The Photochemical Reaction of 1,4-Naphthoquinone Derivatives with Hydrogen Donors

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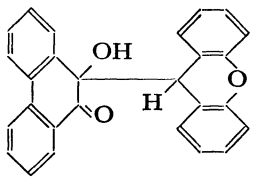
The reaction products of the photochemical reactions of 1,4-naphthoquinone and its methyl- or halogeno-derivatives with xanthene were investigated. Methyl-substituted 1,4-naphthoquinones produce the corresponding 1,4-naphthohydroquinones, but naphthoquinone and its halogeno-derivatives react to give substituted or added products by the xanthyl group in addition to the hydroquinone derivatives. Stable free radicals, which remain unchanged under atmospheric pressure, are also obtained in the latter reactions. The courses of the photochemical reactions were investigated by means of the CIDNP technique, and the reaction mechanism was discussed.

The photochemical reaction of quinones has received extensive interests by many investigators.[1] According to Pfundt,[2] the irradiation of 9,10-phenanthraquinone with xanthene gave the "1,2-adduct", **1**, the reaction was reinvestigated by Maruyama and his co-workers.[3]



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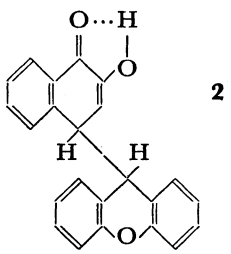

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The irradiation of 1,2-naphthoquinone with xanthene, however, gave a different type of photo-adduct, **2**.[4] Recently the present authors have examined the photochemical reactions of *p*-quinones with xanthene by means of the CIDNP technique[5] and pointed out the formation of unstable intermediates in the course of reactions. Stable products such as hydroquinones and 9,9′-bixanthyl are also formed in the reactions.

In this work, the photochemical reactions of 1,4-naphthoquinone, 2-methyl-1,4-naphthoquinone, 2,3-dimethyl-1,4-naphthoquinone, 2,6-dimethyl-1,4-naphthoquinone, 2-chloro-1,4-naphthoquinone, 2,3-dichloro-1,4-naphthoquinone, 2-bromo-1,4-naphthoquinone, 2,3-dibromo-1,4-naphthoquinone with xanthene dissolved in benzene were mainly studied from the standpoint of stableproduct analyses. Examinations by means of the CIDNP technique were also extended to the above reactions in order to investigate the reaction mechanism.

Results and Discussion

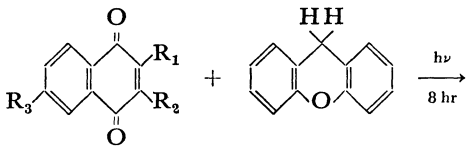
In all of the photochemical reactions described below, a benzene solution of 1,4-naphthoquinone derivatives and xanthene sealed in a glass tube was irradiated by means of a 400W high-pressure mercury arc lamp from the outer side through a 5-cm-thick water layer under ice-water cooling or at room temperature.

Methyl-substituted 1,4-Naphthoquinones. The irradiation for about eight hours of the benzene solution of 2-methyl-1,4-naphthoquinone, **3a**, and xanthene gave 2-methyl-1,4-naphthohydroquinone, **4a**, and 9,9′-bixanthyl in a 70—80% yield. 2,3-Dimethyl-1,4-naphthoquinone, **3b**, and 2,6-dimethyl-1,4-naphthoquinone, **3c**, reacted as well as the **3a** with xanthene to give the corresponding 1,4-naphthohydroquinone derivatives and 9,9′-bixanthyl in good yields. The quantum yields of the naphthoquinone disappearance are tabulated in Table 1.

TABLE 1. QUANTUM YIELDS OF THE DISAPPEARANCE OF 1,4-NAPHTHOQUINONE DERIVATIVES

Quinones	Quantum yields[a]
1,4-Naphthoquinone	0.39
2-Methyl-1,4-naphthoquinone	0.29
2,3-Dimethyl-1,4-naphoquinone	0.12
2-Chloro-1,4-naphthoquinone	0.41

a) Non-degassed benzene solutions were used for the determination. Wavelength of light for excitation was longer than 400 nm.



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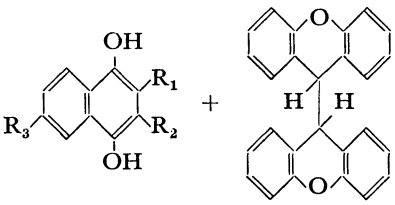

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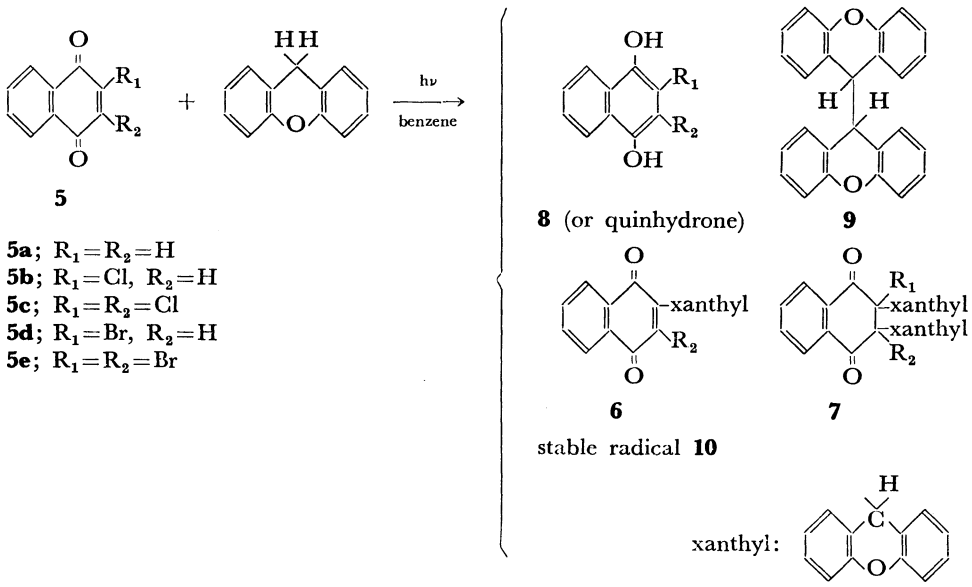
a; R_1=Me, R_2=R_3=H **b**; R_1=R_2=Me, R_3=H **c**; R_1=R_3=Me, R_2=H

