation of the CCT pair of **1b** and oxygen in acetonitrile gave three cyclodimers (**2b**, **3b**, and **5**) and a dimeric ketone (**6**), and that of the CT pair of **1b** and DCNB afforded 1-(4-cyanophenyl)-6-methyl-4-(4-tolyl)-1,2,3,4-tetrahydronaphthalene (**7**) together with the olefin dimers (**2b**:**3b**:**5**=11:11:78). Ketone **6** and diaryltetralin **7** are products from a tetralin-type dimer cation radical trapped by oxygen species (O_2 or $O_2^{\cdot-}$) and DCNB (neutral molecule or anion radical), respectively, as depicted in Scheme 5, because tetralin-type dimer **5** is reported to be produced only through olefin cation radicals.[7b] In fact, benzophenone-sensitized dimerization of **1b** in benzene gave only cyclodimers **2b** and **3b** (20/80) but no tetralin-type dimer **5**.[7b] Therefore, the production of dimeric ketone **6** indicates that the excitation of the CCT pair of **1b** and oxygen caused dissociation of the excited CCT pair into the **1b** cation radical and superoxide anion.

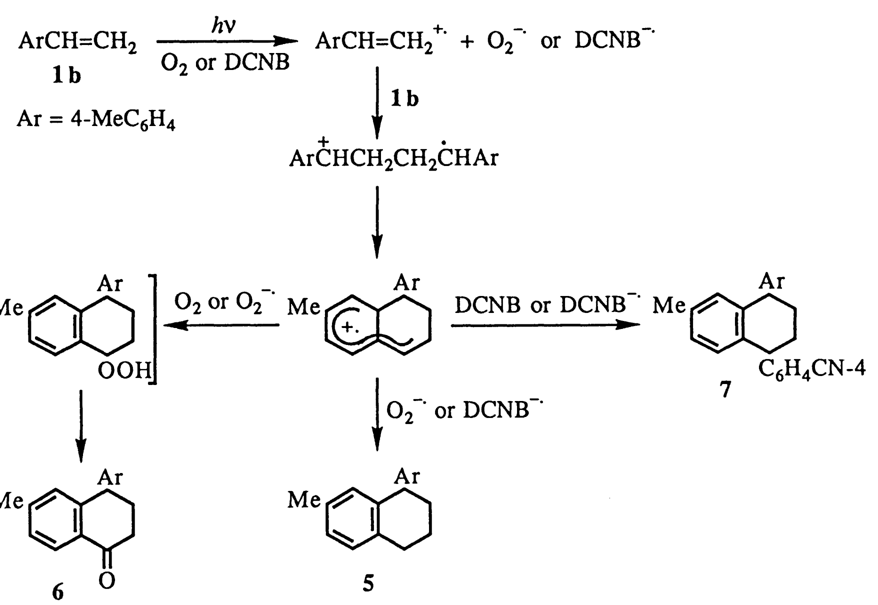
Arnold et al. reported the trapping of triene intermediates through an ene reaction in photochemical electron-transfer dimerization of 1,1-diphenylethene or cross-cycloaddition of 1,1-diphenylethene with 2-methylpropene in the presence of acrylonitrile or methyl acrylate.[9] However, it should be noted that such quenching products of dimer cation radicals as **6** and **7** have scarcely been reported.

Role of Oxygen as an Electron Acceptor. The free energy change (ΔG°) associated with the electron transfer from excited singlet **1** to molecular oxygen or in the CCT pair is given by Eq. 1,[10] where $E(D^+/D)$ and $E(A/A^-)$ are the oxidation potential of donor (D) and the reduction potential of acceptor (A), respectively. The term $e_0^2/\varepsilon a$ is the coulombic energy (ca. 0.06 eV in MeCN) gained by bringing the two ion radical species to encounter distance a in a solvent of dielectric constant ε, and $E_{0,0}$ is the electronic excitation energy of **1** or the CCT pair.

$$\Delta G^\circ(\text{kcal mol}^{-1})=23.06[E(D^+/D)-E(A/A^-)-e_0^2/\varepsilon a]-E_{0,0} \qquad (1)$$

The ΔG° values for electron transfer from excited singlet **1a** to oxygen and in the CCT pairs of **1** with oxygen are estimated to be highly negative as shown in Table 3. These values indicate that the photochemical electron transfer can easily take place as the primary process of the present reactions. Large negative ΔG° values are also estimated for electron transfer from excited singlet **1a** and **1b** to DCNB (Table 3). Thus, the CCT pairs, on excitation, will undergo electron transfer to generate **1** cation radicals and superoxide anions. The former will either add to **1** in the ground state to give dimer cation radicals or undergo back electron transfer to generate **1** triplets.

