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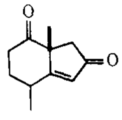
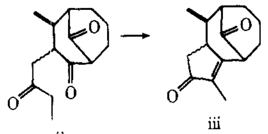


i

(13) As noted above, omission of the crown ether merely resulted in a quantitative recovery of starting material. Using KF and 18-crown-6, we have also been able to effect conversion of ii to iii in 50% yield. This reaction also fails under several of the aforementioned reaction conditions due to cleavage of the acid and base labile bicyclo[3.3.1]nonane-2,9-dione system. The formation of mesityl oxide during KI-dibenzo-18-crown-6 displacements in acetone has been reported: D. J. Sam and H. E. Simmons, *J. Am. Chem. Soc.*, **96**, 2252 (1974).



ii iii

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Photochemistry of Epoxyquinones. 1. Photochemical Reactions of 2-Alkyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinones with Hydrogen Donors[1]

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The photochemical reactions of 2-alkyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinones with good hydrogen donors such as xanthene or 2-propanol gave 2-alkyl-2-hydroxy-2,3-dihydro-1,4-naphthoquinones, 2-alkyl-3-hydroxyl-1,4-naphthoquinones, and 9,9′-bixanthenyl as the main products. For example, the photochemical reaction of 2-methyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone (**1b**) with xanthene gave 2-methyl-2-hydroxy-2,3-dihydro-1,4-naphthoquinone (**3b**), 2-methyl-3-hydroxy-1,4-naphthoquinone (**4b**), 9,9′-bixanthenyl (**5**) and 3,3′-bis(2-methyl-2-hydroxy-2,3-dihydro-1,4-naphthoquinone) (**6**). Isotope effects and the effect of the molar ratio of the reactants on the products distribution suggested that the products **3b** and **6** were formed by hydrogen abstraction of **1b** from xanthene, but the product **4b** was formed by intramolecular rearrangement. The photolysis of 2-methyl-2-hydroxy-3-(9′-xanthenyl)-2,3-dihydro-1,4-naphthoquinone in the absence or in the presence of xanthene also gave the product **3b** or **4b**, respectively, suggesting that the products **3b** and **4b** were formed from the same radical intermediate **10**. The reaction of 2-methyl-2,3-epoxy-3,4-dihydro-4-hydroxynaphthalen-1(2*H*)-one with di-*tert*-butyl peroxalate also gave the product **3b**, together with the epoxyquinone **1b**, suggesting that the product **3b** was also formed by the ring opening rearrangement of the intermediate radical **8**. The photochemical reaction was examined by means of CIDNP. From these data, the reaction mechanism for the formation of the products **3b**, **4b**, **6**, and **5** is presented.

The photochemistry of α,β-epoxy ketones has been well studied in the past.[2] However, little attention has been paid to the photochemistry of epoxyquinones. In this paper we wish to report the photochemical reactions of 2-alkyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinones in the presence of good hydrogen donors. For this work we prepared seven epoxyquinones **1a–g**, and examined their photochemical reactions with hydrogen donors such as xanthene or 2-propanol.

Results and Discussion

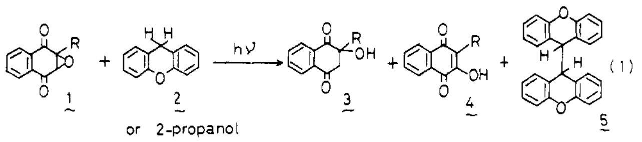
Photoreduction of 2-Alkyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinones with Xanthene or 2-Propanol. A solution of 2-alkyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinones (0.03–0.06 M) and 2 equiv of xanthene in benzene was irradiated in a Pyrex test tube for 10–50 h, using a 300-W high-pressure mercury lamp. Separation of the products by column chromatography and preparative TLC gave 2-alkyl-

Table I. Photoreduction of Epoxynaphthoquinones[a]

