# Photochemical Reduction of 1,2-Naphthoquinones with Xanthen. Investigation by means of a Photo-CIDNP Technique

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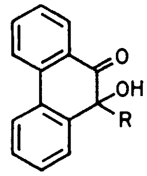
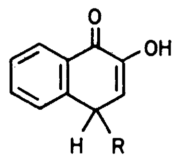
Photochemical reactions of 1.2-naphthoquinone and its derivatives with xanthen. a hydrogen donor, have been investigated. 1.2-Naphthoquinones. in general. produced the stable adducts (2). 9.9'-bixanthenyl. and xanthone together with a small amount of quinhydrones. 4-Substituted 1.2-naphthoquinones. however, gave the corresponding naphthalene-1.2-diols as the major products. Investigation by means of a CIDNP technique indicated the formation of unstable products. judging from the strongly polarized $^1H$ n.m.r. signals. though the unstable intermediates did not accumulate in the reacting solution. Adducts (2). naphthalene-1.2-diols. and 1.2-naphthoquinones themselves also showed polarized $^1H$ n.m.r. signals. From these results. the reaction mechanism was deduced.

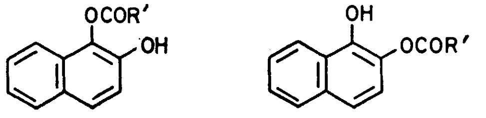
THE photochemical reaction of quinones with hydrogen donors has been investigated by several workers.[1]



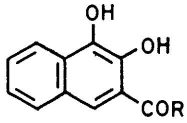
(1)



(2a)



(3)



(4)

R = xanthenyl R′=acyl

Recently we examined the reaction of *p*-quinones [2] and phenanthrene-9,10-quinone [3] with hydrogen donors by means of a photo-CIDNP technique, and pointed out the formation of unstable intermediates in the course of the reactions.

Products in the photochemical reaction of 1,2-naphthoquinone derivatives with xanthen

| | Product [a] | | | | |
|---|---|---|---|---|---|
| Quinone | Adduct (%) | Quinhydrone (%) | $QH_2$ [b] (%) | 9,9′-Bixanthenyl (7) (%) | Xanthone (8) (%) |
| (5a) | (2a) (79) | (6a) (trace) | | 6 | 3 |
| (5a) [c] | (2a) (39) | (6a) (9) | | 20 | 15 |
| (5b) | (2b) (60) | (6b) (2) | | 28 | 7 |
| (5c) | (2c) (44) | (6c) (5) | | 17 | 15 |
| (5d) | (2d) (70) | (6d) (trace) | | 25 | 11 |
| (5e) | (2e) (68) | (6e) (trace) | | 13 | 10 |
| (9a) | | (6′a) (trace) | (10a) (89) | 88 | 11 |
| (9b) | | (6′b) (trace) | (10b) (74) | 52 | 27 |
| (9c) | (11) (15) | (6′c) (58) | | 33 | 24 |
| (9d) | | (6′d) (70) | | 53 | 10 |

[a] Yields are based on the amount of starting material consumed. [b] Naphthalene-1,2-diol. [c] Carbon tetrachloride solution.

Irradiation of phenanthrene-9,10-quinone with xanthen gave the ' 1,2-adduct ' (1).[4] We reported, however, that 1,2-naphthoquinone gave a different type of adduct (2a) in the reaction with xanthen.[5] On the other hand, when aldehyde was used as a solvent, 1,2-naphthoquinone gave the ' 1,4-adduct ' (3) and the ring-acylated photoadduct (4).[6] Thus, the structure of the stable photoadducts depends on the nature of the solvent used.

Photochemical reactions of 1,2-naphthoquinone, and its 3-chloro, 3-methyl, 4-cyano, 4-acetyl, 4-methyl, 4-methoxy, 6-bromo, and 6-methyl derivatives with xanthen in the liquid phase were studied by detailed analyses of the stable products. In addition, photo-CIDNP provided information on the unstable intermediates, leading to the construction of a tentative reaction mechanism.

## RESULTS AND DISCUSSION

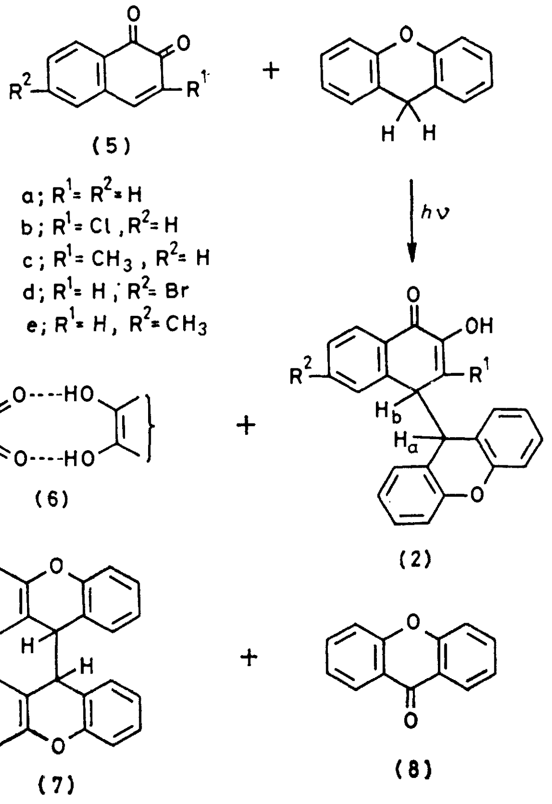
General procedures for photochemical reactions are described elsewhere.[2,5]

*Photochemical Reaction of Substituted* 1,2-*Naphthoquinones* (5) *with Xanthen.*—Irradiation for *ca.* 6 h of a solution of 1,2-naphthoquinone (5a) and xanthen gave 2-hydroxy-4-xanthen-9-ylnaphthalen-1(4*H*)-one (2a), 1,2-,naphthoquinhydrone (6a), 9,9′-bixanthenyl (7), and xanthone (8) in yields of 79, trace, 6, and 3%, respectively.

