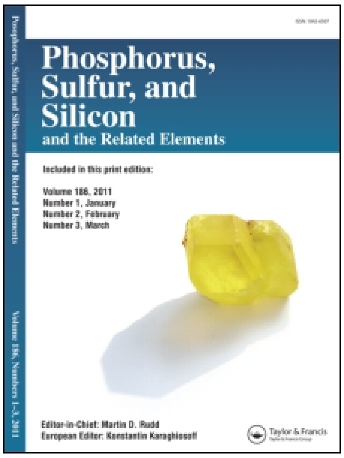

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INTRAMOLECULAR REARRANGEMENT OF BIS(3,4-METHYLENEDIOXYPHENYL) METHYLPHOSPHONATE INDUCED BY SINGLE ELECTRON-TRANSFER OXIDATION

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INTRAMOLECULAR REARRANGEMENT OF BIS(3,4-METHYLENEDIOXYPHENYL) METHYLPHOSPHONATE INDUCED BY SINGLE ELECTRON-TRANSFER OXIDATION

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Photo-sensitized oxidation of bis(3,4-methylenedioxyphenyl) methylphosphonate (**1**) with 9,10-dicyanoanthracene (DCN) in MeCN gave 2-(3,4-methylenedioxyphenyl)-3,4-methylenedioxyphenyl methylphosphonate (**2**) selectively through an intramolecular rearrangement of a 3,4-methylenedioxyphenyl group. Similar results were obtained by oxidation with $Fe(phen)_3^{3+}$ and by γ-radiloysis in 1,2-dichloroethane. Upon direct UV-irradiation of **1** in MeOH, **2** and bis(3,4-methylenedioxy)biphenyl (**3**) were obtained.

Keywords: bis(3,4-methylenedioxyphenyl) methylphosphonate; 9,10-dicyanoanthracene; 2-(3,4-methylenedioxyphenyl)-3,4-methylenedioxyphenyl methylphosphonate; iron(III)(1,10-phenanthroline) perchlorate photolysis; γ-radiloysis

INTRODUCTION

It has been reported that upon direct UV-irradiation bis(4-methoxyphenyl) methylphosphonate in MeOH gave 4,4′-dimethoxybiphenyl and 2,4′,5-trimethoxybiphenyl, which were formed by *ipso*-coupling of two 4-methoxyphenyl groups of the phosphonate via an intramolecular eximer and by intramolecular 1,5-rearrangement of a 4-methoxyphenyl group via a singlet excited monomeric phenyl group, followed by methanolysis, respectively (Scheme 1).[1,2,3]

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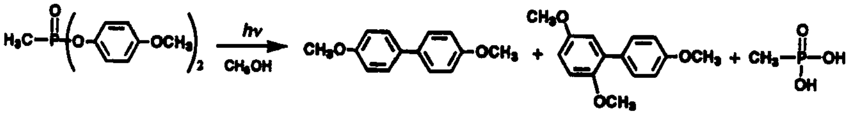
* Corresponding author.



SCHEME I

It has been found that bis(3,4-methylenedioxyphenyl) methylphosphonate (**1**) gave 2-(3,4-methylenedioxyphenyl)-3,4-methylenedioxyphenyl methylphosphonate (**2**) and bis(3,4-methylenedioxy)biphenyl (**3**) under similar conditions. Product **2** was also obtained selectively by photo-sensitized oxidation of **1** with 9,10-dicyanoanthracene (DCA) in MeCN, by oxidation with $Fe(phen)_3^{3+}$, or by γ-radiolysis in 1,2-dichloroethane. In this paper, these formation mechanisms of product **2** will be discussed.

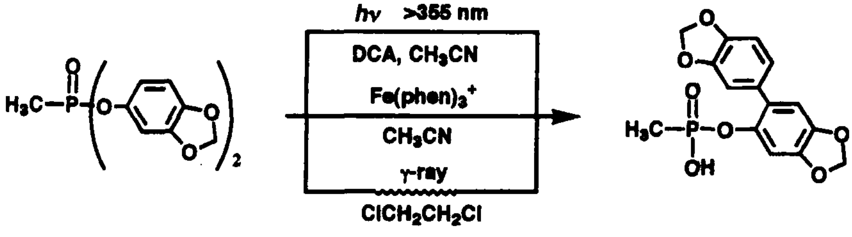
RESULTS AND DISCUSSION

Photosensitized Oxidation with 9,10-Dicyanoanthracene (DCA)

