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Photochemical Electron-transfer Reaction between Aromatic Olefins and Metal Ions. Dependence of the Reaction Course on the Structure of the Olefins

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To investigate the photochemical electron transfer from aromatic olefins to copper(II) or iron(III) ions, a series of substituted styrenes (**1**) was irradiated in the presence of copper(II) or iron(III) salts in methanol, which gave dimethoxylated monomers (**2**) and one or more of three types of dimethoxylated dimers [α,α- (**3**), α,β- (**4**), and β,β-dimers (**5**)]. The formation of these products are reasonably attributed to the participation of the cation radicals of the olefins generated by electron transfer from the excited olefins to the metal ions. Substituents on the substrates are found to govern the reaction products.

Recently, much attention has been paid to the photochemical electron-transfer processes from the viewpoint of mechanistic photochemistry, energy storage, photoimaging, preparative chemistry, *etc.*[1)] On photochemical electron transfer involving styrenes, investigations were reported for the excitation of organic electron acceptors like 1,4-dicyanobenzene or methyl 4-cyanobenzoate followed by electron transfer to their excited state from ground-state styrenes to give the cation radicals of the olefins.[2—4)] On the other hand, few investigation was done for the electron transfer from the excited styrene to an acceptor except a short report by Tsutsumi and Murai that the irradiation of styrene (**1a**) in the presence of copper(II) perchlorate in methanol gave a dimethoxylated monomer **2a** and a dimethoxylated dimer (α,α-dimer **3a**) as isolatable products.[5)]

$$\underset{\textbf{1a}}{\mathrm{PhCH{=}CH_2}} \xrightarrow[\mathrm{Cu^{2+}/MeOH}]{254\ \mathrm{nm}} \underset{\textbf{2a}}{\mathrm{PhCH(OMe)CH_2OMe}}$$

$$+\ \underset{\textbf{3a}\ (\alpha,\alpha\text{-dimer})}{\mathrm{[PhCH(CH_2OMe){-}]_2}}$$

To get deeper insight into the electron transfer from the excited organic compounds, particularly aromatic olefins, to metal ions, a series of styrene derivatives **1** were irradiated in the presence of copperr(II) and iron(III) salts. This paper discribes the results of the reaction; 1) the irradiation gives in addition to **2** and **3**, other isomeric dimethoxylated dimers **4** (α,β-dimer) and **5** (β,β-dimer), 2) the reaction products are similar to those of the electrolysis of the styrene **1** with a platinum anode in the same solvent,[6a)] 3) the reaction course of the cation radicals of **1** is controlled by the substituents on the α-, β-, and *p*-carbons of the olefins **1**.

Results

Photochemical Reaction of Substituted Styrenes in the Presence of Metal Ions in Methanol. In a typical run, styrene (**1a**, 28 mmol) was irradiated in the presence of copper(II) perchlorate (56 mmol) in methanol (300 cm^3) under nitrogen stream at room temperature with a 160-W low pressure mercury lamp for 40 h. After the irradiation, 70% of **1a** was consumed and a dimethoxylated monomer **2a** (yield 41% based on **1a** consumed) was obtained in addition to three types of dimethoxylated dimers [α,α- (**3a**, yield 4%), α,β- (**4a**, 0.7%), β,β- (**5a**, 1.5%)] (see Scheme 1). During the irradiation, a small amount of metallic copper was precipitated. The structure of the products was identified from spectral data in comparison with authentic samples obtained from the anodic oxidation of **1a** in methanol with a platinum or a graphite anode.[6)] The yields of the reaction products were determined by GLPC analysis.

In control experiments, when **1a** was left standing in methanol with $Cu(ClO_4)_2$ for 25 d under nitrogen atmosphere at room temperature without irradiation, **1a** was completely recovered, and also irradiation of **1a** in the presence of $Cu(ClO_4)_2$ in methanol with bromine lamp (effective longer than 400 nm) through a Pyrex filter under nitrogen atmosphere at room temperature gave only a trace amount of **2a**. Moreover, UV spectra of the mixture of **1** and $Cu(ClO_4)_2$ in methanol did not show any new absorption band.