The triplet state of **1** might be responsible for the present reaction. The free energy of the pair of ion



Scheme 5.

Table 3. Free Energy Changes (ΔG°) Associated with Electron Transfer from Excited Singlet 4-Methoxystyrene (**1a**) and 4-Methylstyrene (**1b**) to Oxygen or DCNB

	$E(D^+/D)$	$E(A/A^-)$	$E_{0,0}$	$E_{0,0}$(CCT)[b]	ΔG°
	V[a]	V[a]	kcal mol^{-1}	kcal mol^{-1}	kcal mol^{-1}
1a/O_2	1.15	−1.28	94	78	−39[c] or −23[d]
1a/DCNB		−2.00			−23[c] or −7[d]
1b/O_2	1.38	−1.28	97	78	−39[c] or −18[d]
1b/DCNB		−2.00			−20[c] or −1[d]

a) Vs. Ag/0.1 mol dm^{-3} $AgNO_3$ in MeCN. b) Energies of CCT pairs calculated from the wavelength of their CCT bands. c) Calculated using $E_{0,0}$. d) Calculated using $E_{0,0}$ (CCT).

radicals $\mathbf{1a}^{+\cdot}$ and $O_2^{-\cdot}$ in acetonitrile can be estimated to be 54 kcal mol^{-1} over the ground-state molecules. The singlet excitation energy of **1a** is estimated to be 94 kcal mol^{-1} from its fluorescence spectrum and its triplet excitation energy to be nearly 60 kcal mol^{-1} because styrene has a triplet excitation energy of 62 kcal mol^{-1}.[11] Such estimation enables us to exclude a possibility of production of **1a** triplets through back electron transfer, since this process is endothermic by ca. 6 kcal mol^{-1}. The situation is similar in **1b**.

Therefore, it is reasonable to conclude that on excitation of the CCT pair the resulting olefin cation radical adds to ground-state olefin to give a dimer cation radical to which an electron is reverted from a superoxide anion finally to give the olefin dimer. In the interaction of the cation radical and the olefin molecule to give the dimer cation radical, the aromatic rings substituted in the ethylenic linkage will avoid steric crowding, therefore, to take a trans configuration.

Experimental

^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JMN-MN-100 spectrometer and a JEOL FX-100 spectrometer, respectively. Infrared (IR) and UV spectra were obtained on a Hitachi 260-50 spectrophotometer and a Hitachi 200-20 spectrophotometer, respectively. Mass spectra were determined with a Hitachi RMU-6MC mass spectrometer. The oxidation and reduction potentials were determined by means of cyclic voltammetry in acetonitrile using a Ag/Ag^+ (0.1 mol dm^{-3}) electrode as a reference electrode and 0.1 mol dm^{-3} tetraethylammonium perchlorate as a supporting electrolyte. Irradiations were carried out with a 400-W high-pressure mercury lamp (Riko UVL-400HA) or with a 160-W low-pressure mercury lamp (Riko UVL-160LA).

Materials. 4-Methoxystyrene (**1a**) and 4-methylstyrene (**1b**) were prepared by decarboxylation of the corresponding cinnamic acids as described in the literature.[12] Acetonitrile and benzene were guaranteed reagents and distilled before use.

Contact Charge Transfer (CCT) and Charge Transfer (CT) Absorption Spectra of Styrene Derivatives. A solution of **1a** (0.59 mol dm^{-3}) in acetonitrile or benzene or of **1b** (0.61 mol dm^{-3}) in acetonitrile was placed in a sample cell and a reference cell, and a stream of oxygen was passed for several minutes through the solution in the sample cell. Spectra were measured at room temperature. Immediately after a spectrum was recorded, argon was passed through the solution in the sample cell and a spectrum was again measured.

A solution of **1a** (0.59 mol dm^{-3}) and DCNB (50 mg, 0.39 mmol) was prepared immediately before measurement and placed in a sample cell. In a reference cell was placed an acetonitrile solution of **1a** in the same concentration as in a sample cell.