Photoinduced electron-transfer process between an electron accepter and an electron donor has received increasing attention recently.[4] An electron-deficient photo-sensitizer, such as DCA, oxidizes certain substrates in polar solvents.[5] DCA absorbs light at 400 nm and emitts strong fluorescence bands at 440, 460 and 490 nm in MeCN. The phosphona uenched its fluorescence. When an MeCN solution of **1** (1 mM) and DCA (M) was irradiated for 3 h with light of >355 nm, which was absorbed by only DCA, the only product **2** was obtained in a yield of 31%. This fact suggests that photo-excited DCA oxidized phosphonate **1** to give product **2** through the formation of a cation radical.

Oxidation with Iron(III)(1,10-Phenanthroline) Perchlorate ($Fe(phen)_3^{3+}$)

It is well known that a standard reduction potential of $Fe(phen)_3^{3+}$ is 1.14 volt vs. SCE in MeCN[6,7], which oxidizes certain substrates in polar solvents accompanying a change of color from blue to light brown. An MeCN solution of **1** (1.0 mM) and $Fe(phen)_3^{3+}$ (1.2 mM) was allowed to stand for 2 h at room temperature. Product **2** was obtained in a yield of 24.7%. This fact suggests that the formation of **2** may proceed through a cation radical generated from **1** by an intermolecular single electron oxidation by $Fe(phen)_3^{3+}$ (Scheme 2).



SCHEME 2

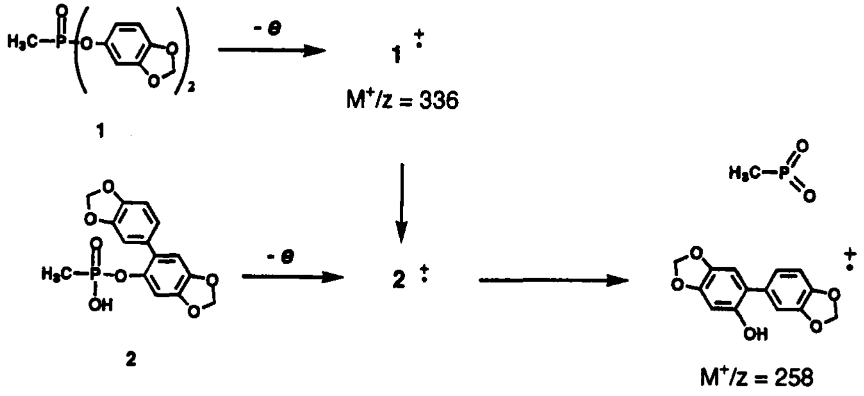
γ-Radiolysis with ^{60}Co in 1,2-Dichloroethane

When a 1,2-dichloroethane solution of **1** (10 mM) was irradiated with ^{60}Co γ-ray for 3 h, the conversion of **1** attained at 46%, and **2** was obtained in a yield of 25% (Scheme 2).

The generation of the high energy cationic species upon γ-irradiation under these conditions has been well known.[8] Therefore, it was suggested that product **2** was formed through a cationic intermediate of **1** generated by intermolecuar hole-transfer in the solution.

Ionization by Electron Impact

Ionization of **1** caused by electron impact (10–20 eV) using a mass spectrometer gave mainly the peaks of m/z = 336 (base peak), 258 and 200. The peak of m/z = 258, which attained at 80% of the base peak abundance, corresponded to the mass number of bis(3,4-methylenedioxy)biphenyl-6-ol$^+$ ($C_{14}H_{40}O_5{}^+$). A similar fragment pattern was also observed in the mass spectrum of **2**, accompanied by



SCHEME 3

several other peaks similar to those of **1** (Scheme 3). This result suggests that **2** may be formed through a cation radical intermediate from **1** generated by electron impact.