1,4-Naphthoquinone and Its Halogeno-derivatives. In the photochemical reactions of 1,4-naphthoquinone and its halogeno-derivatives, other products of the **6** and **7** types, were obtained in addition to the corresponding hydroquinones and 9,9′-bixanthyl. Moreover, stable radicals could be isolated in the reaction of the halogeno-derivatives with xanthene. The relative yields of the respective compounds in the reaction products are profoundly dependent on the temperature, as is shown in Table 2. For example, under ice-water cooling compounds of the **8**, **9**, and **7** types were produced as the main products, but at room temperature

Table 2. Products in the photochemical reaction of 1,4-naphthoquinone derivatives with xanthene[a]

Quinones	Reaction times (hr)	Products (%)				
		Hydroquinone or quinhydrone	9,9′-Bixanthyl	Adduct-1	Adduct-2	Radicals
5a	5[b]	31	17	—	1.5	—
5b	4[b]	48	23	0.5	4	—
5b	5[c]	28	5	2.1	8.6	14
5c	11[c]	trace	trace	24	—	17
5d	5[b]	21	23	2.1	0.8	—
5d	5[c]	3	4	5	trace	23
5e	10[c]	trace	trace	11	—	5.3

a) Equivalent amounts of quinone and xanthene dissolved in benzene were irradiated. Yields were based on the amounts of quinones used. b) Under ice-water cooling. c) At room temperature.
Adduct-1: 2-[9′-Xanthyl]-1,4-naphthoquinone derivatives.
Adduct-2: 2,3-Di-[9′-xanthyl]-1,4-naphthoquinone derivatives.



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5a; $R_1=R_2=H$
5b; $R_1=Cl$, $R_2=H$
5c; $R_1=R_2=Cl$
5d; $R_1=Br$, $R_2=H$
5e; $R_1=R_2=Br$

8 (or quinhydrone) **9**

6 **7**

stable radical **10**

(*ca.* 25 °C) the principal products were of the **8**, **7**, and **10** types and the yield of **9** was considerably reduced. The reactions of **5d** and **5e** followed the same trend. The structures of the **6**—**9** products were determined by means of IR, PMR, mass, and elemental analyses.

Structure of Stable Radicals ***10***. In the photochemical reaction of halogeno-derivatives of 1,4-naphthoquinone with xanthene at room temperature, stable, greenish free radicals could be obtained in fairly high yields. The radicals show a well-resolved ESR hyperfine structure in a tetrahydrofuran solution. The typical ESR spectra of the radicals, which are obtained in the photochemical reaction of 2,3-dichloro- and 2,3-dibromo-1,4-naphthoquinone with xanthene, are shown in Fig. 1.

The analyses of the spectra are straightforward; five groups of lines split further to a quintet. This means that the radical center is at position 9′ and almost all of the unpaired electrons delocalize on the xanthyl moiety. The physical properties of the stable radicals obtained are summarized in Table 3.

When the radicals were then submitted to chromic acid oxidation (or ferric chloride oxidation), they gave 9′-hydroxyderivatives, **12**. Reaction with zinc dust-hydrochloric acid, on the other hand, resulted in the corresponding 2-halogeno-3-[9′-xanthyl]-1,4-naphthohydroquinones, which were subsequently autoxidized in the air to the corresponding naphthoquinone derivatives, **6**. The radicals showed a broad IR absorption due to the hydroxy group in the region of ν_{OH}: 3000—3200 cm^{-1}. Therefore, the radicals were assigned to structure **10**.

Table 3. Physical properties of stable free radicals

Free radicals	**11a**[a]	**11b**[a]	**11c**[a]
Color	green	dark green	black
Decomp. point (°C)	105—107	137	180—182
IR(KBr); (cm^{-1})	3200	3050	3050
ESR coupling constants (gauss) $a_{H_1',8'}$	3.23	3.00	3.30
ESR coupling constants (gauss) $a_{H_3',6'}$	3.90	3.60	3.81
ESR coupling constants (gauss) $a_{H_2',4',5',7'}$	0.79	0.74	0.76
g-Values	2.0029	2.0030	2.0034

a) The structures **11a**, **11b**, and **11c** correspond to the stable radicals **10b**, **10c**, and **10d** respectively.