Other styrene derivatives **1** were likewise irradiated in the presence of $Cu(ClO_4)_2$ in methanol. The results are summarized in Table 1 together with the oxidation potentials of the olefins. The use of iron(III) perchlorate instead of copper(II) perchlorate in the photochemical reaction of **1a—d** in methanol gave **2a** (12%),

$$\underset{\textbf{1a–g}}{\mathrm{ArCR{=}CHR'}} \xrightarrow[\mathrm{Cu^{2+}/MeOH}]{h\nu} \underset{\textbf{2a–g}}{\mathrm{ArCR(OMe)CHR'OMe}}$$

$$+\ \underset{\textbf{3a–c,e}\ (\alpha,\alpha\text{-dimer})}{\mathrm{[ArCR(CHR'OMe){-}]_2}}$$

$$+\ \underset{\textbf{4a}\ (\alpha,\beta\text{-dimer})}{\mathrm{PhCH(OMe)CH_2CH(Ph)CH_2OMe}}$$

$$+\ \underset{\textbf{5a–d,f,g}\ (\beta,\beta\text{-dimer})}{\mathrm{[ArCR(OMe)CHR'{-}]_2}}$$

a: Ar=Ph, R=R′=H; b: Ar=4-ClC$_6$H$_4$, R=R′=H;
c: Ar=Ph, R=Me, R′=H; d: Ar=R=Ph, R′=H;
e: Ar=Ph, R=H, R′=Me; f: Ar=4-MeC$_6$H$_4$, R=R′=H;
g: Ar=4-MeOC$_6$H$_4$, R=R′=H

Scheme 1.

Table 1. Photochemical reaction of styrene derivatives in the presence of copper(II) ion

	ArCR=CHR′ 1	Eox[a)] (V)	Conv. (%)	Dimethoxylated Monomer (2,%)[b)]	Dimethoxylated Dimers (%)[c)] α,α (3)	α,β (4)	β,β (5)
1a	PhCH=CH$_2$	1.95	70	41	4	0.7	1.5
1b	4-ClC$_6$H$_4$CH=CH$_2$	1.76	58	13	35	—	6
1c	PhCMe=CH$_2$[d)]	1.60	54	45	5	—	2
1d	Ph$_2$C=CH$_2$[e)]	1.48	53	39	—	—	2
1e	PhCH=CHMe	1.38	67	12	37	—	—
1f	4-MeC$_6$H$_4$CH=CH$_2$	1.38	63	42	—	—	5
1g	4-MeOC$_6$H$_4$CH=CH$_2$[f)]	1.15	79	trace	—	—	34

a) Oxidation potential *vs.* Ag/0.1 mol/dm^3 AgNO$_3$ in MeCN. b) Yield for **2**: [(moles of 2)/(moles of **1** consumed)]×100. c) Yield for **3**, **4**, or **5**: [(moles of **3**, **4**, or **5**)/(moles of **1** consumed)]×200. d) Another product: PhCMe$_2$OMe (20%). e) Other products: Ph$_2$CO (10%) and Ph$_2$C(OMe)Me (28%). f) Other products: 4-MeOC$_6$H$_4$CH(OMe)Me (12%) and *trans*-1,2-bis(4-methoxyphenyl)cyclobutane (10%).

2b (13%), **2c** (24%), and **2d** (24%), respectively, but did not afford any other isolatable products.

