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Photochemical Reaction of 1,2-Naphthoquinone and Its Derivatives with Xanthene[1]

Kazuhiro MARUYAMA and Akio TAKUWA*
Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606
**Department of Chemistry, Faculty of Literature and Science, Shimane University, Matsue*

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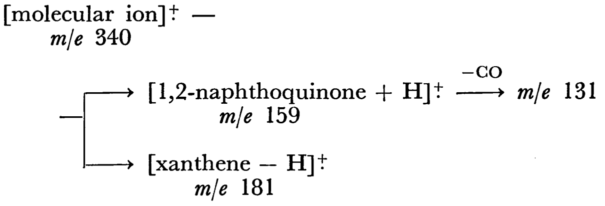
In contrast to other *o*-quinones, photochemical reaction of 1,2-naphthoquinone with xanthene gave a 1 : 1 adduct in which xanthene moiety is attached to position C_4, *i.e.*, 1,4-dihydro-2-hydroxy-4-xanthyl-1-ketonaphthalene (**2a**). The analogous photo-adducts, **2b**, **2c**, and **2d**, were obtained by the photochemical reaction of 3-chloro-1,2-naphthoquinone, 3-bromo-1,2-naphthoquinone, and 6-bromo-1,2-naphthoquinone with xanthene, respectively. The dynamic aspect of these reactions was also examined using the CIDNP technique and the reaction mechanism was discussed.

When *o*-quinones are irradiated in solution in the presence of hydrogen donors, "1,2-adduct" or "1,4-adduct"[2] is generally obtained corresponding to nature of the solvent used.[3] For example, Rubin[4] has shown that phenanthraquinone was irradiated in alkyl benzenes to give "1,2-adduct" and in ethers to give "1,4-adduct," respectively. Thus, the photochemical reactions of *o*-quinones, especially of phenanthraquinone, with hydrogen donors have been extensively investigated. However, the photochemical reaction of 1,2-naphthoquinone has not yet been described presumably from the view of its instability. However, it has been reported that the photochemical reactions of 1,2-naphthoquinone derivatives with aromatic aldehyde and stilbene[5] gave "1,4-adduct" and dioxin, respectively. Photochemical reaction of 1,2-naphthoquinone, 3-chloro-1,2-naphthoquinone, 3-bromo-1,2-naphthoquinone, and 6-bromo-1,2-naphthoquinone with xanthene as hydrogen donor were investigated in this work.

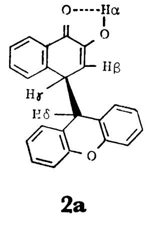
Results and Discussion

Reaction Products and Structure Determination. Equimolar 1,2-naphthoquinone and xanthene dissolved in benzene was irradiated in the usual glass tube for five hours. Photo-adduct precipitated is unstable in polar solvent or to a prolonged irradiation, it decomposes gradually to 1,2-naphthoquinone, its quinhydrone, 9,9′-bixanthyl, and some tarry matters. The structure of the photo-adduct was confirmed by the followings: the mild oxidation of the adduct, **2a**, with potassium permanganate gave phthalic acid and xanthone. The IR spectrum of **2a** exhibited the presence of both of intramoleculary hydrogen bonded hydroxyl group (3375 cm^{-1}) and chelated carbonyl (1640 cm^{-1}) group. The peaks at *m/e* 340, 181, 159, and 131 found in the mass spectrum of **2a** were interpreted in the term of scheme 1.



Scheme 1.

Elemental analysis and these results described above indicate that **2a** is a 1 : 1 adduct of 1,2-naphthoquinone and xanthene. The NMR spectrum of **2a** is shown in Fig. 1 and Table 1. The assignment of corresponding protons in Table 1 were confirmed by the followings. The signal at δ : 1.55 disappeared on addition of deutrium oxide in the sample, therefore it is due to hydroxyl proton (H_α). When the signal at δ : 3.93 (quartet) was irradiated by the spin decoupling technique, the doublet signals at δ : 4.54 and 5.76 changed to singlet, respectively. The signal at δ : 4.54 could not be observed with the photo-adduct which was obtained by the photochemical reaction of 1,2-naphthoquinone with xanthene-9-d_2, and at the same time the signal at δ : 3.93 changed to doublet. These results indicate that H_γ coupled with H_β and H_δ, respectively and thus H_δ is assigned to methine proton of xanthene moiety in the photo-adduct. Analogous photo-adducts having similar structure (**2b**, **2c**, and **2d**) were obtained by the photochemical reaction of 3-chloro-1,2-naphthoquinone, 3-bromo-1,2-naphthoquinone, and



2a

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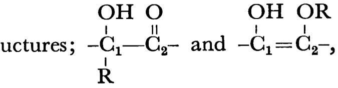
[1] A part of this work was reported by K. Maruyama and A. Takuwa, *Chem. Lett.*, **1972** 135.