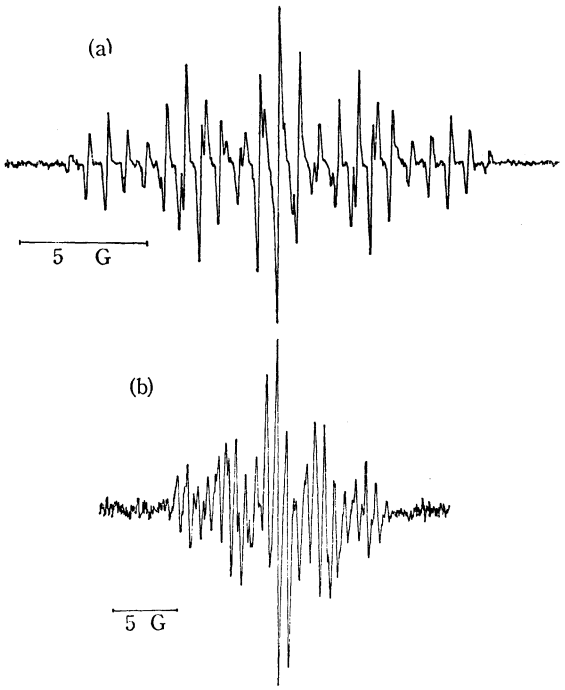
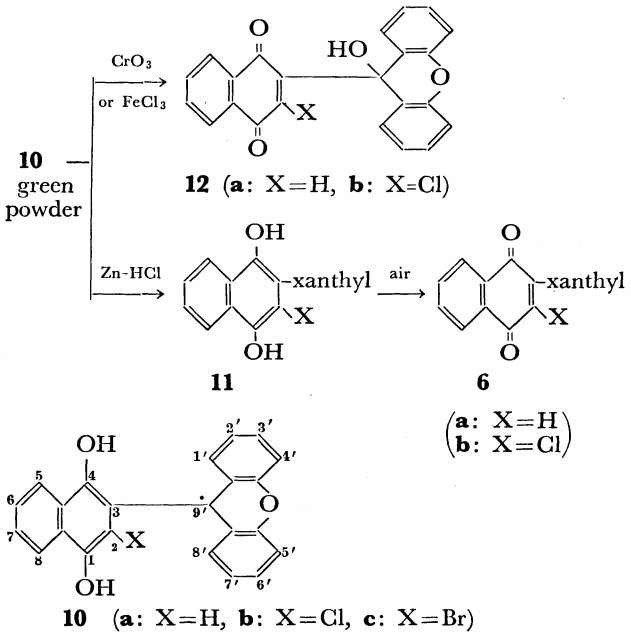
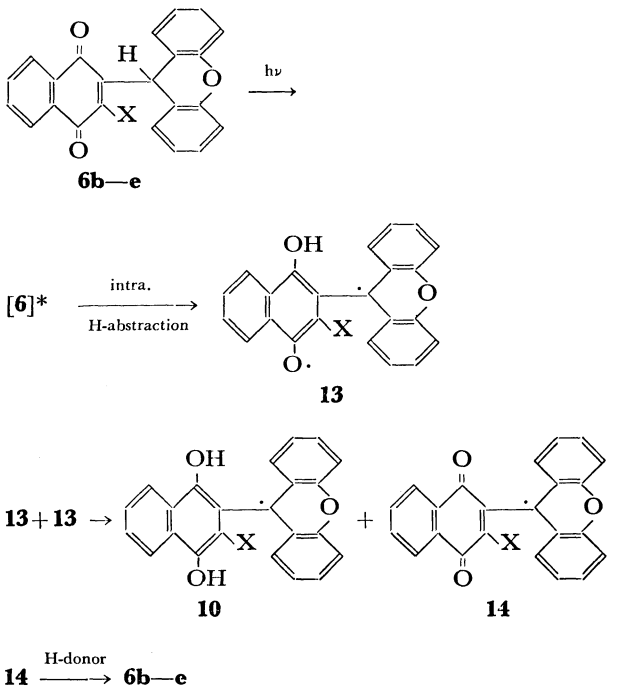


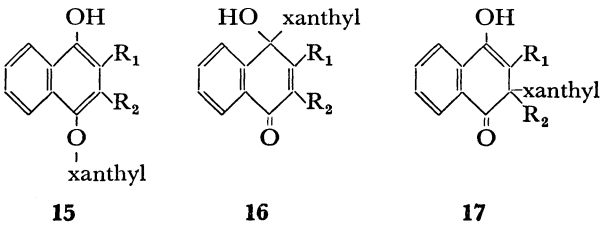
Fig. 1. ESR spectrum of stable radical (**10c**) obtained in the reaction of 2,3-dichloro-1,4-naphthoquinone with xanthene(a) and in the reaction of 2,3-dibromo-1,4-naphthoquinone with xanthene(b).



Thus, **5b** and **5d** convert to the same product, **10a**; **5c**, to **10b**, and **5e**, to **10c**. The radicals are stable in the solid state, but they gradually change to non-radical substances in a solution (*e.g.*, solvent THF). These radicals may be produced *via* photo-induced intramolecular hydrogen abstraction of the primary products, **6b—e**, accumulated in the reacting system, as is shown in the following equations;



CIDNP Measurements and Reaction Mechanism. 1,4-Naphthoquinone derivatives examined in this work have n→π^* absorption bands in the region of λ_{max}: 420—440 nm (ε: 20—60). The molecules of 1,4-naphthoquinone derivatives excited by the n→π^* transition could be converted to the triplet state via inter-system crossing. The excited molecules in the triplet state can abstract hydrogen from xanthene to give the triplet radical pair, **18**—radical pair consisting of a semiquinone radical and a xanthyl radical—in the solvent cage. By means of the CIDNP technique we have previously investigated the photochemical reactions of 1,4-naphthoquinone derivatives with xanthene and pointed out the formation of the **15**, **16**, and **17** reaction intermediates.[5] These reaction intermediates decomposed thermally to give a solvent-separated semiquinone radical and xanthyl radical.