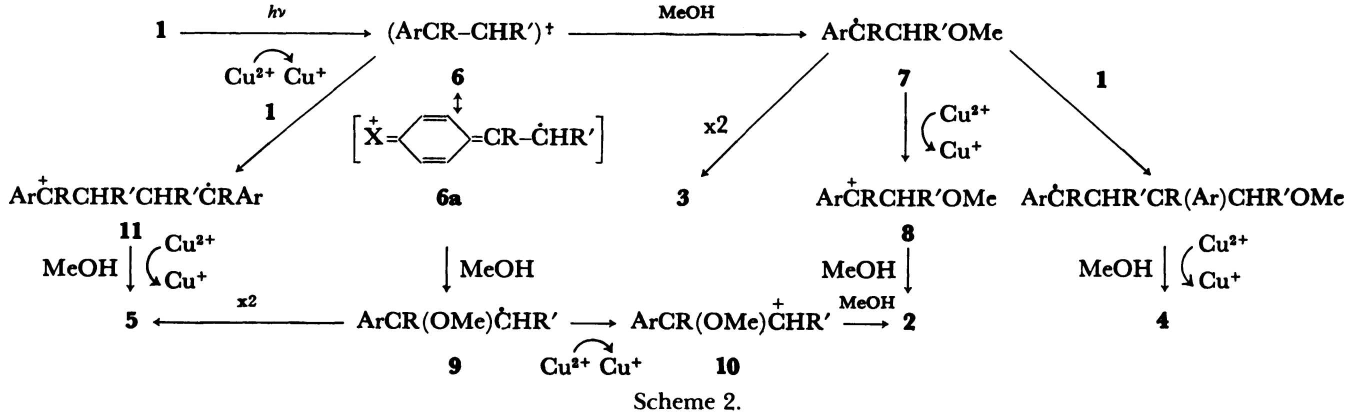
Discussion

Substituent Effect on the Selectivity for Products. As Table 1 shows, **1a**, **1b**, and **1c** with the higher oxidation potentials among **1**'s afforded **2**, α,α-dimer **3**, and β,β-dimer **5**, accompanied by α,β-dimer **4** from **1a**. On the other hand, **1d**, **1f**, and **1g** with the lower oxidation potentials gave no α,α-dimer **3** but exclusively β,β-dimer **5** together with **2**. On the basis of the above selectivity for the production of the dimethoxylated dimers, **1a**, **1b**, and **1c** are now classified as group I olefins, while **1d**, **1f**, and **1g** as group II olefins. **1e** is classified as group I in view that irradiation of **1e** with Cu(ClO$_4$)$_2$ in methanol gave exclusively α,α-dimer **3e** together with **2e** but no β,β-dimer **5e**, although **1e** has the same oxidation potential as **1f** of group II. As the above results indicate, the selectivity for production of dimethoxylated dimers is governed by the substituent on the α-, β-, or *p*-carbon of **1**; group II olefins with electron-donating groups such as *p*-methyl or *p*-methoxyl group tend to produce β,β-dimer **5** selectively, while group I olefins without electron-donating groups on the aromatic nucleus tend to give α,α-dimer **3** rather than β,β-dimer **5**.

Mechanism. Formation of the various products is satisfactorily understood in terms of a mechanism depicted in Scheme 2.

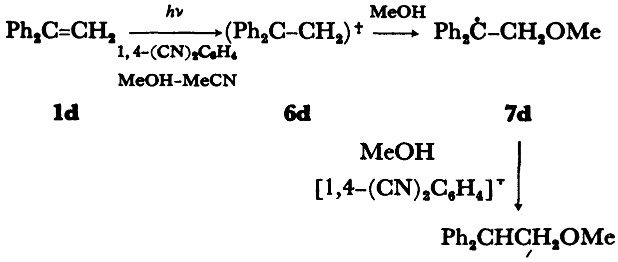
The initial step after the excitation of **1** is certainly the electron transfer from the excited state of **1** to the metal ions to generate the cation radical **6**.

In group I olefins, the production of α,α-dimer **3** seems to be plausible only through dimerization of radical **7**, which results from the addition of methanol to β-carbon of the cation radical **6**. Also, radical **7** will collapse into α,β-dimer **4** through addition to the olefins, or be further oxidized by copper(II) ion into carbocation **8** finally giving rise to **2**. However, in the photochemical reactions of group II olefins, production of neither α,α-dimer **3** nor α,β-dimer **4** suggests that radical **7** does not participate as a reaction intermediate. In cation radicals **6** arising from group II olefins as compared with those arising from group I olefins, the positive charge tends to be more highly distributed on the aromatic ring and concurrently the unpaired electron must have higher density on the terminal carbon. This situation can be schematically expressed by a resonance canonical form (**6a**) and was actually observed in ESR spectrum of the cation radicals of *N*,*N*-dimethylalkenamines generated by electrolysis.[7)] Therefore, **6** from group II olefins, owing to their higher spin density on their terminal carbon atoms, will more facilely add to olefins than those from group I olefins finally leading to β,β-dimer **5**, and consequently, due to the less positive charge population on their terminal carbon atoms, will react with methanol on their α-carbon atoms to give radical **9**, which will be further oxidized by copper(II) ion to give carbocations **10** finally affording **2**.[8)]



Scheme 2.