Determination of the structure of (2a) was described previously.[5] 3-Chloro-1,2-naphthoquinone (5b), 3-methyl-1,2-naphthoquinone (5c), 6-bromo-1,2-naphthoquinone (5d), and 6-methyl-1,2-naphthoquinone (5e) gave similar products as summarized in the Table (see also Scheme 1).

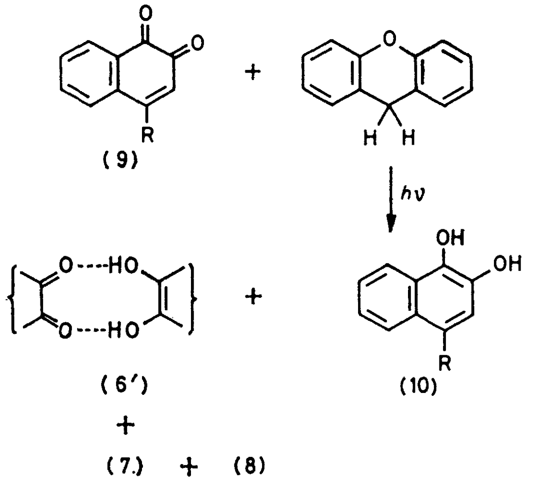
*Photochemical Reaction of* 4-*Substituted* 1,2-*Naphthoquinones* (9) *with Xanthen.*—In the photochemical reaction of 4-substituted 1,2-naphthoquinones (9) with xanthen the corresponding naphthalene-1,2-diols, 1,2-naphthoquinhydrone (6′), 9,9′-bixanthenyl (7), and xanthone (8) were obtained in good yields without any adduct (see Scheme 2 and Table).

4-Substituted naphthalene-1,2-diols (10a and b) were obtained in the reaction of 4-cyano- (9a) and 4-acetyl-1,2-naphthoquinone (9b) in good yields, but 4-methyl- (9c) and 4-methoxy-1,2-naphthoquinone (9d) gave a very low yield of the reduction products. After irradiation of (9c and d) for *ca.* 30 h in the presence of xanthen, these quinones were recovered in yields of 33 and 88%, respectively. These results indicated (10c and d) initially formed in the reacting system might be easily oxidised to the corresponding quinones upon isolation, since (10c and d) prepared by reduction of (9c and d) were easily oxidised to the starting materials in benzene solution on treatment with air or silica gel.



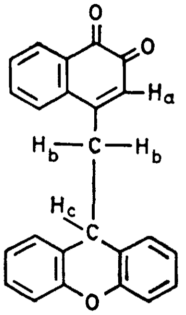
SCHEME 1

The reaction of 4-methyl-1,2-naphthoquinone (9c) gave an unexpected yellow adduct (11) (11.5%) in addition to the usual products (6′c), (7), and (8). The adduct (11) was identified by the following spectroscopic properties. The i.r. spectrum showed absorption bands at 1 695 (weak) and 1 655 (strong) cm$^{-1}$, characteristic of the carbonyl groups of 1,2-naphthoquinones.[7] The $^1$H n.m.r. spectrum showed signals at δ 2.99 (2 H, d, $J$ 8.0 Hz, H$_b$), 4.35 (1 H, t, $J$ 8.0 Hz, H$_c$), 5.77 (1 H, s, H$_a$), and 7.00—8.15 (12 H, m). The nuclear spin–spin interactions between H$_b$ and H$_c$ were confirmed by the spin-decoupling technique. When H$_b$ were irradiated, the triplet for H$_c$ changed to a singlet, and *vice versa*. The corresponding adduct obtained from the photochemical reaction of (9c) with $[9\text{-}^2H_2]$xanthen showed no signal at δ 4.35 and the doublet at δ 2.99 changed to a singlet. In addition, the mass spectrum of (11) supported the structure, $m/e$ 352 ($M^+$), 181 [(xanthen moiety)$^+$], and 172 [(quinone moiety)$^+$]. From these results, structure (11) was assigned to the yellow adduct. The mechanism of formation of (11) still remains to be clarified.