Photochemical Reaction. a) Isolation of Reaction Products. ***cis*-1,2-Bis(4-methoxyphenyl)cyclobutane (2a).** 4-Methoxystyrene (2 g, 15 mmol) was irradiated in acetonitrile (250 cm^3) with a 160-W low-pressure mercury lamp under a nitrogen stream at room temperature. After 48 h, 4-methoxystyrene was completely consumed as determined by GLPC analysis. Column chromatography of the concentrated reaction mixture on silica gel with hexane as eluent gave an oily product, the structure of which was determined as *cis*-1,2-bis(4-methoxyphenyl)cyclobutane (**2a**) based on the following spectral data. GLPC analysis showed that the product contained the trans isomer (**3a**) (**2a**/**3a**=91/9).

2a: oil; MS: *m/z* 268 (M^+), 240, 225, 134 ($M^+/2$, 100%), 119; ^{1}H NMR ($CDCl_3$) δ=2.36 (q, 4H, CH_2), 3.64 (s, 6H, OMe), 3.68 (m, 2H, CH), 6.52—6.84 (q, 8H, aromatic H); ^{13}C NMR ($CDCl_3$) δ=157.4 (s), 133.7 (s), 128.8 (d), 113.0 (d), 55.0 (q), 44.5 (d), 24.5 (t).

***trans*-1,2-Bis(4-methoxyphenyl)cyclobutane (3a).**[7a] Irradiation of **1a** (500 mg, 3.7 mmol) in acetonitrile (5 cm^3) under oxygen atmosphere with a 400-W high-pressure mercury lamp through a Pyrex filter for 24 h gave trans dimer **3a** (320 mg, 64%) after separation by chromatography on silica gel with benzene as eluent.

3a: oil; MS: *m/z* 268 (M^+), 266, 240, 225, 160, 134 ($M^+/2$, 100%) 119; ^{13}C NMR ($CDCl_3$) δ=158.0 (s), 136.8 (s), 127.6 (d), 113.7 (d), 55.2 (q), 47.8 (d), 26.0 (t).

***cis*-1,2-Bis(4-tolyl)cyclobutane (2b).**[7b] 4-Methylstyrene (1.8 g, 15 mmol) was irradiated in acetonitrile (250 cm^3) with a 160-W low-pressure mercury lamp under an argon stream at room temperature for 48 h. The solvent was evaporated in vacuo and the residue was separated by chromatography on silica gel to give **2b** (1 g, 56%) and trace amounts of **3b** and **5**.

2b: oil; MS: *m/z* 236 (M^+), 208, 193, 178, 132, 118 ($M^+/2$, 100%), 90; ^{13}C NMR ($CDCl_3$) δ=138.6 (s), 134.7 (s), 128.3(d), 127.8 (d), 44.9 (d), 24.6 (t), 21.0 (q).

***trans*-1,2-Bis(4-tolyl)cyclobutane (3b).**[7b] A solution (3 cm^3) of **1b** (216 mg, 1.83 mmol) in acetonitrile was irradiated in the presence of benzophenone (100 mg, 0.55 mmol) in a uranium glass tube with a 400-W high-pressure mercury lamp under argon atmosphere at room temperature to give **2b** and **3b** in a ratio of 30/70 but no tetralin dimer **5**.

3b: MS: m/z 236 (M^+), 234, 221, 219, 206, 193, 191, 179, 178, 144, 118 ($M^+/2$, 100%), 105, 90.

1-(4-Tolyl)-7-methyl-1,2,3,4-tetrahydronaphthalene (5).[7b)] Oil; MS: m/z 236 (M^+), 221, 208, 193, 144 ($M^+-4\text{-}MeC_6H_4$, 100%), 129, 118; ^{13}C NMR ($CDCl_3$) δ=144.5 (s), 139.1 (s), 135.1 (s), 134.8 (s), 134.3 (s), 130.4 (d), 128.7 (d), 128.6 (d), 126.6 (d), 45.0 (d), 33.3 (t), 29.3 (t), 21.0 (t and q).

6-Methyl-4-(4-tolyl)-1,2,3,4-tetrahydronaphthalen-1-one (6). 4-Methylstyrene (1.8 g, 15 mmol) was irradiated in acetonitrile (60 cm^3) under oxygen atmosphere with a 400-W high-pressure mercury lamp through a Pyrex filter at room temperature. After 72 h, **1b** was completely consumed as determined by GLPC analysis and **6** was separated from other dimers (**2b**, **3b**, and **5**) by chromatography on silica gel using benzene as eluent.