[2] In general, photo-adducts of *o*-quinone with RH having the next structures;  $\overset{OH}{\underset{R}{-C_1}}-\overset{O}{\overset{\|}{C_2}}-$ and $-\overset{OH}{C_1}=\overset{OR}{C_2}-$, are used to call "1,2-adduct" and "1,4-adduct", respectively.

[3] A. Schönberg, G. O. Schneck, and O. A. Neumüller, "Preparative Organic Photochemistry", Springer-Verlag, New York, Inc. (1968).

[4] M. B. Rubin, *J. Org. Chem.*, **28**, 1949 (1963). M. B. Rubin and P. Zwitkowits, *ibid.*, **29**, 2362 (1964).

[5] A. Schönberg, N. Latif, P. Moubasher, and A. Sina, *J. Chem. Soc.*, **1951**, 1364. A. Schönberg, W. I. Awad, and G. A. Mousa, *J. Amer. Chem. Soc.*, **77**, 3850 (1955). A, Mustafa, A. H. E. Narash, A. K. E. Mansour, and S. M. A. E. Omran, *ibid.*, **78**, 4306 (1956).

TABLE 1. NMR DATA OF **2a**—**2d** IN $CDCl_3$ (δ-VALUES FROM TMS)

	H_α	H_β	H_γ	H_δ	Aromatic-H	Coupling constant (Hz)
2a	1.55 b	5.76 d	3.93 q	4.54 d	5.50—7.95 m	J=4.5, J=3.8
2b	1.62 b	—	4.15 d	4.96 d	6.15—7.93 m	J=3.5
2c	1.61 b	—	4.11 d	4.85 d	5.98—7.80 m	J=3.6
2d	1.61 b	5.78 d	4.03 q	4.62 d	5.95—8.00 m	J=4.4, J=3.6

b=broad, d=doublet, q=quartet, m=multiplet

Assignments of protons correspond to the structural formula of **2a**.

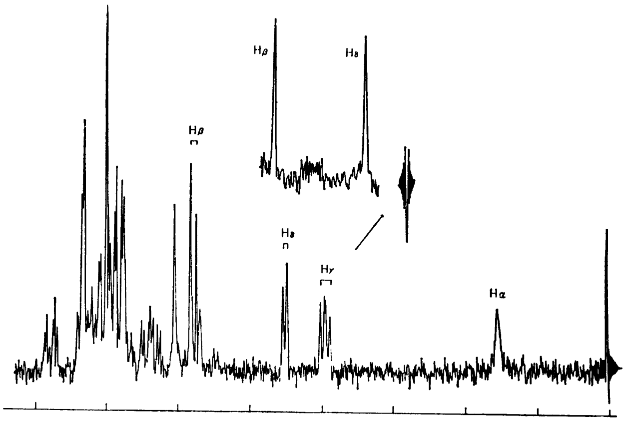
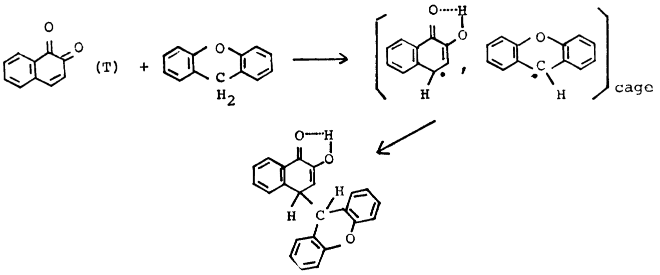


Fig. 1. NMR spectrum of **2a** in $CDCl_3$.

6-bromo-1,2-naphthoquinone with xanthene. The NMR spectra of these photo-adducts are summarized in Table 1.

Reaction Mechanism and CIDNP. 1,2-Naphthoquinones have a maximum absorption band owing to n–π^* transition at 520—527 nm (ε, 66—162) in chloroform.[6] 1,2-Naphthoquinone and its halogeno derivatives in benzene are excited *via* n–π^* to their photochemically active triplet states. The excited species abstract hydrogen from xanthene and simultaneously radical pair may be formed in solvent cage. The resulting radical pair is to be coupled to produce the photo-adduct. When the radical pair couples to give such a photo-adduct, the proton at the nearest-neighbor to the coupling center may give rise to the polarized PMR signals.[7] In the examination of the photochemical reaction of 1,2-naphthoquinone with xanthene in benzene by CIDNP technique, we could recognize the strongly polarized PMR signals only at δ : 4.34 (doublet, enhanced absorption), and δ : 3.93 (quartet, enhanced emission) signals. (Fig. 2). The CIDNP signals of photochemical reaction of 3-chloro-1,2-naphthoquinone with xanthene are shown in Fig. 3. Photochemical reaction of 6-bromo-1,2-naphthoquinone and 3-bromo-1,2-naphthoquinone with xanthene revealed the analogous polarized PMR signals in Figs. 2 and 3, respectively. The chemical shifts of these polarized PMR signals coincided with the δ-values of H_γ and H_δ in photo-adducts (**2a**–**2d**) as shown in Table 1. These phenomena indicate that the C_4-position of semiquinone radical coupled with xanthyl radical to give adduct. "1,2-Adduct" or "1,4-adduct" was not produced even in the course of reaction. If it was produced, a singlet polarized PMR signal (due to methine proton of xanthene moiety) should be observed as an instance of photochemical reaction of phenanthraquinone with xanthene.[8] The CIDNP