a; R = CN, b; R = COCH$_3$, c; R = CH$_3$, d; R = OCH$_3$

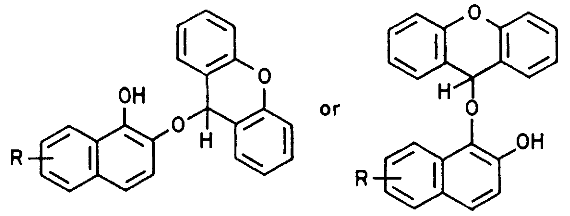
SCHEME 2



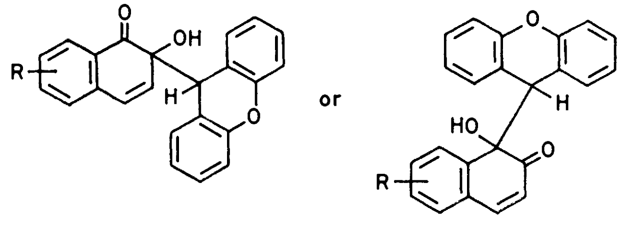
(11)

*Photo-CIDNP Measurements.*—Figure 1 shows $^1$H n.m.r. spectra observed for the reaction of 1,2-naphthoquinone with xanthen. Spectra (a) and (b) were observed before and during irradiation, respectively. Comparing (b) with (a), new, strong, polarized signals 1—6 appear in (b). When irradiation is cut off the polarized signals disappear within a few seconds. Spectrum (c) observed during the course of the photoreaction of 1,2-naphthoquinone with $[9\text{-}^2H_2]$xanthen clearly indicates that three polarized signals, *i.e.*, signals 2, 4, and 5, are due to the methine protons of the xanthen moiety in the product, since they disappear in (c). Further, it is concluded that the other signals 1, 3, and 6 in (b) are derived from the ring protons of the quinone or the quinone moiety of the adduct. Signal 6 in (b) (emission; double doublet) changes into a doublet in (c).

The polarized signals 3, 4, and 6 could be easily assigned to the stable adduct (2a) by comparison with $^1$H n.m.r. spectrum of the corresponding isolated adduct [they correspond to $R^1$ = H, $H_a$, and $H_b$ of (2a), respectively]. By comparison of the chemical shifts of the polarized signals with those observed in the photochemical reaction of 1,4-naphthoquinone with xanthen,[2] the absorption-polarized signals 2 (δ 6.05) and 5 (δ 3.98) may be assigned to the methine protons of the xanthen moiety in the unstable products (12) and (13), respectively. These assignments are further supported by comparison of these results with those observed for the reaction of 3-methyl-1,2-naphthoquinone with xanthen (Figure 2).



1,4 – adduct
(12)



1,2 – adduct
(13)

Signals 5 (absorption, doublet) and 7 (emission, doublet) shown in Figure 2(b) correspond respectively to $H_a$ and $H_b$ of the stable adduct (2c). Comparing Figure 2(b) with 2(c) we may assign signals 2 (δ 6.13) and 6 (δ 3.99) to the methine protons of the unstable products (12) and (13), respectively. Signal 3 is due to 4-H of 3-methyl-1,2-naphthoquinone. However, signals 1 and 4, though they are undoubtedly due to the protons of the quinone or the quinone moiety of the adduct, cannot be assigned exactly. In addition, five polarized signals [8—12 in Figures 2(b) and (c)] in the methyl region were observed. These correspond to the methyl groups of stable or unstable products. The methyl protons of the stable adduct (2c) showed the emission-polarized signal 9. Signals 8 (emission) and 12 (absorption) correspond to the methyl protons of 3-methylnaphthalene-1,2-diol and 3-methyl-1,2-naphthoquinone, respectively. The other polarized signals 10 and 11 should be due to the methyl protons of unstable products.

The $^1$H n.m.r. spectra observed during the course of the photochemical reaction of the 6- and 4-methyl derivatives of 1,2-naphthoquinone with xanthen are shown in Figures 3 and 4, respectively. The signals are assignable to the structure as shown in Figures 3 and 4. One of the two emission-polarized signals [signal 1 in Figure 3(b)] corresponds to the methyl group of 6-methylnaphthalene-1,2-diol and the other, signal 4, corresponds to the methyl group of quinone itself. Signal 3 in Figure 3(b) is assignable to the methyl group of the stable adduct (2e), and the other absorption-polarized signal 2 may be due to the methyl group of the unstable products.

In Figure 4 we find an analogous polarization pattern in the methyl group region. The absorption-polarized signal 5 corresponds to the methyl group of 4-methylnaphthalene-1,2-diol. The emission-polarized signals 3 (δ 1.44) and 6 (δ 5.80) in Figure 4(b) correspond to the methyl protons and 3-H of 4-methyl-1,2-naphthoquinone. The other absorption-polarized signals (1, 2, and 4) are probably due to the methyl protons of unstable products.