In addition to the strongly polarized PMR signals due to these intermediates, other polarized PMR signals corresponding to the isolated stable products could be observed. The PMR spectra observed during the course of the photochemical reactions of 1,4-naphthoquinone and its halogeno-derivatives with xanthene are shown in Figs. 2—4; Fig. 2 shows the PMR polarized signals observed in the reactions of 1,4-naphthoquinone with xanthene, Fig. 3, those of 2-chloro-1,4-naphthoquinone, and Fig. 4, those of 2,3-dichloro-1,4-naphthoquinone. The polarized PMR signals due to the stable products could be easily assigned to the

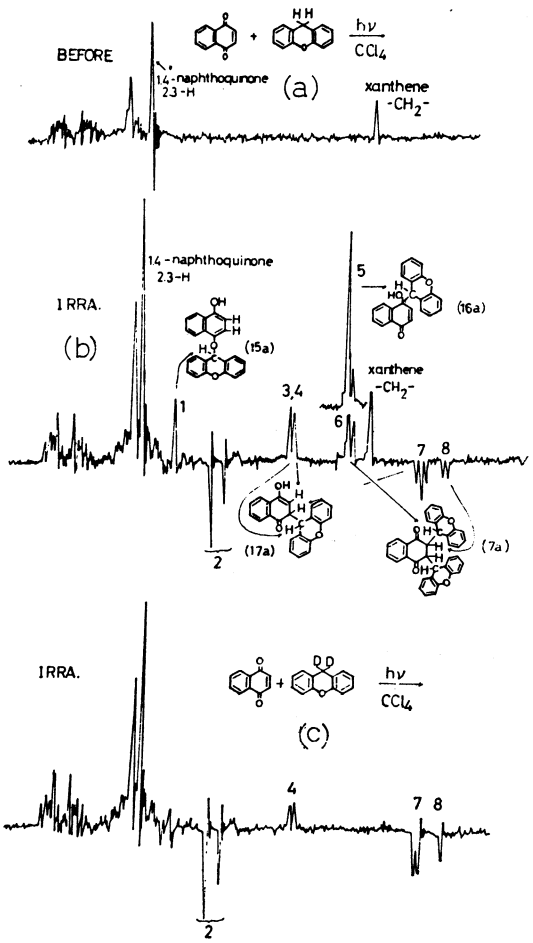


Fig. 2. PMR spectra observed in the photochemical reaction of 1,4-naphthoquinone with xanthene.
(a): before irradiation, (b): during irradiation; (c): during irradiation, when xanthene-9-d_2 was used.
Signals 2 in the Figure should be assigned to 2,3-protons of **16a**[15].

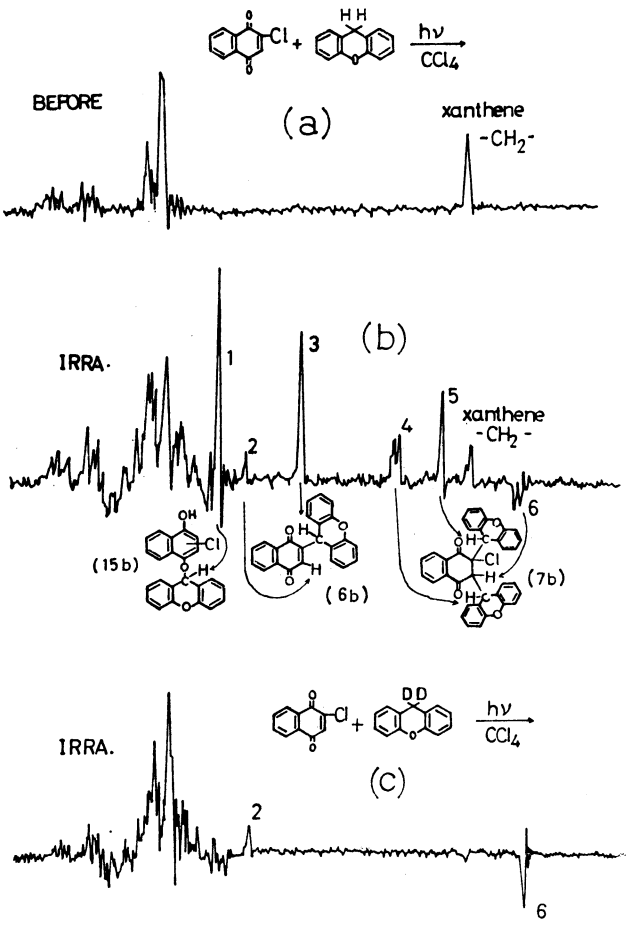


Fig. 3. PMR spectra observed in the photochemical reaction of 2-chloro-1,4-naphthoquinone with xanthene.
(a): before irradiation, (b): during irradiation, (c): during irradiation, when xanthene-9-d_2 was used.

respective compounds by comparison with the PMR spectra of the isolated products, but one can determine those due to reaction intermediates by comparison with the polarized PMR signals observed in the reaction of the corresponding quinones with xanthene-9-d_2 and their chemical shifts. The structures thus determined are indicated in Figs. 2—4. According to the CKO theory,[6] the polarized signals are developed by the reaction products formed through a radical process, regardless of their stabilities. Although these photochemical reactions obviously proceed through radical processes, fairly vigorous liberation of hydrogen halides could be observed in the course of the reactions of **5b**, **5c**, **5d**, and **5e**. This may be interpreted in terms of the decomposition of the thermally-unstable intermediates to give the substituted derivatives of 1,4-naphthoquinone by means of the xanthyl group. Since the structure of the reaction intermediates formed in the reacting system, as well as the stable products, could be determined by means of the CIDNP technique and by stable-product analyses, the following possible reaction scheme can be proposed. The disproportionation of the semiquinone radical (Step iv) was unambiguously confirmed by means of the CIDNP technique, the details were reported in a previous report.[5] The temperature dependence of the stable-product distributions described in Table 2 can be ingeniously interpreted by taking into consideration Steps v and vi; at higher temperatures the yield of 9,9′-bixanthyl is considerably reduced, and that of the stable radical is increased. The process of the stable free radical formation has already been considered in Section 3. In the photochemical reaction of 1,4-naphthoquinone with xanthene, Steps vii, viii, and ix might be unimportant.

The photochemical reactions of 1,4-naphthoquinone derivatives with thioxanthene proceeded quite smoothly, as those with xanthene, but the products were the corresponding hydroquinones, quinhydrones and 9,9′-bithioxanthyl, with the exceptions of **5b** and **5d**. In the phothochemical reactions of **5b** or **5d** with thioxanthene, a small amount of the adduct corresponding to **6b** was isolated in addition to the compounds described above.