Scheme 2.

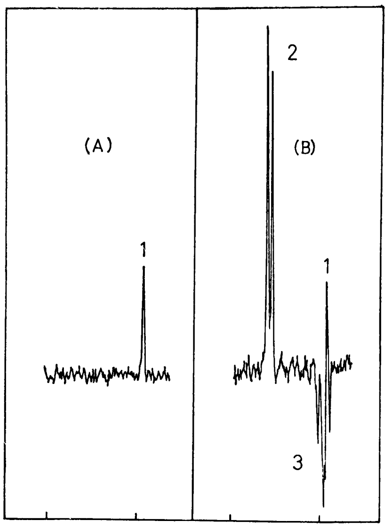


Fig. 2. Polarized PMR spectrum observed in the reaction of 1,2-naphthoquinone with xanthene in benzene solution.

A) Before irradiation. Signal 1: methylene protons of xanthene.

B) During the cource of irradiation. Signal 1: methylene protons of xanthene. Signal 2: absorption polarized signals, which correspond to the methine proton (H_δ) of xanthene rest in photo-adduct, **2a**. Signal 3: emission polarized signals, which correspond to the 4-position proton (H_γ) of quinone rest in photo-adduct, **2a**.

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[6] R. W. A. Oliver, R. M. Rashman, and A. W. Somerville, *Tetrahedron*, **24**, 4067 (1968).

[7] For example, K. Maruyama, H. Shindo, T. Otsuki, and T. Maruyama, This Bulletin, **44**, 2756 (1971), and other papers cited in this paper.

[8] K. Maruyama, T. Maruyama, and H. Shindo, This Bulletin, **44**, 585 (1971); **44**, 2000 (1971); **44**, 2789 (1971); **44**, 2885 (1971).

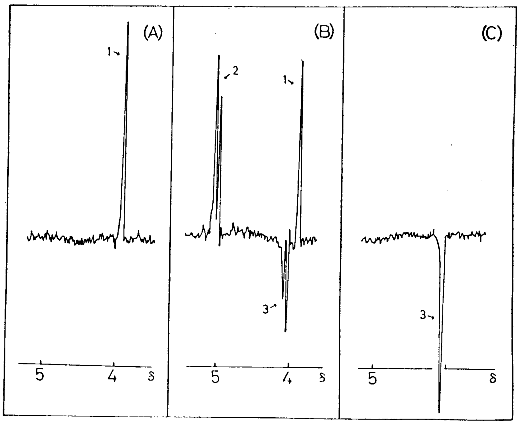

Fig. 3. Polarized PMR spectrum observed in the reaction of 3-chloro-1,2-naphthoquinone with xanthene in benzene solution.

A) Before irradiation. Signal 1: methylene protons of xanthene.

B) During the course of irradiation. Signal 1: methylene protons of xanthene. Signal 2: absorption polarized signals, which correspond to the methine proton (H_δ) of xanthene rest in photo-adduct, **2b**. Signal 3: emission polarized signals, which correspond to the 4-position proton (H_γ) of quinone rest in photo-adduct, **2b**.

C) Enhanced emission signal observed during irradiation in the reaction of 3-chloro-1,2-naphthoquinone with xanthene-9-d_2. Signal 3 due to the 4-position proton of the quinone rest in photo-adduct.

signal of the photochemical reaction of 3-chloro-1,2-naphthoquinone with xanthene-9-d_2 is shown in Fig. 3-C. The doublet enhanced absorption signals (due to the methine proton of xanthene moiety) in Fig. 3-B could not be observed and singlet enhanced emission signal was only observed corresponding to the doublet enhanced emission signal in Fig. 3-B. Therefore, the doublet enhanced absorption signals and enhanced emission signal in Fig. 3-B correspond to the proton of quinone moiety and the methine proton of xanthene moiety, respectively.