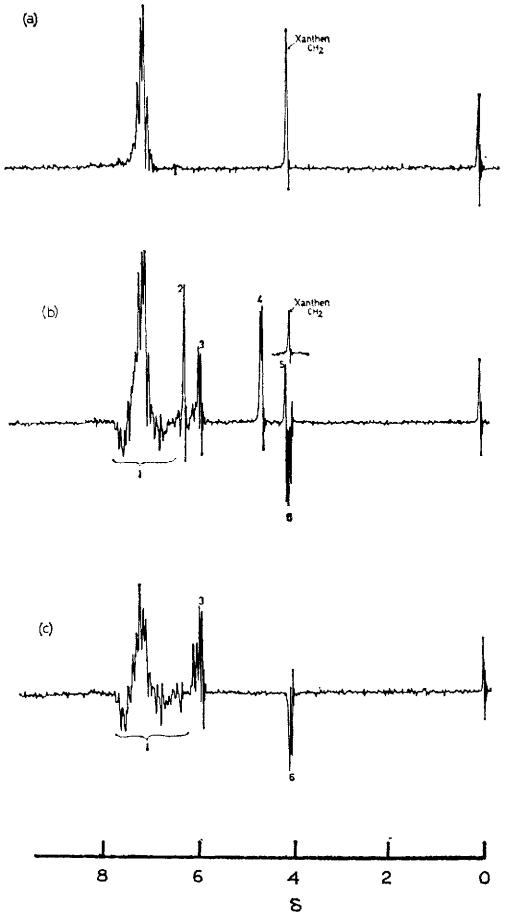


FIGURE 1 $^1$H N.m.r. spectra observed for the photochemical reaction of 1,2-naphthoquinone with xanthen: (a) before irradiation; (b) during irradiation; (c) during irradiation using [9-$^2H_2$]xanthen (solvent, carbon tetrachloride)

In the photochemical reaction of 4-methoxy-1,2-naphthoquinone with xanthen, strong polarized $^1$H n.m.r. signals similar to those observed in the reaction of 4-methyl-1,2-naphthoquinone were also observed. Both methyl protons and 3-H of 4-methoxy-1,2-naphthoquinone also showed emission-polarized signals.

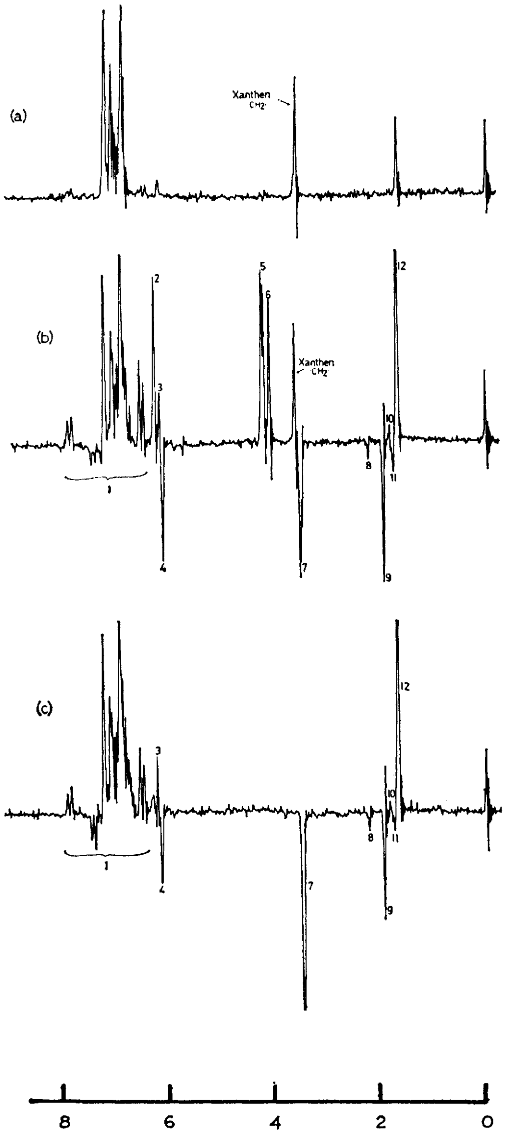


FIGURE 2 $^1$H N.m.r. spectra observed for the photochemical reaction of 3-methyl-1,2-naphthoquinone with xanthen: (a) before irradiation; (b) during irradation; (c) during irradiation using [9-$^2H_2$]xanthen (solvent, [$^2H_6$]benzene)

Thus, it was concluded that the 1,4-adduct (12) and the 1,2-adduct (13) were formed in the reacting system, but they were not stable enough to be isolated. As the methyl protons of methyl-substituted 1,2-naphthoquinone and those of the corresponding naphthalene-1,2-diol both showed strong polarizations, it may be deduced that two solvent-separated 1,2-naphthosemiquinone radicals disproportionate to yield 1,2-naphthoquinone and naphthalene-1,2-diol. This is substantiated by the following evidence: both the ring protons of *p*-benzoquinone and hydroquinone produced in the disproportionation of *p*-benzosemiquinone radical showed strong emission- and absorption-polarized signals, respectively.[8]

*Reaction Mechanism.*—1,2-Naphthoquinone derivatives examined in this work have an *n*–π* absorption band in the region $\lambda_{max.}$ 470—530 nm (ε *ca.* 100). 1,2-Naphthoquinone derivatives excited by the *n*–π* transition could convert into the triplet state *via* intersystem crossing (i.s.c.). The excited molecule in the triplet state can abstract hydrogen from xanthen to give a triplet radical pair (14) consisting of 1,2-naphthosemiquinone and xanthenyl in the solvent cage. Combination of these radicals in the cage may occur, giving stable and unstable products. The unstable products could decompose thermally or photochemically to give solvent separated 1,2-naphthosemiquinone (16) and xanthenyl (17). Radical (16) will disproportionate to give a 1,2-naphthoquinone and a naphthalene-1,2-diol. 9,9′-Bixanthenyl is formed by coupling of two molecules of radical (17). Xanthone is formed by trapping of oxygen dissolved in the solvent by radical (17).