For the methanolysis of the cation radical **6**, electron transfer between **1d** and excited electron acceptors like 1,4-dicyanobenzene and 1-cyanonaphthalene in methanol was reported to give anti-Markownikoff adduct of methanol to the olefin through the formation of radical **7d** as an intermediate.[2d] It is noticeable that, in the present reaction of group I olefins, methanolysis of the intermediate cation radical **6** occurs by the same orientation as the above reaction, however, for group II olefins, methanolysis of the cation radical **6** proceeds by a different orientation giving **9**.



$$\mathrm{Ph_2C{=}CH_2} \xrightarrow[\substack{1,4\text{-}(\mathrm{CN})_2\mathrm{C_6H_4}\\ \mathrm{MeOH\text{-}MeCN}}]{h\nu} (\mathrm{Ph_2C\text{-}CH_2})^{\dagger} \xrightarrow{\mathrm{MeOH}} \mathrm{Ph_2\dot{C}\text{-}CH_2OMe} \xrightarrow[{[1,4\text{-}(\mathrm{CN})_2\mathrm{C_6H_4}]^{\mathsf{T}}}]{\mathrm{MeOH}} \mathrm{Ph_2CHCH_2OMe}$$

1d　**6d**　**7d**

The free-energy change (ΔG) for the electron-transfer processes from the excited olefin to metal ions is given by Eq. 1,[9] where $E(D/D^+)$ and $E(A^-/A)$ are the oxidation potential of the donor (D) and the reduction potential of the acceptor (A), respectively, and $e_0{}^2/\varepsilon\alpha$ is the energy gained by bringing the two ion radicals to the encounter distance (α) in a solvent of dielectric constant ε (methanol, ε_{25°=32.7) and estimated to be 0.065 eV (1.5 kcal/mol) in methanol. The singlet energies, E_s, of 4-methoxystyrene and styrene are obtained from the fluorescence spectrum or literature,[10] respectively. In Table 2 are listed the calculated values of ΔG for the olefins. The electron-transfer process from the excited olefins to copper(II) ion is shown to be exothermic.

$$\Delta G(\mathrm{kcal/mol}) = 23.06[E(D/D^+) - E(A^-/A) - e_0^2/\varepsilon\alpha] - E_s \quad (\mathrm{kcal/mol}) \quad (\mathrm{Eq.\ 1})$$

The proposed mechanism in Scheme 2 requires the second electron transfer from radical **7** or radical **9** to metal ions. The free-energy change of this process cannot be easily estimated because the oxidation potentials of radical **7** and **9** cannot be measured.[11] However, their oxidation potentials seem to lie at more cathodic levels than the reduction potentials of the metal ions. Therefore, the second electron-transfer process seems also exothermic as reported by Kochi *et al.*[12–14]

TABLE 2. SINGLET ENERGIES OF THE OLEFINS AND CALCULATED ΔG VALUES, USING Eq. 1, FOR THE ELECTRON-TRANSFER PROCESS INVOLVING THE SINGLETS OF THE OLEFINS AND COPPER(II) ION

	Eox/V[a]	Ered/V[b]	E_s (kcal/mol)	ΔG (kcal/mol)
$\mathrm{PhCH{=}CH_2}$	1.95	—	98[c]	−33
$\mathrm{4\text{-}MeOC_6H_4CH{=}CH_2}$	1.15	—	94[d]	−48
$\mathrm{Cu(ClO_4)_2}$	—	−0.88		

a) Oxidation potential. b) Reduction potential. c) Taken from S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, New York (1973), p. 20. d) Obtained from the fluorescence spectrum.

Experimental

The IR spectra were obtained from a Hitachi 260-50 infrared spectrophotometer and a Hitachi 260-10 infrared spectrophotometer. The NMR spectra were recorded on a JEOL JNM-MH-100 spectrometer, a JEOL-FX-100 spectrometer, and a JEOL-FX-90Q spectrometer. The mass spectra were determined with a Hitachi RMU-6MC mass spectrometer. Gas-liquid phase chromatographic analysis was performed on a Hitachi 163 gas chromatograph equipped with a flame ionization detector.

Materials. Styrene, 4-chlorostyrene, α-methylstyrene, 1,1-diphenylethylene, and *trans*-β-methylstyrene were commercial samples from Wako Pure Chemical Industries. 4-Methylstyrene and 4-methoxystyrene were prepared by decarboxylation of the corresponding cinnamic acids as described in the literature.[15] Copper(II) perchlorate and iron(II) perchlorate were purchased from Kanto Chemical.