Experimental

Materials. 1,2-Naphthoquinone (mp 121—122 °C) was prepared by the oxidation of 1-amino-2-naphthol hydrochloride with ferric chloride.[9] 6-Bromo-1,2-naphthoquinone (mp 156 °C) was prepared by the oxidation of 6-bromo-2-naphthol with Fremy's salt.[6] 3-Chloro-1,2-naphthoquinone (mp 171 °C)[10] and 3-bromo-1,2-naphthoquinone (mp 164 °C)[11] were prepared by the chlorination and bromination of 1,2-naphthoquinone, respectively. Xanthene-9-d_2 was prepared by the reduction of xanthone with lithium aluminium deuteride.[12] Xanthene commercially available was further purified by recrystallization.

Spectra. Infrared spectra were taken with Jasco IR-G and Hitachi 215 infrared spectrometers with KBr disc. NMR spectra were observed with a JEOL C-60 HL spectrometer in $CDCl_3$(saturated) as a solvent and TMS as an internal indicater.

Photochemical Reaction. A typical photochemical reaction was accomplished as the following: 1,2-Naphthoquinones (0.5 mmol) and xanthene (0.5 mmol) dissolved or suspended in benzene was irradiated in ordinary glass tube by 300 W high-pressure mercury arc lamp through 5—10 cm thick water layer at 0—5 °C. Yield was nearly 50—60% in all cases.

Analyses of Photochemical Products. 1,4-Dihydro-2-hydroxy-4-xanthyl-1-ketonaphthalene (**2a**): A suspension of 1,2-naphthoquinone and xanthene in benzene was irradiated for 5 hr. A white needles deposited was collected and recrystallized from benzene–petroleum at ordinary temperature; White needles, mp 121—123 °C (dec.); IR, ν_{OH}: 3375, $\nu_{C=O}$: 1640 cm^{-1}). Elemental analysis, Found, C: 81.31, H: 4.81%. Calcd for $C_{23}H_{16}O_3$, C: 81.16, H: 4.74%. Oxidation of **2a** with potassium permanganate in acetone–water solution gave phthalic acid, mp 190—190.5 °C and xanthone, mp 173 °C, undepressed on admixture with an authentic specimen.

*1,4-Dihydro-2-hydroxy-3-chloro-4-xanthyl-1-ketonaphthalene (**2b**).* Irradiation of the benzene solution of 3-chloro-1,2-naphthoquinone and xanthene was for 4 hr. The characteristic orange-red color of the quinone faded to pale yellow. Removal of the benzene under reduced pressure left a yellowish brown solid mass. It was washed with petroleum ether and then small amount of benzene, and recrystallized from benzene–petroleum ether, pale yellow leaves, mp 157—158 °C (dec.); ν_{OH}: 3375 cm^{-1}, $\nu_{C=O}$: 1665 (w), 1640(vs) cm^{-1}, Found; C: 73,63, H: 3.86%, Calcd for $C_{23}H_{15}ClO_3$, C: 73.70, H: 4.03%.

*1,4-Dihydro-2-hydroxy-3-bromo-4-xanthyl-1-ketonaphthalene (**2c**)* Separation and purification were the analogous work-up described above, pale yellow prism, mp 143—144 °C (dec.); ν_{OH}: 3375 cm^{-1}, $\nu_{C=O}$: 1665 (w), 1640 (vs) cm^{-1}; Found, C: 65.85, H: 3.54%, Calcd for, $C_{23}H_{15}BrO_3$, C: 65.81, H: 3.61%.

*1,2-Dihydro-2-hydroxy-4-xanthyl-6-bromo-1-ketonaphthalene (**2d**).* Irradiation of the benzene solution of 6-bromo-1,2-naphthoquinone and xanthene was for 2 hr. The characteristic reddish brown color of the quinone faded to almost colorless. Benzene was removed under reduced pressure, and the resulting brown solid was washed with petroleum ether and then with benzene containing 50% petroleum ether, and recrystallized from benzene–petroleum ether; white needles, mp 130—131 °C (dec.); ν_{OH}: 3375 cm^{-1}, $\nu_{C=O}$: 1640 cm^{-1}; Found, C: 65.71, H: 3.54%, Calcd for $C_{23}H_{15}BrO_3$, C: 65.89, H: 3.61%.

CIDNP Examination. Investigation of these photochemical reactions by CIDNP technique was performed using JEOL C-60 HL spectrometer, equipped with the modified NMR probe for the photo-irradiation. The detailed method used was described in this Bulletin by K. Maruyama *et al.*[7]

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[9] A. H. Blatt, "Organic Syntheses" Coll. Vol. 2, p. 430 (1948).

[10] T. Zincke, *Ber.*, **19**, 2497 (1886).

[11] T. Zincke, *ibid.*, **19**, 2495 (1886).

[12] A. Mustafa and M. K. Hilmy, *J. Chem. Soc.*, **1952**, 1345.