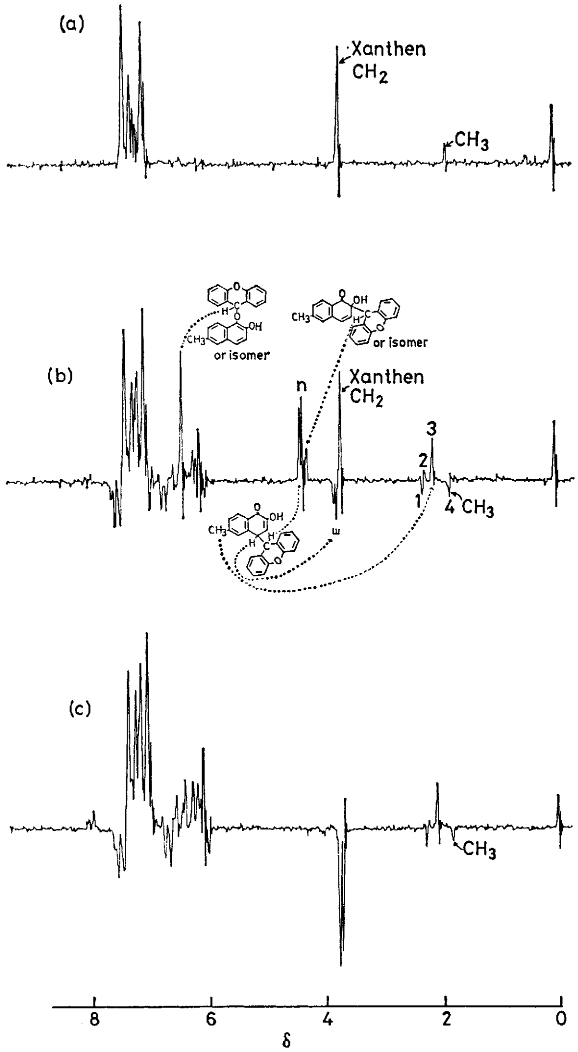
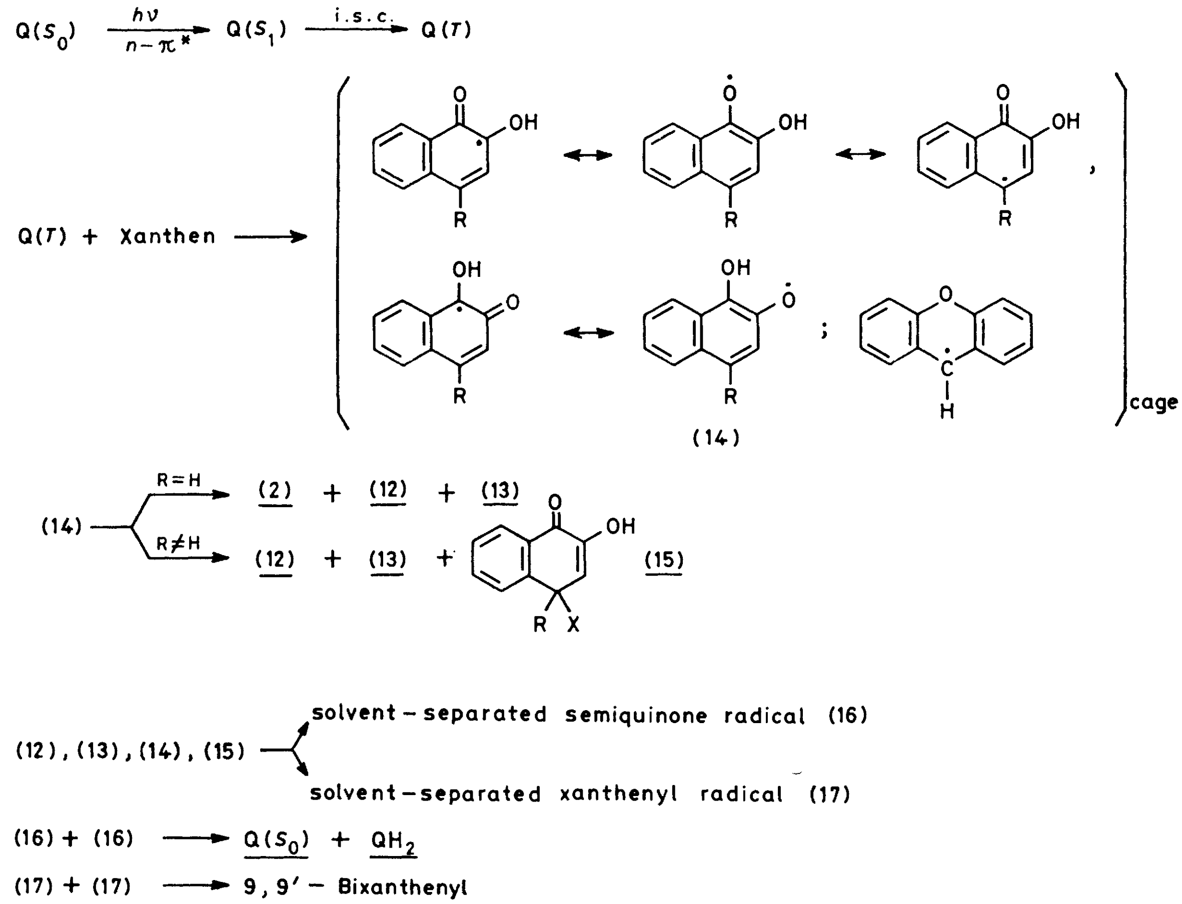


FIGURE 3 $^1$H N.m.r. spectra observed for the photochemical reaction of 6-methyl-1,2-naphthoquinone with xanthen: (a) before irradiation; (b) during irradiation; (c) during irradiation using [9-$^2H_2$]xanthen (solvent, [$^2H_6$]benzene)

These sequences are summarized in Scheme 3.