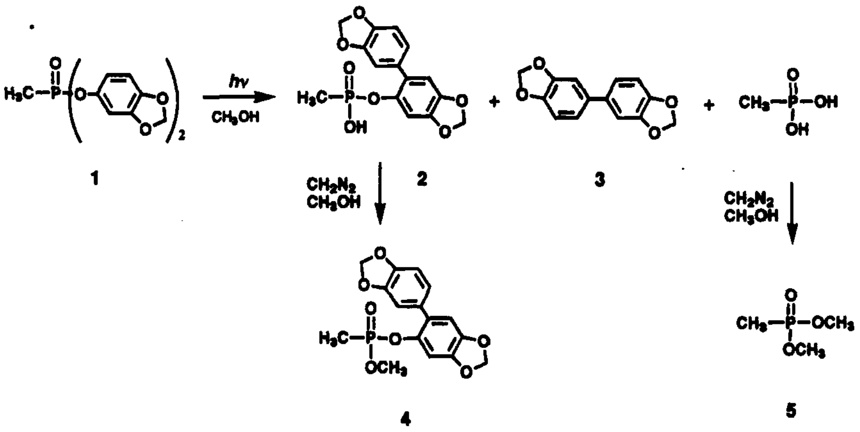
Direct Photolysis

Upon UV-irradiation of **1** (10^{-2} mM) in MeOH for 1 h (conversion 72%), two products **2** (60%, $\phi = 0.117$) and **3** (6%, $\phi = 0.017$) were given. After treatment of the photolyzed product with diazomethane, the methyl ester of **2** (**4**) (58%) and dimethyl methylphosphonate (**5**)(5.5%) were obtained (Scheme 4).

Fluorescence Spectra

Figure 1 shows a fluorescence spectrum of **1** in MeOH (10^{-4} M). Only one emission band having a maximum at 326 nm was observed.

This spectrum was different apparently from that of bis(4-methoxyphenyl) methylphosphonate, which consisted of two emission bands (325 and 360 nm) arising from a monomeric singlet excited species (monomer) and an intramolecular excimer.[2)] By a single photon-counting method it was revealed that the emission band of **1** consisted of two components having different lifetimes of 2.5 (at 326 nm) and 18 ns (at 400 nm). The shorter lifetime may be assigned to the monomer by comparison with an emission spectrum of diethyl (3,4-methylenedioxyphenyl) phosphate. From Stren-Volmer analysis by quenching a



SCHEME 4

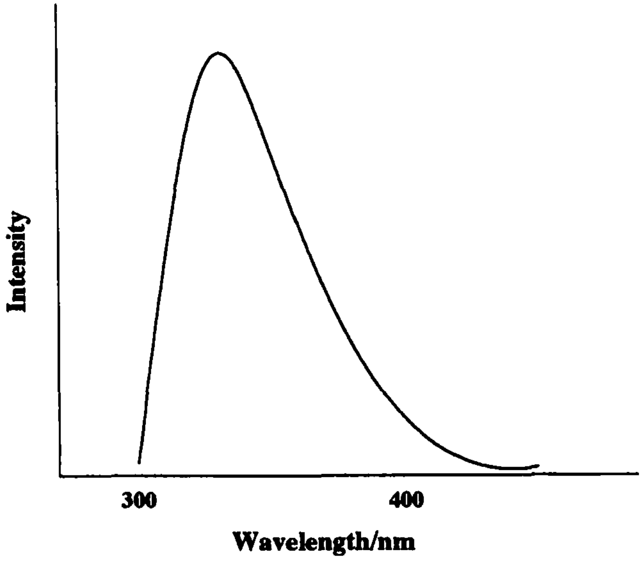


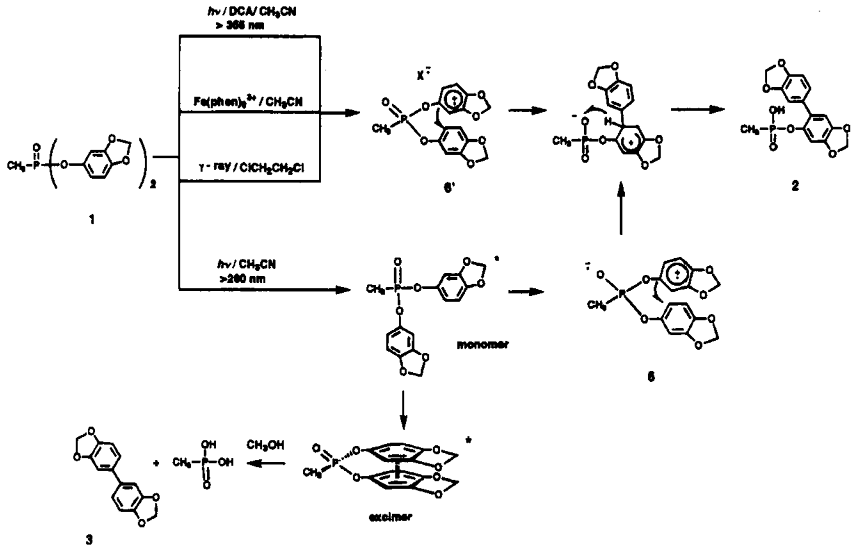
FIGURE 1 Fluorescence spectrum of **1** in methanol (0.1 mM, λex = 280 nm).