Experimental

Materials. 1,4-Naphthoquinone (mp 125—126 °C) commercially available was further purified by sublimation.

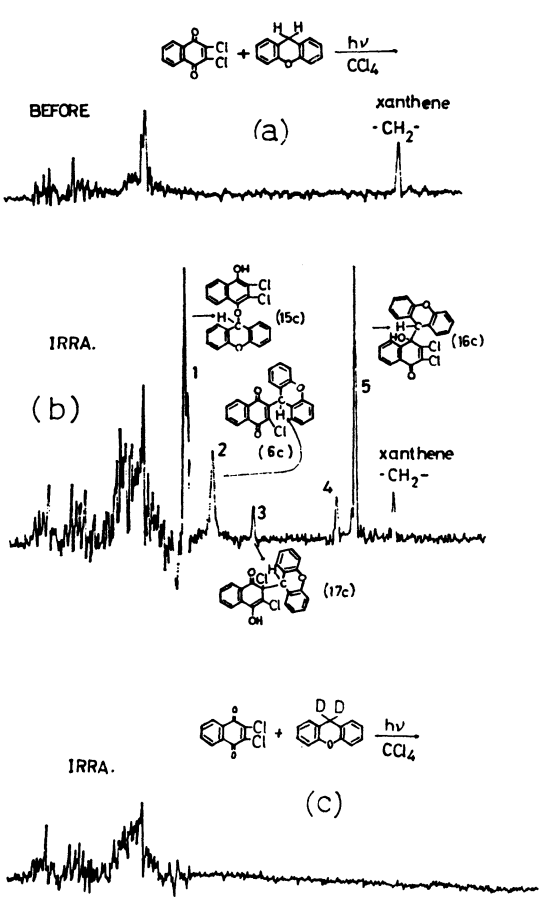
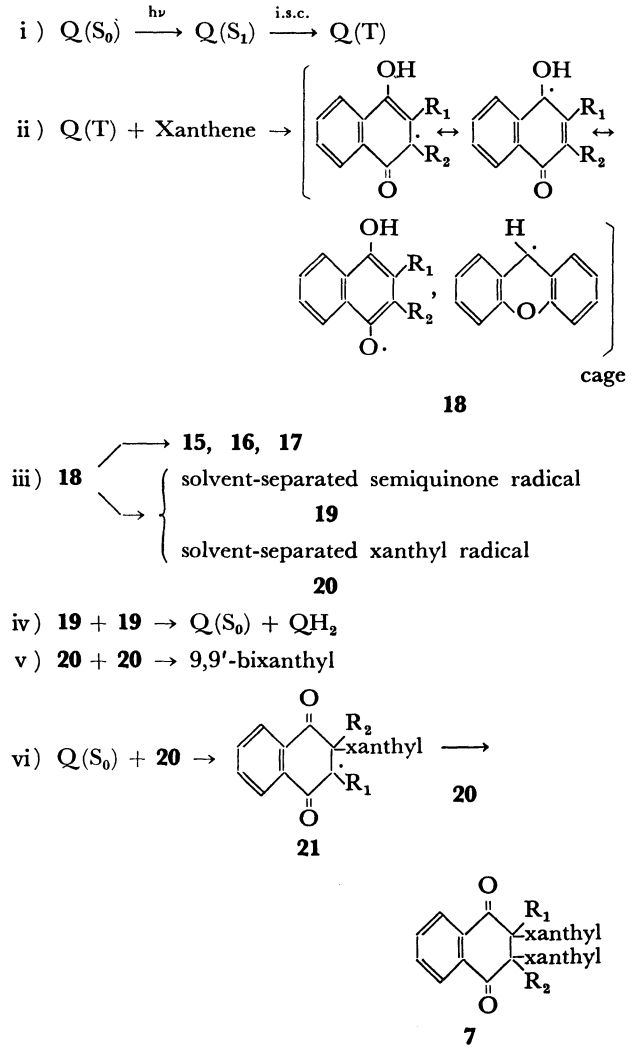


Fig. 4. PMR spectra observed in the photochemical reaction of 2,3-dichloro-1,4-naphthoquinone.
(a): before irradiation, (b): during irradiation, (c): during irradiation, when xanthene-9-d_2 was used.

2-Methyl-1,4-naphthoquinone (mp 104—105 °C),[7] 2,3-dimethyl-1,4-naphthoquinone (mp 126—127 °C),[8] and 2,6-dimethyl-1,4-naphthoquinone (mp 139 °C),[9] were prepared by the oxidation of the corresponding methylnaphthalenes with chromic acid. 2-Chloro-1,4-naphthoquinone (mp 116—117 °C) was prepared by the oxidation of 2,4-dichloronaphthol with chromic acid.[10] 2,3-Dichloro-1,4-naphthoquinone (mp 197—198 °C) commercially available was further purified by recrystallization. 2-Bromo-1,4-naphthoquinone (mp 135 °C) was prepared by the dibromination of 1,4-naphthoquinone, followed by dehydrobromination with sodium acetate.[11] 2,3-Dibromo-1,4-naphthoquinone (mp 220 °C) was prepared by the bromination of 2-bromo-1,4-naphthoquinone.[11] Xanthene commercially available was further purified by recrystallization. Thioxanthene (mp 130—131 °C) was prepared by the reduction of thioxanthone with lithium alminium hydride.[12] Thioxanthone was prepared by heating thiosalicyclic acid and benzene in conc. sulfuric acid.[13] Xanthene-9-d_2 was prepared with lithium aluminium deuteride.

Spectra. Infrared spectra were taken with a JASCO IR-G spectrophotometer, using a KBr disc. PMR spectra were observed with a JEOL PS-100 100 Hz spectrometer in suitable solvents using TMS as the internal standard. Ultraviolet spectra were recorded by means of a Shimadzu UV-200 spectrophotometer. ESR spectra were measured at room temperature using a JEOL X-band PE-3X spectrometer in THF.