The methine proton polarization of the xanthen moiety in stable and/or unstable products may be predicted from the Kaptein equation (i),[9] in which each symbol has the signs written underneath.*,† The observed enhanced absorption-polarized signals are in complete coincidence with prediction.

$$\Gamma_{ne} = \mu\cdot\varepsilon\cdot\Delta g\cdot a \qquad \text{(i)}$$
$$= + + - - \equiv +$$



SCHEME 3 Compounds underlined show polarised signals. Q = 1,2-Naphthoquinone; $QH_2$ = naphthalene-1,2-diol; X = xanthenyl radical

## EXPERIMENTAL

Instruments were described previously.[2,6] Yields are based on starting materials consumed.

*Materials*.—1,2-Naphthoquinones were prepared by literature methods or by the oxidation of naphthol with Fremy's salt.[6,11] Commercial xanthen and [9-$^2H_2$]xanthen prepared by the reduction of xanthone with $LiAlD_4$ [12] were used.

General procedures for photochemical reactions were described previously.[2,5]

*Photochemical Reaction of* 1,2-*Naphthoquinones* (5) *with Xanthen*.—(*i*) 1,2-*Naphthoquinone* (5a). A benzene or carbon tetrachloride solution of (1 mmol) and xanthen (2 mmol) was irradiated for 6 h with ice–water cooling. After the usual work-up, the following products were obtained: 1,2-naphthoquinhydrone (6a), dark violet crystals, $\nu_{max.}$ 3 250 cm$^{-1}$; unchanged xanthen (200 mg); 9,9′-bixanthenyl (7) (7 mg), m.p. 211—212°; xanthone (8) (3.5 mg), m.p. 174°; 2-hydroxy-4-xanthen-9-ylnaphthalen-1(4*H*)-one (2a) (270 mg), silky needles (from benzene–petroleum), m.p. 121—122° (decomp.), $\nu_{max.}$ 3 375 and 1 640 cm$^{-1}$, $\delta[(CD_3)_2CO]$ 4.27 (1 H, dd, $H_b$), 4.92 (1 H, d, $H_a$), 5.90 (1 H, d, naphthalene 3-H), and 6.02—8.03 (13 H, m).

(*ii*) 3-*Chloro*-1,2-*naphthoquinone* (5b). A benzene solution of (5b) (1 mmol) and xanthen (1 mmol) was irradiated for 20 h at 15°. After the usual work-up, the following products were obtained: 3-chloro-1,2-naphthoquinhydrone (6b) (5 mg), $\nu_{max.}$ 3 300 cm$^{-1}$; 9,9′-bixanthenyl (41 mg); xanthone (10 mg); unchanged quinone (33 mg); 3-chloro-2-hydroxy-4-xanthen-9-ylnaphthalen-1(4*H*)-one (2b) (186 mg), silky needles (from benzene), m.p. 157—158 °C, $\nu_{max.}$ 3 375 and 1 655 cm$^{-1}$, $\delta[(CD_3)_2CO]$ 4.25 (1 H, d, $H_b$), 4.95 (1 H, d, $H_a$), 6.24—7.75 (12 H, m), and 8.21 (1 H, s, exchanged with $D_2O$).

(*iii*) 3-*Methyl*-1,2-*naphthoquinone* (5c). A benzene solution of (5c) (1 mmol) and xanthen (1 mmol) was irradiated for 24 h at room temperature. After the usual work-up, the following products were obtained: 3-methyl-1,2-naphthoquinhydrone (6c) (8 mg), dark violet crystals, $\nu_{max.}$ 3 275 cm$^{-1}$; unchanged xanthen (32 mg); unchanged

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* The *g* value of semiquinone radical is larger than that of carbon radicals without exception.

† The sign of the hyperfine coupling constant (*a*) of the α hydrogen of carbon radicals is assumed to be negative.[10]

quinone (49 mg); 9,9′-bixanthenyl (25 mg); xanthone (22 mg); 2-hydroxy-3-methyl-4-xanthen-9-ylnaphthalene-1(4*H*)-one (2c) (112 mg), needles (from benzene–petroleum), m.p. 127—129°, $\nu_{max.}$ 3 380 and 1 639 cm$^{-1}$, $\delta$(CDCl$_3$) 2.15 (3 H, s), 3.73 (1 H, d, H$_b$), 4.40 (1 H, d, H$_a$), and 6.10—7.55 (13 H, m).

3-Methylnaphthalene-1,2-diol was prepared by the reduction of (5c) with $Na_2S_2O_4$ as crystals, m.p. 96—97°, $\nu_{max.}$ 3 500 cm$^{-1}$. It was easily oxidized to (5c) in benzene solution with air or in silica gel. The chemical shift of the methyl group ($\delta$ 2.30) of 3-methylnaphthalene-1,2-diol in [$^2H_6$] benzene coincided with signal 8 in Figure 2(b).

