

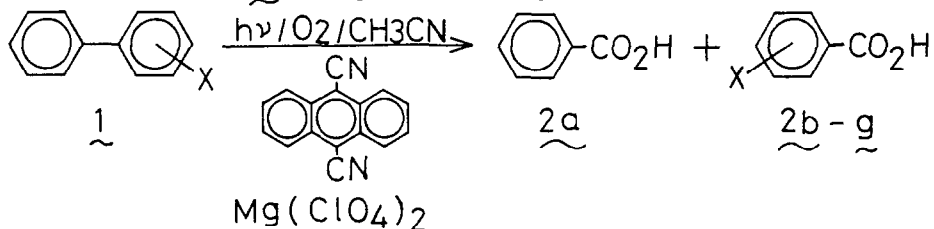
ELECTRON-TRANSFER MEDIATED PHOTOOXYGENATION OF BIPHENYL  
AND ITS DERIVATIVES IN THE PRESENCE OF  $Mg(ClO_4)_2$

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Summary: The 9,10-dicyanoanthracene-sensitized photooxygenation of biphenyl and its derivatives in the presence of  $Mg(ClO_4)_2$  in acetonitrile brought about the oxidative cleavage of benzene nucleus to give benzoic acid and its derivatives.

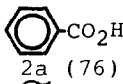
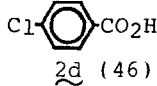
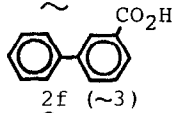
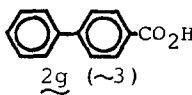
Electron-transfer mediated photooxygenation of organic compounds has received much attention in recent years.<sup>1-6</sup> A component ring of polycyclic aromatic compounds and an alkyl-substituent of alkyl benzenes can be oxidized by this photoreaction.<sup>2-3</sup> However, little is known about the photooxygenation of benzene ring in phenyl group-containing compounds.<sup>4</sup> We have recently demonstrated that the electron-transfer mediated photoisomerization and photooxygenation of 1,2-diarylcyclopropanes bearing electron-donating substituents were remarkably enhanced by the addition of metal salts such as  $Mg(ClO_4)_2$  and  $LiBF_4$ .<sup>6</sup> We now report a novel photooxygenation of biphenyl and its derivatives in the presence of  $Mg(ClO_4)_2$  under mild conditions.

Irradiation of a dry acetonitrile solution of biphenyl (1a) (1 mmol) in the presence of  $Mg(ClO_4)_2$  (0.5 mmol) and a catalytic amount (0.02 mmol) of 9,10-dicyanoanthracene (DCA) under oxygen bubbling with a 300 W high-pressure mercury lamp for 3 h gave benzoic acid (2a) as a sole isolable product in 76% yield. Only a small amount of DCA was consumed during the reaction. Control experiments showed that 1a was quantitatively recovered in the absence of DCA.



a; X = H, b; X = o-OMe, c; X = p-OMe, d; X = p-Cl,  
e; X = o-Ph, f; X = m-Ph, g; X = p-Ph, h; X = p-Et

Table 1. Product Distributions, Fluorescence Quenching Rate Constants in the DCA-Sensitized Photooxygenation of Biphenyls and Terphenyls, and Oxidation Potentials of Biphenyls and Terphenyls

Substrate	$E_{p/2}^{ox}$ (V) <sup>a</sup>	$\Delta G$ (kJ mol <sup>-1</sup> ) <sup>b</sup>	$k_q$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> ) <sup>c</sup>	Conv (%) <sup>d</sup>	Products (%) <sup>e</sup>
<u>1a</u> X=H	1.45	-34.4	$4.6 \times 10^9$	95	 2a (76)
<u>1b</u> X=o-OMe	1.20	-58.5	$1.5 \times 10^{10}$	95	2a (35)
<u>1c</u> X=p-OMe	1.15	-63.3	$2.1 \times 10^{10}$	≥ 98	2a (72)
<u>1d</u> X=p-Cl	1.50	-29.5	$3.9 \times 10^9$	95	2a (23)  2d (46)
<u>1e</u> X=o-Ph	1.30	-48.8	$1.2 \times 10^{10}$	95	2a (60)
<u>1f</u> X=m-Ph	1.43	-36.3	$9.4 \times 10^9$	95	2a (54)  2f (~3)
<u>1g</u> X=p-Ph	1.35	-44.0	$7.0 \times 10^9$	95	2a (40)  2g (~3)
<u>1h</u> X=p-Et	1.35	-44.0	$1.6 \times 10^{10}$	≥ 98	1i (100)
<u>1i</u> X=p-C(=O)CH <sub>3</sub>	1.55	-24.7	$3.8 \times 10^8$	< 2	(~0)
<u>1j</u> X=p-CN	1.65	-15.1	$3.1 \times 10^7$	< 2	(~0)