Reaction Scheme.

Photochemical Reactions. A typical photochemical reaction was performed as follows; 1,4-naphthoquinone derivatives (1—2 mmol) and one or two equivalents of xanthene were dissolved in 30 ml of benzene, and the solution was irradiated in an ordinary glass tube from outside by a 400W high-pressure mercury arc lamp through a water layer 5—10 cm thick under ice-water cooling or at room temperature.

i) Photochemical Reactions of Methyl-substituted 1,4-Naphthoquinone, 3, with Xanthene. A soluiton of 2-methyl-1,4-naphthoquinone, **3a** (300 mg, 1.7 mmol), and two equivalents of xanthene was irradiated for 8 hr. 2-Methyl-1,4-naphthohydroquinone, **4a**, thus deposited was filtered off, washed with benzene, and recrystallized from acetic acid. The filtrate was evaporated under reduced pressure and the residue was chromatographed on silica gel. Elution with light petroleum gave 9,9'-bixanthyl in 70—80% yield. 2,3-Dimethyl-1,4-

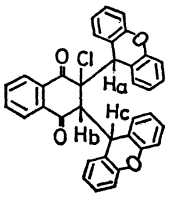
naphthoquinone, **3b**, and 2,6-dimethyl-1,4-naphthoquinone, **3c**, reacted with xanthene as smoothly as **3a** to give **4b**, **4c**, and 9,9′-bixanthyl. 2-Methyl-1,4-naphthohydroquinone, **4a**; white needles(readily turned violet in the air), mp 152 °C; ν_{OH} 3320 cm^{-1}. 2,3-Dimethyl-1,4-naphthohydroquinone, **4b**; white crystals (readily turned black), mp 141 °C; IR(KBr): ν_{OH} 3300 cm^{-1}, 2,6-Dimethyl-1,4-naphthohydroquinone, **4c**; white crystals tinged with violet; mp 175—176 °C; IR(KBr): ν_{OH} 3260 cm^{-1}. 9,9′-Bixanthyl; colorless needles; mp 211—211.5 °C.

*ii) Photochemical Reaction of 1,4-Naphthoquinone, **5a**, with Xanthene.* A solution of **5a** (632 mg, 4 mmol) and xanthene (4 mmol) in 30 ml of benzene was irradiated under ice-water cooling (at 0—5 °C) for hr 5. Dark violet needles of quinhydrone, **8a**, (195 mg, 31%) were deposited and then filtered off. The filtrate was evaporated under reduced pressure, and the residue was chromatographed on a column of florisil. Elution with light petroleum gave 9,9′-bixanthyl (120 mg, 17%). Elution with light petroleum–benzene (1 : 1 v/v) gave unreacted 1,4-naphthoquinone. Elution with benzene gave white crystals of 2,3-dixanthyl-2,3-dihydro-1,4-naphthoquinone, **7a** (31 mg, 1.5%). Quihydrone, **8a**; mp 165—166 °C, IR (KBr): ν_{OH} 3250 cm^{-1}. 2,3-Dixanthyl-2,3-dihydro-1,4-naphthoquinone, **7a**; mp 196 °C, IR(KBr): $\nu_{C=O}$ 1675 cm^{-1}, $\nu_{=C-O-}$ 1250 cm^{-1}. PMR($CDCl_3$) δ: 7.8—6.1(m, 20H), 4.30(d, 2H, methine protons of the xanthyl moleties), 3.12(d, 2H, 2,3-protons of the quinone moiety), J=4.0 Hz. Found: C, 83.20; H, 4.54%. Calcd for $C_{36}H_{24}O_4$: C, 83.06; H, 4.65%. Mass *m/e*: 520(M^+), 362, 338, 181.

*iii) Photochemical Reactions of 2-Chloro-1,4-naphthoquinone, **5b**, with Xanthene.* A solution of **5b** (964 mg, 5 mmol) and xanthene (5 mmol) in 60 ml of benzene was irradiated for 4 hr under ice-water cooling(at 0—5 °C). The violet leaflets quinhydrone, **8b**, (470 mg, 48%) thus deposited were filtered off, washed with petroleum-benzene, and recrystallized from petroleum–benzene(4 : 1 v/v). The filtrate was evaporated under reduced pressure to *ca.* 3 ml. Petroleum ether was added to the resulting solution, and crude solids were filtered off and recrystallized from peroleum–benzene to give colorless crystals of 2-chloro-2,3-dixanthyl-2,3-dihydro-1,4-naphthoquinone, **7b** (110 mg, 4%). The mother liquors from the filtration of **7a** were evaporated under reduced pressure, and the resulting residue was chromatographed on silica gel. Elution with petroleum gave 9,9′-bixanthyl (203 mg, 23%). Elution with petroleum–benzene(5 : 1 v/v) gave yellow needles of 2-xanthyl-1,4-naphthoquinone, **6b** (9 mg, 0.8%).

In the photochemical reaction of **5b** at room temperature, a solution of **5b** (385 mg, 2 mmol) and the equivalent mol of xanthene was irradiated for 5 hr. Greenish solids of **10b** (107 mg, 14%) were deposited, and filtered off, washed with petroleum–benzene. The greenish solids were proved to consist of free radicals by means of ESR spectroscopy. The filtrate was evaporated under reduced pressure to *ca.* 3 ml, and treated with petroleum; then the quinhydrone, **8b**, and **7b** deposited were collected and dissolved in petroleum–benzene (5 : 1 v/v) under heating. The quinhydrone was dissolved, and insoluble **7b** was separated out. The recrystallization of crude **7b** gave pure crystals (95 mg, 9%). When a hot solution containing quinhydrone was cooled, violet leaflets of quinhydrone, **8b** (94 mg, 24%), were obtained. The mother liquors left after the filtration of **8b** and **7b** were evaporated, and the resulting residue was chromatographed on silica gel. 17 mg of 9,9′-bixanthyl (5%) and 14 mg of **6b** (2.1%) were thus obtained.