(*iv*) 6-*Bromo*-1,2-*naphthoquinone* (5d). A benzene solution of (5d) (1 mmol) and xanthen (1 mmol) was irradiated for 5 h at room temperature. After the usual work-up, the following products were obtained: unchanged xanthen (26 mg); 9,9′-bixanthenyl (20 mg); xanthone (20 mg); 6-bromo-2-hydroxy-4-xanthen-9-ylnaphthalen-1(4*H*)-one (2d) (293 mg), needles (from benzene–petroleum), m.p. 130—131°, $\nu_{max.}$ 3 375 and 1 640 cm$^{-1}$, $\delta$(CDCl$_3$) 3.97 (1 H, dd, H$_b$), 4.55 (1 H, d, H$_a$), 5.89 (1 H, d, naphthalene 3-H), and 6.07—7.75 (12 H, m).

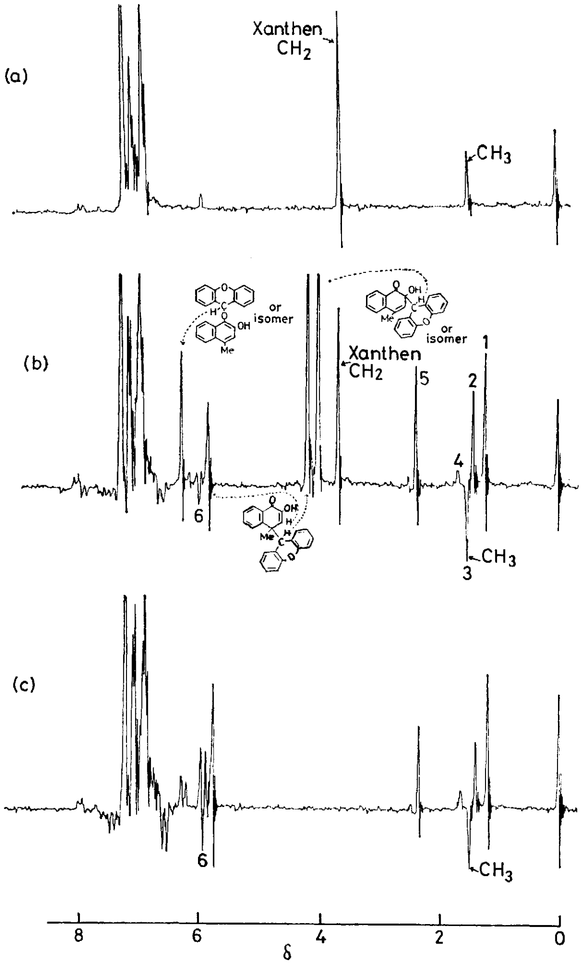

FIGURE 4 $^1$H N.m.r. spectra observed for the photochemical reaction of 4-methyl-1,2-naphthoquinone with xanthen: (a) before irradiation; (b) during irradation; (c) during irradiation using [9-$^2H_2$]xanthen (solvent, [$^2H_6$]benzene)

(*v*) 6-*Methyl*-1,2-*naphthoquinone* (5e). A benzene solution of (5e) (3 mmol) and xanthen (3.5 mmol) was irradiated for 8 h with ice–water cooling. After usual work-up, the following products were obtained: unchanged xanthen (190 mg); 9,9′-bixanthenyl (58 mg); xanthone (48 mg); 2-hydroxy-6-methyl-4-xanthen-9-ylnaphthalen-1(4*H*)-one (2e) (725 mg), crystals (from benzene), m.p. 140—142° (decomp.), $\nu_{max.}$ 3 375 and 1 642 cm$^{-1}$, $\delta$(CDCl$_3$) 2.40 (3 H, s), 3.93 (1 H, dd, H$_b$), 4.54 (1 H, d, H$_a$), 5.82 (1 H, d, naphthalene 3-H), and 5.87—7.76 (12 H, m).

6-Methylnaphthalene-1,2-diol was prepared by the reduction of (5e) with $Na_2S_2O_4$; silky needles which turn dark brown in air, m.p. 74—74.5°, $\nu_{max.}$ 3 330 cm$^{-1}$. The chemical shift of the methyl group ($\delta$ 2.15) of 6-methylnaphthalene-1,2-diol in [$^2H_6$]benzene coincided with signal 1 in Figure 3(b).

(*vi*) 4-*Cyano*-1,2-*naphthoquinone* (9a). A benzene solution of (9a) (1 mmol) and xanthen (2 mmol) was irradiated for 6 h with ice–water cooling. After the usual work-up, the following products were obtained: unchanged xanthen (180 mg); 9,9′-bixanthenyl (160 mg); xanthone (22 mg); quinhydrone (6′a) (15 mg); 4-cyanonaphthalene-1,2-diol (10a) (165 mg), crystals (from benzene), m.p. 208°.[13]

(*vii*) 4-*Acetyl*-1,2-*naphthoquinone* (9b). A benzene solution of (9b) (1 mmol) and xanthen (1 mmol) was irradiated for 10 h at room temperature. After the usual work-up, the following products were obtained: 9,9′-bixanthenyl (95 mg); xanthone (50 mg); 4-acetylnaphthalene-1,2-diol (10b) (150 mg), needles (from benzene–methanol), m.p. 162—164°, $\nu_{max.}$ 3 250 cm$^{-1}$.