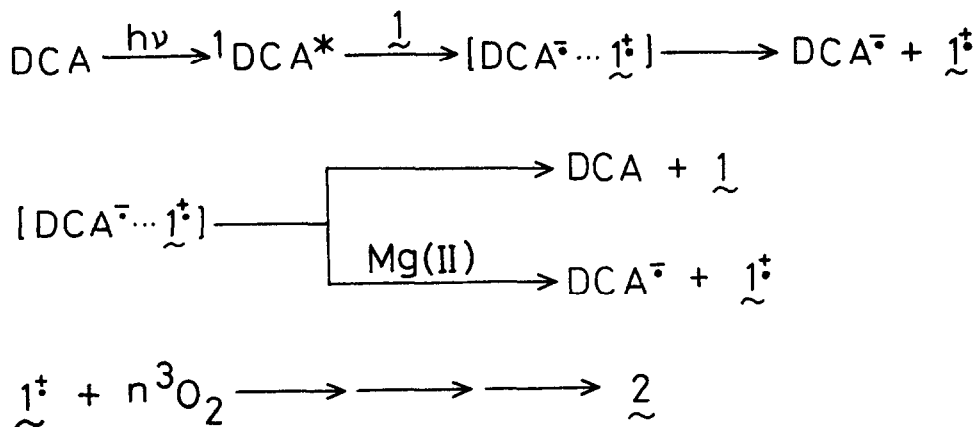
<sup>a</sup> Oxidation potentials were obtained by cyclic voltammetry: Pt electrode, tetraethylammonium perchlorate (0.1 mol/dm<sup>3</sup>) in CH<sub>3</sub>CN vs. Ag/Ag<sup>+</sup>.

<sup>b</sup> Calculated value in CH<sub>3</sub>CN; see ref. 7. <sup>c</sup> Rate constants for fluorescence quenching of DCA in aerated CH<sub>3</sub>CN solutions; [DCA] =  $1.0 \times 10^{-4}$  mol/dm<sup>3</sup>;  $\tau$ (DCA, air) = 12.8 ns from ref. 6. <sup>d</sup> Conversions obtained by irradiations in the presence of Mg(ClO<sub>4</sub>)<sub>2</sub>. <sup>e</sup> Isolated yields based on the substrates used.

The photooxygenation of several substituted biphenyls and terphenyls were also studied. The results are summarized in Table 1. In the photooxygenation of o- and p-methoxybiphenyls (1b-c), the benzene ring bearing methoxy group was selectively oxidized, giving 2a with high efficiency; o- and p-methoxybenzoic acids (2b-c) were not detected by GLC analyses. With p-chlorobiphenyl (1d), both substituted and unsubstituted benzene rings were competitively oxidized to give 2a and p-chlorobenzoic acid (2d) in a 1:2 ratio. In the cases of o-, m-, p-terphenyls (1e-g), the central benzene ring was preferentially oxidized; indeed, the photooxygenation of terphenyls gave 2a as a major product along with a small amount of m- or p-phenylbenzoic acid (2f-g), depending on the structure of terphenyls. On the other hand, the photooxygenation of p-ethylbiphenyl (1h) resulted in the oxidation of ethyl group to give p-acetylbiphenyl (1i) in a quantitative yield.<sup>3</sup> No reaction occurred with 1i and p-cyanobiphenyl (1j) which bear electron-withdrawing groups on the benzene ring.

Singlet oxygen is not responsible for the formation of 2a from 1a. When 1a was irradiated in acetonitrile in the presence of singlet oxygen sensitizers such as rose bengal and methylene blue, 1a was completely recovered even after the prolonged irradiation.

The fluorescence of DCA in acetonitrile was efficiently quenched by 1a-h, but with less efficiency by 1i-j. The free energy changes ( $\Delta G$ ) for one-electron transfer from 1a-h to the excited singlet DCA ( $^1\text{DCA}^*$ ) were estimated to be negative. The photooxygenation of 1a did not occur in less polar solvents such as benzene and ethyl acetate. The rates for the formation of 2a,d from 1a-d were enhanced by a factor of 2-5 by the addition of  $\text{Mg}(\text{ClO}_4)_2$  compared with those in the absence of  $\text{Mg}(\text{ClO}_4)_2$ . On the other hand, the photooxygenation of 1a-d was completely quenched by the addition of 1,4-diazabicyclo[2.2.2]octane ( $0.005 \text{ mol dm}^{-3}$ ).



Scheme 1.

These results could be explained in terms of the electron transfer mechanism as shown in Scheme 1. Radical cation  $\underline{1}^+$  generated by the photoinduced electron transfer from a substrate  $\underline{1}$  to  $^1\text{DCA}^*$  is a key intermediate for the photooxygenation. Since the fluorescence of DCA in acetonitrile was not quenched by  $\text{Mg}(\text{ClO}_4)_2$  and also the fluorescence quenching rate of DCA by  $\underline{1a}$  in the presence of  $\text{Mg}(\text{ClO}_4)_2$  was the same as that in the absence of  $\text{Mg}(\text{ClO}_4)_2$ , the role of  $\text{Mg}(\text{ClO}_4)_2$  in the photooxygenation probably is the suppression of a back-electron transfer from  $\text{DCA}^-$  to  $\underline{1}^+$ . However, the detailed pathway for the formation of an oxidized product  $\underline{2}$  from  $\underline{1}^+$  is unclear at present.<sup>8</sup>

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8. The addition of  $\text{CCl}_4$  in the reaction system did not accelerate the DCA-sensitized photooxygenation of  $\underline{1a}$ . Therefore, involvement of a free radical mechanism may be excluded.

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