fluorescence band at 326 nm by oxygen, $k_q\tau_m = 40\ M^{-1}$ was obtained. Another $k_q\tau_e$ at 400 nm could not be determined due to lower emission intensity and overlapping with a large emission band of product **2**.

The formation processes of both **2** and **3** were also quenched by oxygen in different ways, and the $k_q\tau$ values for **2** and **3** were 42 and 88 M^{-1}, respectively. The former $k_q\tau$ agreed nearly with the $k_q\tau_m$. Therefore, it was concluded that the formation of **2** might proceed through a singlet excited monomer rather than an intramolecular excimer.

Finally, the mechanism of formation of **2** might be as follows; upon UV-irradiation a singlet excited species having a cationic aryl group **6** may be given by photo-chemical intramolecular charge-transfer from an aryl group to phosphoryl oxygen. The aryl cation may give **2** through intramolecular nucleophilic 1,5-rearrangement of the aryl group.

The similar cation radical intermediates **6′** were given by one-electron oxidation with DCA-photosensitized, with $Fe(phen)_3^{3+}$, by γ-radiolysis in dichloroethane. The intermediates **6** and **6′** must have similar reactivities. In these intermediates, a cationic aryl group may attack at the neighboring aromatic ring (ortho-position) to give **2** (Scheme 5).



SCHEME 5

EXPERIMENTAL

Apparatus

Melting points were obtained with a Yanagimoto micro melting point apparatus. CHN microanalyses were obtained with a Perkin-Elmer Model 240 analyzer. UV-visible spectra were recorded on a Hitachi 150–20 spectrometer. Steady-state fluorescence spectra were recorded on a Hitachi 850 type fluorescence spectrometer. ^{1}H- and ^{13}C-NMR spectra were determined in $CDCl_3$ with tetramethylsilane as an internal standard on a JOEL EX-270 spectrometer. GLC analyses were carried out by use of a Shimadzu GC-7A with a column of 2% Silicone OV-17 on Chrom. GC-MS spectra were recorded with a JMS-DX 300 and high-resolution mass spectra were also obtained on a JMS-01SG-2 instrument. HPLC analyses were carried out by use of a Shimadzu LC-10AS instrument with a column of Shiseido CAPCELL PAK C18 AG 120. Photolyses were carried out with a 300 W high pressure mercury lamp EHBW-300, or a 60 W low pressure mercury lamp ELJ-60 (Eikosha Co., Ltd.).

Material. Bis(3,4-Methylenedioxyphenyl) Methylphosphonate (1)

A mixture of 3,4-methylenedioxyphenol and triethylamine in ether was added dropwise into an ether solution of one-half amount of methylphosphonyl dichloride. After usual workup, the crude product was chromatographed on silica gel (eluent: chloroform/hexane = 1 : 3) to give a product. mp 71–73 °C, (Found: C, 53.47; H, 3.93; P, 9.44%.

$C_{15}H_{13}O_7P$ requires: C, 53.58; H, 3.90; P, 9.21%). UV λ_{max} (MeOH) 287.2 nm(ϵ/$M^{-1}cm^{-1}$ 8480), (MeCN or THF) 288.8 nm(8510). $^1H(CDCl_3; Me_4Si)$ δ = 6.70(m, 6H), 5.96(s, 4H), 1.74(d, J_{PH} = 17.5 Hz, 3H). m/z = 336(M^+; 100), 258(90), 200(10), 184(10), 138(15), 167(5), 121(5).