Epoxyquinone 1	Registry no.	H donor	Irradiation time, h	% recovered epoxyquinone 1	Isolated yields, %[b] 3	4	5
a, R = H	15448-58-5	Xanthene[d]	10		29		58
b, R = Me	15448-59-6	Xanthene	13		42	16	57
b, R = Me		2-Propanol[e]	20[c]	28	20	24	
c, R = Et	53948-59-7	Xanthene	15	~10	37	22	50
d, R = Pr	63534-40-7	Xanthene	15	22	18	12	36
e, R = *i*-Pr	20175-90-0	Xanthene	15	15	43		53
f, R = CH₂Ph	63534-41-8	Xanthene	15	42	14	12	22
g, R = t-Bu	63534-42-9	Xanthene	50	No reaction			

[a] The solution of the epoxyquinones (0.03–0.06 M) and 2 equiv of xanthene (0.6–0.12 M) in benzene was irradiated using a 300-W high-pressure mercury lamp. [b] Yields of recovered epoxyquinones and products were based on the epoxyquinones and xanthene used. [c] The solution of **1b** (0.053 M) in 2-propanol was irradiated. [d] Registry no.: 92-81-1. [e] Registry no.: 67-63-0.

2-hydroxy-2,3-dihydro-1,4-naphthoquinones (**3**), 2-alkyl-3-hydroxy-1,4-naphthoquinones (**4**), and 9,9′-bixanthenyl (**5**) as the main products (eq 1). The results are summarized in Table I. The major products in the presence of xanthene were 2-alkyl-2-hydroxy-2,3-dihydro-1,4-naphthoquinones (**3**) rather than 2-alkyl-3-hydroxy-1,4-naphthoquinones (**4**), as shown in Table I. On the other hand, the photoreduction of **1b** in 2-propanol gave 2-methyl-3-hydroxy-1,4-naphthoquinones (**4b**) as a major product rather than 2-methyl-2-hydroxy-2,3-dihydro-1,4-naphthoquinone (**3b**). In the photochemical reaction of the epoxyquinone **1b** with xanthene, the dimeric product **6** was also obtained in a low yield (4%), in addition to **3b**, **4b**, and **5** (eq 2). The structures of these products were determined by IR, UV, NMR, mass spectra, elemental analyses, and chemical reactions. The IR spectrum of **3b** showed two characteristic bands at 3390 and 1680 cm^{-1} due to the hydroxy and carbonyl groups, respectively. The NMR spectrum showed the methyl proton as a singlet at δ 1.44 and the methylene protons at C-3 as the AB quartet at δ 3.09 and 3.29 (J = 16 Hz), in agreement with the structure **3b**. The confirmation of structure **3b** was also given by the chemical evidence. The dehydration of **3b** with sodium acetate gave 2-methyl-1,4-naphthoquinone.[3] 2-Methyl-3-hydroxy-1,4-naphthoquinone (phthiocol) (**4b**) was identical with an authentic sample synthesized by the treatment of **1b** with concentrated sulfuric acid.[4] The IR spectrum of the compound **6** showed two characteristic bands at 3450 and 1690 cm^{-1} due to the hydroxy and carbonyl groups, respectively. The NMR spectrum of **6** showed two equivalent methyl protons at δ 1.12 (s, 6 H) and methine protons at δ 2.83 (s, 2 H). The mass spectrum showed no parent peak, but fragment peaks at m/e 360 ($M^+ - 18$), 342, 327, 318, 300, 271, 243, and 215. From these data, **6** is compatible with 3,3′-bis(2-methyl-2-hydroxy-2,3-dihydro-1,4-naphthoquinone). Actually, the dimeric structure of **6** was confirmed by the following reaction. When a solution of **6** and sodium acetate in acetic acid was refluxed, ready dehydration occured to give known 3,3′-bis(2-methyl-1,4-naphthoquinone).[5]



a, R = H; b, R = Me; c, R = Et; d, R = Pr; e, R = *i*-Pr; f, R = CH₂Ph; g, R = *t*-Bu