Preparation of Authentic Samples. Authentic samples of dimethoxylated monomers **2** (except for **2c**) and dimethoxylated dimers (except for **3b**, **3c**, and **3e**) were prepared by anodic oxidation of olefins **1** in methanol.[6]

Preparation of 1,2-Dimethoxy-1-phenylpropane (2e). Metallic sodium (1 g, 43 matom) was dissolved in 100 cm^3 of methanol and then freshly distilled β-methylstyrene (4.5 g, 38 mmol) was added to the mixture. The mixture was subjected to constant-current (1 A) elctrolysis at a platinum plate anode (approximate area 60 cm^2) with a platinum wire as a cathode and SCE as a reference electrode under argon atmosphere at room temperature for 2 h. Because a current was not able to be maintained at 1 A after 2 h, constant-current electrolysis was continued at 0.1 A for 3 h. The electrolysis mixture was diluted with water (300 cm^3) and extracted with dichloromethane (80 cm^3×2). The organic layer was washed with water, dried ($\mathrm{Na_2SO_4}$), and analyzed by GLPC. The products obtained by evaporation of the dichloromethane solution were separated with flash-column chromatography.[16] The structures of the products were determined on the basis of their spectral data and elemental analysis.

PhCH(OMe)CH(Me)OMe (2e), erythro-*form*: Bp 59 °C/4 mm; MS: *m/z* 180 (M$^+$), 149, 121 (100%), 117, 105, 91; IR (neat): 1100 cm^{-1}, $\nu_{\mathrm{C\text{-}O}}$; ^{1}H-NMR ($\mathrm{CDCl_3}$): δ=1.12 (d, J=8 Hz, 3H, Me), 3.16 (s, 6H, 2MeO), 3.18 (m, 1H, CH), 4.14 (d, J=4 Hz, 1H, CH), 7.30 (s, 5H, Ph); ^{13}C-NMR ($\mathrm{CDCl_3}$): δ= 139.2 (s), 128.0 (d), 127.4 (d), 86.0 (d), 80.6 (d), 57.1 (q), 57.0 (q), 14.3 (q); Found: C, 73.30; H, 8.92%. Calcd for $\mathrm{C_{11}H_{16}O_2}$: C, 73.29; H, 8.94%. *threo*-form: Bp 62 °C/4 mm: MS: *m/z* 180 (M$^+$). 149, 121 (100%), 117, 105, 91; IR (neat): 1100 cm^{-1}, $\nu_{\mathrm{C\text{-}O}}$; ^{1}H-NMR ($\mathrm{CDCl_3}$): δ=0.92 (d, J=7 Hz, 3H, Me), 3.24 (s, 3H, OMe), 3.40 (s, 3H, OMe), 3.50 (m, 1H, CH), 4.08 (d, J=7 Hz, 1H, CH), 7.28 (s, 5H, Ph); ^{13}C-NMR ($\mathrm{CDCl_3}$): δ=139.1 (s), 128.2 (d), 127.8 (d), 127.6 (d), 87.4 (d), 80.0 (d), 57.3 (q), 57.0 (q), 15.6 (q); Found: C, 73.19; H, 8.86%. Calcd for $\mathrm{C_{11}H_{16}O_2}$: C, 73.29; H, 8.94%.

Measurements of the Oxidation Potentials of Styrenes. Cyclic voltammetric data were obtained using a three-electrode cell with a Hokuto HA-201 potentiostat and a Hokuto HB-104 function generator. The working electrode was a platinum wire (1 mm diameter) sealed into glass and a counter electrode was a platinum gauze. A Ag/$\mathrm{AgNO_3}$ (0.1 mol/dm^3)

electrode was used as a reference electrode and 0.1 mol/dm^3 tetraethylammonium perchlorate as supporting electrolyte. The current-potential curves were recorded directly from the output of the potentiostat on a Rika Denki RW-11 X-Y recorder. The measured value for **1d** agreed well with the reported value.[17)]