Photosensitized Oxidation with DCA

An MeCN solution of **1** (1 mM) was irradiated in the presence of DCA (0.5 mM) in a Pyrex cell with a high pressure Hg lamp fitted with a filter ($BiCl_3$/HCl solution >355 nm) for 3 h. The reaction was followed by GLC analyses (conversion 35%). After MeOH was evaporated off, the product was isolated with column chromatography using silica gel (eluent; benzene and MeOH/C_6H_6 mixture). The product was confirmed to be 2-(3,4-methylenedioxyphenyl)-3,4-methylenedioxyphenyl methylphosphonate (**2**) as a colorless viscous oil in a yield of 31% as follows. Found: C, 53.20; H, 3.89; P, 9.39%. $C_{15}H_{13}O_7P$ requires: C, 53.58; H, 3.90; P, 9.21%. $^1H(CDCl_3; Me_4Si)$ δ = 1.03(3H, d, J_{PH} = 17.2), 3.35(1H, s), 5.88(2H, s), 5.91(2H, s), 6.70(1H, s), 6.78(1H, d, J = 7.9, 6.88(1H, dd, J = 8.3, 1.7 Hz), 6.98(1H, d, J = 1.7 Hz), 7.10(1H, s). m/z = 258(100), 200(10), 128(5). After methylation of **2** with diazomethane, m/z was 350(M^+; 10), 258(100), 200(5). After hydrolysis of **2** with a 6 N HCl solution under refluxing conditions for 3 h, a result of GCMS analysis showed a m/z of 258(M^+), which was corresponding to the m/z of bis(3,4-methylenedioxy)-biphenyl-5-ol.

Oxidation with $Fe(phen)_3{}^{3+}$

$Fe(phen)_3{}^{3+}(ClO_4)_3 \cdot H_2O$ was prepared by the reaction of iron(II) sulfate and 1,10-phenanthroline, followed by oxidation with chlorine and treatment with sodium perchlorate.6) An MeCN solution of **1** (10 mM) and $Fe(phen)_3{}^{3+}$ (1.2 mM) was allowed to stand for 2 h at room temperature. The color of the reaction mixture changed from blue to light brown. The product **2** was obtained in a yield of 24.7% (conversion 31.0% by HPLC analysis).

γ-Radiolysis with ^{60}Co in 1,2-Dichloroethane

A 1,2-di-chloroethane solution of **1** (10 mM) was irradiated under argon atmosphere with γ-ray from ^{60}Co (using a the source at dose rate of 1.8×10^4 rd/min, in Radiation Laboratory, Osaka University) for 3 h at ambient temperature. When the conversion of **1** was attained at 46%, the product **2** was also obtained in a yield of 25% as a main product. The formation of small amount of other products was also observed, but they could not be identified.

Direct Photolysis

A 200 ml MeOH solution of **1**(10^{-2} M) was charged in a doughnut type quartz cell with 10 mm thick, and argon was bubbled through the solution to purge off dissolved air. Irradiation was carried out with a 300 W high pressure mercury lamp at ambient temperature for 1 h (conversion 72%). The products were separated with column chromatography using silica gel (eluent; benzene and MeOH/C_6H_6 mixture), One of the products was confirmed to be **2** (60%, ϕ = 0.117). Another product was confirmed to be bis(3,4-methylenedioxy)biphenyl (**3**, 6%, ϕ = 0.017) by elementary analysis, ^{1}H NMR and mass spectra. mp 141–142 °C; ^{1}H(CDCl$_3$; Me$_4$Si) δ = 5.98(4H, s), 6.83(2H, d, J = 7.6), 6.96(2H, d, J = 7.6, 1.0), 6.98(2H, s). ^{13}C(CDCl$_3$; Me$_4$Si) δ = 101.1, 107.5, 108.5, 120.3, 135.4, 146.8, 148.1. m/z = 242 (M$^+$; 100), 120 (10). It was also confirmed by comparison with the GLC-retention time and the mass spectrum of the authentic sample, prepared by the coupling reaction of 4-bromo-1,2-methylenedioxybenzene in the presence of NiBr$_2$(PPh$_3$)$_2$/Zn/Et$_4$NI in THF at 50°C for 5 h.$^{9)}$

Measurement of Quantum Yield

The quantum yields were measured as follows: A 3-ml MeOH solution of **1**(1.0×10^{-2} M) saturated with argon gas in a quartz cell (10 mm × 10 mm) was irradiated using a low-pressure Hg lamp (60 W). Photolysis was carried out up to 10% conversion. Actinometry was carried out by use of a potassium trioxalatoferrate(III) solution.$^{10)}$ The product yields were determined by HPLC and GLC after methylation.