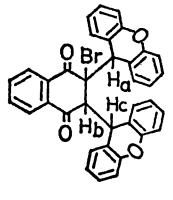
Quinhydrone, **8b**; mp 141—142 °C, IR(KBr): ν_{OH} 3360 cm^{-1}. 2-Chloro-2,3-dixanthyl-2,3-dihydro-1,4-naphthoquinone, **7b**; mp 186 °C(decomp.), IR(KBr): $\nu_{C=O}$ 1700 cm^{-1} (due to carbonyl group bearing a chlorine atom at the equatorial position), 1675 cm^{-1}. PMR($CDCl_3$) δ: 8.08—6.36(m, 20H), 4.98(d, H_c), 4.43(s, H_a), 3.76(d, H_b), J_{bc}=4.0 Hz. In the PMR spectrum of the adduct corresponding to **7b** obtained from the photochemical reaction of **5b** with xanthene-9-d_2, the two signals at δ: 4.98 and 4.43 disappeared and the signal at δ: 3.76 changed to a singlet. Found: C, 78.11; H, 4.19; Cl, 6.12%. Calcd for $C_{36}H_{23}O_4Cl$: C, 77.90; H, 4.18; Cl, 6.39%. 2-Xanthyl-1,4-naphthoquinone **6b**; mp 196 °C, IR(KBr): $\nu_{C=O}$ 1650 cm^{-1}. PMR(CCl_4) δ: 7.0—8.3 (m, 12H), 6.31(s, 1H, proton at position 3 of the quinone moiety), 5.76(s, 1H, methine proton of the xanthene moiety). UV($CHCl_3$): λ_{max} (log ε), 430 nm(1.43), 340 nm(3.60), 286 nm(3.88), 254 nm(4.46). Found: C, 81.72; H, 4.06%. Calcd for $C_{23}H_{14}O_3$: C, 81.64; H, 4.17%. Stable radical, **10b**; greenish powder; mp 105—107 °C(decomp.), IR(KBr): ν_{OH} 3200 cm^{-1}.



7b

*iv) Photochemical Reaction of 2-Bromo-1,4-naphthoquionne, **5d**, with Xanthene.* A solution of **5d** (1165 mg, 5 mmol) and xanthene (5 mmol) in 60 mg of benzene was irradiated for 5 hr under ice-water cooling (at 0—5 °C). Four products were isolated by the same treatment as in the case of **5b**. 250 mg (21%) of quinhydrone, **8d**, 210 mg(23%) of 9,9′-bixanthyl, 35 mg(2.1%) of **6b**, and 25 mg(0.8%) of 2-bromo-2,3-dixanthyl-2,3-dihydro-1,4-naphthoquinone **7d** were obtained. In the photochemical reaction of **5d** at room temperature, a solution of **5d** (354 mg, 1.5 mmol) and xanthene (1.5 mmol) was irradiated for 5 hr. The greenish solids, **10d**, deposited (117 mg, 23%) were filtered off, and washed with benzene–petroleum ether. The greenish solids were proved to be free radicals by means of ESR spectroscopy. The filtrate was evaporated under reduced pressure, and the resulting residue was chromatographed on silica gel. Small amounts 9,9′-bixanthyl and 25 mg(5%) of **6b** were thus obtained.

Quinydrone, **8d**; dark-violet leaflets; mp 113—115 °C, IR(KBr): ν_{OH} 3400 cm^{-1}. 2-Bromo-2,3-dixanthyl-2,3-dihydro-1,4-naphthoquinone, **7d**; white crystals; mp 151—152 °C, IR(KBr): $\nu_{C=O}$ 1700, 1780 cm^{-1}. PMR($CDCl_3$) δ: (m, 20H), 5.16(d, H), 4.56(s, H), 3.93(d, H), J_{bc}=4.0 Hz. Elemental and mass analyses could not be done, because **7d** was unstable and gradually decomposed. However, IR and PMR spectra showed the same patterns as those of **7b**. Stable radical, **10d**; greenish powder; mp *ca.* 110 °C (decomp.). **10d** and **10b** had almost the same decomposing points, and their chromic-acid oxidations gave the same



7d

product. Their ESR and IR spectra were, then, quite similar.

*v) Photochemical Reaction of 2,3-Dichloro-1,4-naphthoquinone, **5c**, with Xanthene.* A solution of **5c** (454 mg, 2 mmol) and xanthene (2 mmol) was irradiated for 11 hr. The dark-greenish solids thus deposited were filtered off, and washed with benzene. 130 mg(17%) of dark-greenish solids, **10c**, were thus obtained. The filtrate was evaporated under reduced pressure, and the resulting residue was chromatographed on silica gel. Elution with benzene gave red needles of 2-chloro-3-xanthylnaphthoquinone, **6c**, (178 mg, 24%). The dark-greenish solids were proved to be free radicals by means of ESR spectroscopy.

Stable radical, **10c**; dark-greenish powder; mp 135—140 °C(decomp.), IR(KBr): ν_{OH} 3050 cm^{-1}. 2-Chloro-3-xanthyl-1,4-naphthoquinone **6c**; PMR($CDCl_3$) δ: 7.5—8.2 (m, 4H), 6.7—7.3(m, 8H), 6.16(s, 1H), IR(KBr): $\nu_{C=O}$ 1660 cm^{-1}. UV($CHCl_3$): λ_{max} (log ε) 483 nm(1.80), 340 nm(3.75), 280 nm(4.18), 252 nm(4.30). Found: C, 73.98; H, 3.38; Cl, 9.77%. Calcd for $C_{23}H_{13}O_3Cl$: C, 74.11; H, 3.51; Cl, 9.51%. Mass *m/e*: 372(M^+), 337, 181.