6: oil; MS: m/z 250 (M^+, 100%), 235, 222, 208; IR (neat): 1670 cm^{-1}, $\nu_{C=O}$; ^{1}H NMR ($CDCl_3$) δ=2.34 (s, 3H, CH_3), 2.30—2.65 (m, 4H, CH_2CH_2), 4.0—4.25 (m, 1H, CH), 6.7—8.0 (m, 7H, aromatic H); ^{13}C NMR ($CDCl_3$) δ=197.7, 146.4, 144.3, 140.7, 136.2, 130.6, 129.8, 129.2, 128.4, 127.9, 127.2, 44.8, 36.5, 31.9, 21.7, 21.0. The phenylhydrazone of **6**, mp 131—133 °C (decomp); Found: C, 84.73; H, 7.10; N, 8.26%. Calcd for $C_{24}H_{24}N_2$: C, 84.66; H, 7.10; N, 8.22%.

1-(4-Cyanophenyl)-6-methyl-4-(4-tolyl)-1,2,3,4-tetrahydronaphthalene (7). 4-Methylstyrene (1.8 g, 15 mmol) was irradiated in the presence of 1,4-dicyanobenzene (1 g, 8 mmol) in acetonitrile (250 cm^3) with a high-pressure mercury lamp under a nitrogen stream at room temperature. After 44 h, the solvent was evaporated in vacuo and silica-gel chromatography of the residue gave dimers (**3b** and **5**, trace) and **7** (570 mg, 21%) as a 1 : 1 mixture of cis and trans isomers, the assignment of which was based on ^{13}C NMR spectrum.

7: colorless amorphous; mp 111—112 °C from hexane-methanol; MS: m/z 337 (M^+), 245 (100 %), 234, 219, 208; IR (KBr): 2210 cm^{-1}, $\nu_{C\equiv N}$; ^{1}H NMR ($CDCl_3$) δ=1.6—2.1 (m, 4H, CH_2CH_2), 2.16 and 2.18 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 3.95—4.35 (m, 2H, 2CH), 6.6—7.55 (m, 11H, aromatic H); ^{13}C NMR ($CDCl_3$) δ=153.3, 153.2, 144.0, 143.9, 139.6, 136.3, 136.1, 135.7, 135.3, 135.2, 132.1, 131.0, 130.7, 129.9, 129.6, 129.0, 128.6, 127.5, 127.3, 119.0, 109.9, 45.7, 45.6, 45.3, 44.8, 30.9, 30.1, 29.7, 21.0. Found: C, 89.03; H, 6.87; N, 4.16%. Calcd for $C_{25}H_{23}N$: C, 88.97; H, 6.87; N, 4.15%.

b) Determination of Product Yields. Irradiations with a High-Pressure Mercury Lamp. A solution (3 cm^3) of 4-methoxystyrene (238 mg, 1.78 mmol) in acetonitrile or benzene was irradiated under oxygen or nitrogen atmosphere in a Pyrex tube or a uranium glass tube with a 400-W high-pressure mercury lamp for 16 h at room temperature. The yields of all products were determined by GLPC analysis on a Hitachi 163 gas chromatograph equipped with a flame ionization detector using 2-m columns of 5% polyethylene glycol 20M and 5% Silicone GE SE-30.

A solution (3 cm^3) of **1b** (216 mg, 1.86 mmol) in acetonitrile was irradiated under oxygen or nitrogen atmosphere in a Pyrex or a uranium glass tube with a 400-W high-pressure mercury lamp at room temperature for 20 h using a merry-go-round apparatus. The yields of the products were determined by GLPC analysis.

A solution (3 cm^3) of **1a** (238 mg, 1.78 mmol) in acetonitrile was irradiated in the presence of **4a** (56 mg, 0.41 mmol) or DCNB (50 mg, 0.39 mmol) in a Pyrex or a uranium glass tube with a high-pressure mercury lamp under nitrogen atmosphere at room temperature. The yields of products were determined by GLPC analysis.

Irradiations with a Low-Pressure Mercury Lamp. A solution (3 cm^3) of **1a** (238 mg, 1.78 mmol) in acetonitrile was irradiated in a quartz tube with a 160-W low-pressure mercury lamp under oxygen or nitrogen atmosphere for 16 h at room temperature. The yields of products were determined by GLPC analysis.

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