Quenching Fluorescence by Oxygen

Six 3-ml MeOH solutions of **1**(1.0×10^{-4} M) were charged in six separate quartz cells (10 mm × 10 mm). An argon, air, 40, 60, 80% oxygen/nitrogen or oxygen gas was bubbled into the solutions until saturating at 20°C for 10 min, respectively. Concentrations of oxygen in these solutions were evaluated from their solubility in MeOH to be 0.0, 1.51, 3.82, 5.72, 7.63 and 9.54 × 10^{-3} M, respectively. Their emission spectra were recorded on a fluorescence spectrometer. The $k_q\tau$ was determined by the following Stern-Volmer equation [1],

$$I^0/I = 1 + k_q\tau[O_2] \qquad (1)$$

Where I and I^0 are the intensities of the fluorescence of **1** in the presence and absence of oxygen, respectively, and k_q is a quenching rate constant and τ is a fluorescence lifetime.

Quenching the Formation of Product by Oxygen

Six 3-ml MeOH solutions of **1** (1.0 × 10^{-2} M) saturated with the prescribed concentration of oxygen were prepared, respectively, and the quantum yields of **2** (ϕ_2) and **3** (ϕ_3) were measured. The $k_q\tau$'s were determined by the following equations; for **2**

$$\phi^0{}_2/\phi_2 = 1 + k_{q2}\tau_2[O_2] \qquad (2)$$

Equation [3] is based on the assumption that product **3** was formed through the excimer, which is not equilibrated with the monomer

$$(\ \phi^0{}_3/\phi_3)/(\phi^0{}_2/\phi_2) = 1 + k_{q3}\tau_3[O_2] \qquad (3)$$

where ϕ and ϕ^0 are quantum yields of formation of products in the presence and absence of oxygen, respectively, k_{q2} *and* k_{q3} are quenching rate constants of **2** and **3** by oxygen, respectively, and τ_2 and τ_3 are the lifetimes of the monomeric excited species and the excimer.

References

[1] Okamoto, Y., Nakamura, M., Shi, M. and Takamuku, S. (1992) *Photochemistry and Photobiology*, **56**, 403.
[2] Nakamura, M., Sawasaki, K., Okamoto, Y. and Takamuku, S. (1994) *J. Chem. Soc. Perkin Trans.*, **1**, 141.
[3] Nakamura, M., Shi, M., Okamoto, Y. and Takamuku, S. (1995) *J. Photochem. and Photobiology*, **85**, 111.
[4] Mariano, P. S. and Stavinoha, J. L. (1984) *Synthetic Organic Photo-chemistry*, ed by W. M. Horspool, Plenum Press, New York, p. 199.
[5] Eriksen, J. and Foote, C. S. (1978) *J. Phys. Chem.*, **82**, 2659; Eriksen, J. and Foote, C. S. (1980) *J. Am. Chem. Soc.*, **102**, 6083; Schaap, A. P., Siddiqui, S. and Gagnon, S. D. (1983) *J.*

Am. Chem. Soc. **105**, 5139; Xu, J., He, J. and Qian, Y. (1991) *J. Chem. Soc., Chem. Commun.*, 714.

[6] Schilt, A. A. and Taylor, R. C. (1959) *J. Inorg. Nucl. Chem.*, 9, 211.

[7] $Fe(phen)_3^{3+} + e^- \rightarrow Fe(phen)_3^{3+}$ 1.14 volt vs. SCE in MeCN (CRC *Handbook of Chemistry and Physics*, 54th ed. by Weast, R. C. 1973–1974 CRC Press Ohio, D-120.

[8] Kira, A., Arai, S. and Imamura, M. (1973) *Int. J. Radiat. Phys. Chem.*, **5**, 127.

[9] Iyoda, M., Otsuka, H., Sato, K., Nisato, N. and Oda, M. (1990) *Bull. Chem. Soc. Jpn.*, **63** 80.

[10] Murov, L. S. (1973) *Handbook of Photochemistry*; Marcel Dekker, New York, p 89.