*vi) Photochemical Reaction of 2,3-Dibromo-1,4-naphthoquinone, **5e**, with Xanthene.* A solution of **5e** (632 mg, 2 mmol) and xanthene (2 mmol) in 60 ml of benzene was irradiated for 10 hr. The black solids deposited were filtered off, and washed with benzene. 53 mg(5.3%) of black solids, **10d**, were thus obtained. The solids were proved to consist of free radicals by means of ESR spectroscopy. The filtrate was evaporated, and the resulting residue was chromatographed on silica gel. Elution with benzene gave red needles, which proved to be 2-bromo-3-xanthyl-1,4-naphthoquinone **6e** (107 mg, 11%).

Stable radical, **10e**; black powder; mp 181—182 °C(decomp.), IR(KBr): ν_{OH} 3050 cm^{-1}. 2-Bromo-3-xanthyl-1,4-naphthoquinone, **6e**; mp 210 °C(decomp.), IR(KBr): $\nu_{C=O}$ 1667 cm^{-1}. UV($CHCl_3$): λ_{max} (log ε) 490 nm(1.85), 340 nm (3.54), 290 nm(4.23), 254 nm(4.29). PMR($CDCl_3$) δ: 7.0—8.4(m, 12H), 6.36(s, 1H): Found: C, 66.49; H, 3.08; Br, 19.02%. Calcd for $C_{23}H_{13}O_3Br$: C, 66.20; H, 3.14; Br, 19.14%.

vii) Photochemical Reactions of 1,4-Naphthoquinone Derivatives with Thioxanthene. A solution of 1,4-naphthoquinone derivatives, **3a** and **5a—e** (2 mmol), and thioxanthene(4 mmol) in 30 ml of benzene was irradiated for 6—8 hr. Naphthohydroquinones, quinhydrones, and 9,9′-bithioxanthyl were thus obtained in nearly quantitative yields. In the photochemical reaction of **5b** or **5d** with thioxanthene, small amounts of the adduct corresponding to **6b** were isolated. 9,9′-Bithioxanthyl; white needles; mp>300 °C. 2-Thioxanthyl-1,4-naphthoquinone; orange needles; mp 236—237 °C, IR(KBr): $\nu_{C=O}$ 1650 cm^{-1}. PMR($CDCl_3$) δ: 7.04—8.0(m, 12H), 6.36(s, 1H), 5.74(s, 1H). Mass *m/e*: 354(M^+), 337, 197.

*Oxidation of Stable Free Radicals, **10b—d**.* A dilute aqueous chromic acid solution was added to a solution of stable free radicals, **10b, 10c,** or **10d** (100 mg), in acetic acid(30 ml) until the green solution turned reddish yellow. A 100-ml portion of water was then added to the solution, and it was extracted with ether. The dried extract was evaporated, and resulting residue was separated on thin-layer chromatography. 2-[9′-Hydroxyxanthyl]-1,4-naphthoquinone, **12a**, from **10b** and **10d**, and 2-chloro-3-[9′-hydroxyxanthyl]-1,4-naphthoquinone, **12b**, from **10c**, in about 30% yield.

2-[9′-Hydroxyxanthyl]-1,4-naphthoquinone, **12a**; red needles; mp 226—227 °C, IR(KBr): ν_{OH} 3490 cm^{-1}, $\nu_{C=O}$ 1660 cm^{-1}. PMR($CDCl_3$) δ: 6.92—8.10(m, 13H), 3.20 (s, 1H, -OH). Found: C, 78.25; H, 4.05%. Calcd for $C_{23}H_{14}O_4$: C, 77.96; H, 3.98%. Mass *m/e*: 354(M^+), 337, 197. 2-Chloro-3-[9′-hydroxyxanthyl]-1,4-naphthoquinone, **12b**; orange yellow needles; mp 165 °C (decomp.), IR(KBr): ν_{OH} 3370 cm^{-1}. $\nu_{C=O}$ 1680, 1640 cm^{-1} (the two IR absorptions due to carbonyl groups indicate the existence of chelated and non-chelated carbonyl groups, coinciding with the existence of an intramolecularly-hydrogen-bonded hydroxyl group). PMR($CDCl_3$) δ: 8.22—6.88(m, 12H), 6.84(s, 1H, -OH). Found: C, 71.38; H, 3.40; Cl, 9.35%. Calcd for $C_{23}H_{13}O_4Cl$: C, 71.04; H, 3.38; Cl, 9.12%. Mass *m/e*: 388(M^+), 371, 352, 336, 279, 197.

ESR Spectroscopy. ESR spectra of **10b—e** were observed at room temperature by the use of a JEOL X-band PE-3X spectrometer. THF used as a solvent was dried with metallic sodium and purified by distillation. Samples dissolved in THF were thoroughly degassed by four freeze-pump-thaw cycles and sealed. The ESR coupling constants and *g*-values of **10b—e** were measured by using Fremy's salt (a_N: 13.0 gauss, *g*: 2.0055) as a standard.

CIDNP Examinations. An investigation of these photochemical reactions by the CIDNP technique was performed using a JEOL C-60 HL spectrometer, equipped with a modified NMR probe for the photo-irradiation. The details of the method used were previously described in this Bulletin by Maruyama and his co-workers.[3]

Determination of Quantum Yields. A solution of 1,4-naphthoquinone derivatives(0.1 M) and xanthene(0.2 M) was irradiated with a 400W high-pressure mercury arc lamp through a uv-cut filter (Toshiba VY-42). The intensity was determined by means of a potassium ferrioxalate actinometer.[14] The rate of quinone disappearance was determined spectroscopically.

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15) Signal 2 was erroneously assigned to 2,3-protons of quinone moiety in structure **15** in the previous report,[5] but this should be corrected to be assigned to 2,3-protons of quinone moiety in structure **16**.