Irradiation of Styrenes with Copper(II) Salt in Methanol. A solution of styrenes **1** (5 g, 28—48 mmol) in methanol (300 cm^3) containing copper(II) perchlorate (21—36 g, 56—96 mmol) was irradiated under a nitrogen stream at room temperature with a 160-W low pressure mercury lamp (Riko UVL-160LA) for 49 h. The reaction mixture was diluted with water (500 cm^3) and extracted with dichloromethane (100 cm^3×2). The organic layer was washed with water and dried (Na_2SO_4). After evaporation of the solvent, the residue was subjected to flash-column chromatography[16)] on silica gel to give **2**, **3**, **4**, and **5**. The structures of the products (**2**, **3**, **4**, and **5**) were confirmed from their spectral data and elemental analysis, or by comparison of their spectral data with those of authentic samples. The organic layer was analyzed by GLPC to determine the yields of the products (Table 1).

1,2-Dimethoxy-2-phenylpropane (2c): Oil; bp 64 °C/3 mm; MS: *m/z* 165, 149, 134 (100%); IR (neat): 1070—1140 cm^{-1}, $\nu_{C\text{-}O}$; ^{1}H-NMR ($CDCl_3$): δ=1.52 (s, 3H, Me), 3.10 (s, 3H, OMe), 3.30 (s, 3H, OMe), 3.40—3.50 (ss, 2H, OCH_2), 7.15—7.50 (m, 5H, aromatic H); ^{13}C-NMR ($CDCl_3$): δ= 142.5 (s), 128.1 (d), 127.2 (d), 126.5 (d), 80.8 (t), 78.9 (s), 59.5 (q), 50.6 (q), 20.1 (q); Found: C, 72.97; H, 9.02%. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%.

1,4-Dimethoxy-2,3-bis(4-chlorophenyl)butane (3b): Mp 127—128 °C; MS: *m/z* 342 (M^++2), 340 (M^+), 310, 308, 172, 170 (M^+/2), 169, 156, 139; IR (KBr): 1100 cm^{-1}, $\nu_{C\text{-}O}$; ^{1}H-NMR ($CDCl_3$): δ=3.08 (s, 6H, 2MeO), 3.16—3.34 (broad, 6H, 2CH and $2CH_2$), 7.20 (s, 8H, aromatic H); ^{13}C-NMR ($CDCl_3$): δ= 140.4 (s), 132.4 (s), 129.8 (d), 128.5 (d), 74.5 (t), 58.9 (q), 47.7 (d); Found: C, 63.81; H, 5.93; Cl, 20.80%. Calcd for $C_{18}H_{20}Cl_2O_2$: C, 63.72; H, 5.94; Cl, 20.90%.

1,4-Dimethoxy-2,3-dimethyl-2,3-diphenylbutane (3c): Oil; a 1:1 mixture of *meso*- and *dl*-form; MS: *m/z* 221, 149 (M^+/2, 100%), 134; IR(neat): 1100 cm^{-1}, $\nu_{C\text{-}O}$; ^{1}H-NMR ($CDCl_3$): δ= 1.30 and 1.40 (s, 6H, 2Me), 3.15 and 3.18 (s, 6H, 2MeO), 3.34 and 3.60 (m, 4H, $2OCH_2$), 6.80—7.40 (m, 10H, 2Ph); ^{13}C-NMR ($CDCl_3$): δ=142.9 (s), 128.7 (d), 126.8 (d), 125.9 (d), 78.1 (t), 58.8 (q), 47.8 (s), 47.6 (s), 20.6 (q), 20.3 (q); Found: C, 80.44; H, 8.58%. Calcd for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78%.

2,5-Dimethoxy-3,4-diphenylhexane (3e): Mp 175—176 °C; MS: *m/z* 267, 209 (100%), 150; IR(KBr): 1130—1070 cm^{-1}, $\nu_{C\text{-}O}$; ^{1}H-NMR ($CDCl_3$): δ=0.74 (d, 6H, 2Me), 3.20 (m, 2H, 2CH), 3.20 (s, 6H, 2MeO), 3.22 (broad, 2H, 2CH), 7.24—7.60 (m, 10H, 2Ph); ^{13}C-NMR ($CDCl_3$): δ=140.9 (s), 130.4 (d), 127.7 (d), 126.1 (d), 76.1 (d), 56.3 (q), 54.3 (d), 17.0 (q); Found: C, 80.69; H, 8.82%. Calcd for $C_{20}H_{26}O_2$: C, 80.54; H, 8.72%.

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