(*viii*) 4-*Methyl*-1,2-*naphthoquinone* (9c). A benzene solution of (9c) (1 mmol) and xanthen (1 mmol) was irradiated for 38 h at room temperature. After the usual work-up, the following products were obtained: 4-methyl-1,2-naphthoquinhydrone (6′c) (100 mg), dark violet crystals, $\nu_{max.}$ 3 400 cm$^{-1}$; unchanged xanthen (35 mg); 9,9′-bixanthenyl (49 mg); xanthone (49 mg); (9c) (56 mg); 4-xanthen-9-ylmethyl-1,2-naphthoquinone (11) (56 mg), yellowish orange needles (from benzene–petroleum), m.p. 155—156° (decomp.), $\nu_{max.}$ 1 695w and 1 655s cm$^{-1}$, *m*/*e* 352 ($M^+$, 28%), 181 (100), 172 (45), 144 (30), and 115 (64), $\delta$(CDCl$_3$) 2.99 (2 H, d, *J* 8.0 Hz, H$_b$), 4.35 (1 H, t, *J* 8.0 Hz, H$_c$), 5.77 (1 H, s, H$_a$), and 7.00—8.15 (12 H, m).

4-Methylnaphthalene-1,2-diol was prepared by the reduction of (9c) with $Na_2S_2O_4$, silky needles which readily turn violet in air, m.p. 64—66°, $\nu_{max.}$ 3 350 cm$^{-1}$. The diol was easily oxidized to (9c) or (6′c) in benzene on treatment with air or silica gel. The chemical shift of the methyl group 4-methylnaphthalene-1,2-diol in [$^2H_6$]benzene coincided with signal 5 in Figure 4(b).

(*ix*) 4-*Methoxy*-1,2-*naphthoquinone* (9d). A benzene solution of (9d) (1.06 mmol) and xanthen (1.5 mmol) was irradiated for 24 h at 15°. After the usual work-up, the following products were obtained: 4-methoxy-1,2-naphthoquinhydrone (6′d) (23 mg), dark green powder, $\nu_{max.}$ 3 300 cm$^{-1}$; xanthen (62 mg); 9,9′-bixanthenyl (112 mg); xanthone (22 mg); and (9d) (167 mg).

*Photo-CIDNP Examination*.—The investigation of the photochemical reactions by CIDNP was performed using a JEOL MH-100 spectrometer, equipped with a modified n.m.r. probe for photoirradiation (light source, 500 W high-pressure xenon arc lamp). Details were reported previously.[2]

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REFERENCES

[1] J. M. Bruce, *Quart. Rev.*, 1967, **21**, 405, and references cited therein.

[2] K. Maruyama, T. Otsuki, and A. Takuwa, *Chem. Letters*, 1972, 131; K. Maruyama, T. Otsuki, A. Takuwa, and S. Arakawa, *Bull. Chem. Soc. Japan*, 1973, **46**, 2470; K. Maruyama and S. Arakawa, *ibid.*, 1974, **47**, 1960.

[3] K. Maruyama, H. Shindo, and T. Maruyama, *Bull. Chem. Soc. Japan*, 1971, **44**, 585; K. Maruyama, T. Otsuki, H. Shindo, and T. Maruyama, *ibid.*, pp. 2000, 2756, 2789; K. Maruyama and T. Otsuki, *ibid.*, 1971, **44**, 2885; K. Maruyama, A. Takuwa, T. Otsuki, and S. Kako, *Bull. Inst. Chem. Res., Kyoto Univ.*, 1972, **50**, 348; K. Maruyama, T. Otsuki, and Y. Naruta, *Bull. Chem. Soc. Japan*, 1976, **49**, 791.

[4] G. Pfundt, Dissertation, Göttingen; *cf.* A. Schönberg, 'Preparative Organic Photochemistry,' Springer, Berlin, 1968, p. 184.

[5] K. Maruyama and A. Takuwa, *Chem. Letters*, 1972, 135; K. Maruyama and A. Takuwa, *Bull. Chem. Soc. Japan*, 1973, **46**, 1529.

[6] K. Maruyama and A. Takuwa, *Chem. Letters*, 1974, 471; A. Takuwa, *Bull. Chem. Soc. Japan*, 1976, **49**, 2790; 1977, **50**, 2973.

[7] St. Berger and A. Rieker, 'Identification and Determination of Quinones,' in 'The Chemistry of the Quinonoid Compounds,' ed. S. Patai, Wiley, 1974, part II, p. 193.

[8] unpublished work.

[9] R. Kaptein, *Chem. Comm.*, 1971, 732; *J. Amer. Chem. Soc.*, 1972, **94**, 6251.

[10] H. Fischer, 'Structure of Free Radicals by E.S.R. Spectroscopy,' in 'Free Radicals,' ed. J. K. Kochi, Wiley–Interscience, New York, 1973, vol. 2, p. 435.

[11] H. J. Teuber and N. Götz, *Chem. Ber.*, 1954, **87**, 1236.

[12] A. Mustafa and M. K. Hilmy, *J. Chem. Soc.*, 1952, 1343.

[13] A. Schönberg, W. I. Awad, and G. A. Mousa, *J. Amer. Chem. Soc.*, 1955, **77**, 3850.