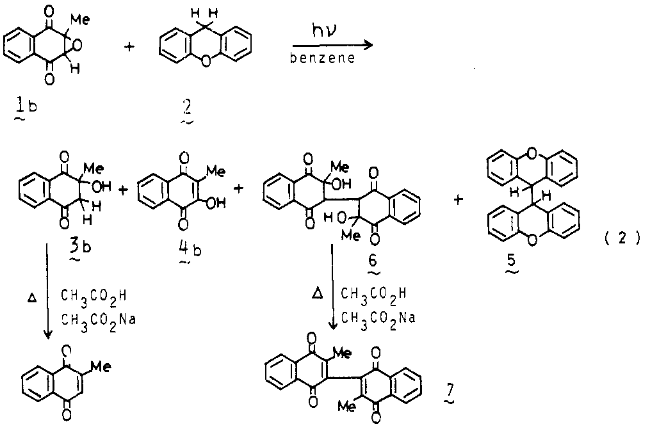


Table II. Quantum Yields[a] for the Disappearance of 1 and the Formation of 3

Epoxyquinone 1	Φ_1[b]	Φ_3[c]
a, R = H	0.73	~0.3
b, R = Me	0.55	0.19
c, R = Et	0.44	0.20
d, R = Pr	0.25	0.06
e, R = *i*-Pr	0.19	0.16
f, R = CH₂Ph	<0.05	
g, R = *t*-Bu	<0.05	

[a] Measured in benzene solution of epoxyquinones **1** (0.05 M) and xanthene (0.1 M) at 313 nm, using potassium ferrioxalate actinometry. [b] Quantum yield for the disappearance of epoxyquinones **1**. [c] Quantum yield for the formation of **3**.

Table III. Isotope Effects on the Photochemical Reaction of the Epoxyquinone 1b with Xanthene[a]

	Yields of products, % 3b	4b	6	5	Recovery, % 1	2
Xanthene	48	20	15	65	17	35
Xanthene-9-d_2	27	30	5	*b*	38	*b*

[a] A solution of **1b** (0.1 M) and xanthene (0.2 M) in benzene was irradiated for 6 h. Yields of products were determined by NMR. [b] Not determined.

Furthermore, we measured quantum yields for the disappearance of epoxyquinones **1a–g** and for the formation of the reduction products **3a–e**, in order to investigate the reactivity of the epoxyquinones **1a–g**. With increasing bulkiness of 2-alkyl substituents, quantum yields for the disappearance of the **1a–g** decreased as shown in Table II, indicating the overwhelming importance of steric factors in the reactions.

In order to investigate the reaction mechanism, we examined the photochemical reaction of the epoxyquinone **1b** with xanthene in detail. Table III shows yields of products and recovered starting materials in the photochemical reaction of **1b** and xanthene or xanthene-9-d_2. When xanthene-9-d_2 was used, the yields of **3b** and **6** decreased, while the yield of phthiocol **4b** increased. This is highly indicative that the products **3b** and **6** are formed via the hydrogen abstraction by

Table IV. Photochemical Reaction of the Epoxyquinone 1b and Xanthene in Benzene (5 mL). Effect of the Molar Ratio of Reactants[a]

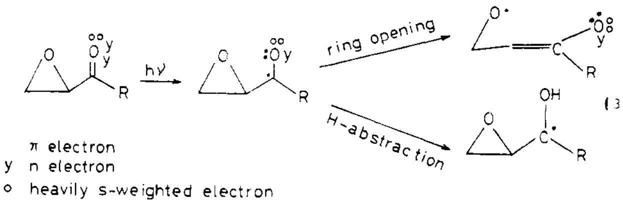
Reactant, mmol		Product, mmol				Recovery, mmol	
1b	**2**	**3b**	**4b**	**6**	**5**	**1b**	**2**
0.25	1.0	0.17	0.05	0.03	0.45	0.00	0.55
0.50	1.0	0.27	0.08	0.06	0.60	0.09	0.40
1.0	1.0	0.34	0.06	0.12	0.70	0.48	0.30
2.0	1.0	0.35	0.07	0.15	0.78	1.43	0.22
0.50	0.50	0.20	0.06	0.05	0.43	0.19	0.07
0.50	0.25	0.14	0.03	0.05	0.23	0.28	0.02

[a] Irradiation time, 10 h. The yields of products were determined by NMR.

the excited epoxyquinone from xanthene. Phthicol **4b** may be produced by intramolecular photoisomerization of **1b.**

The yields of products and recovered starting materials were also examined in benzene solutions at various concentrations of the reactants, and are listed in Table IV. With increasing the amount of **1b** to **2** the yields of **3b** and **6** increased, but that of **4b** was rather insensitive.

The photochemical reaction of α,β-epoxy ketones is generallized as shown in eq 3, using Zimmermann's notation.[6]

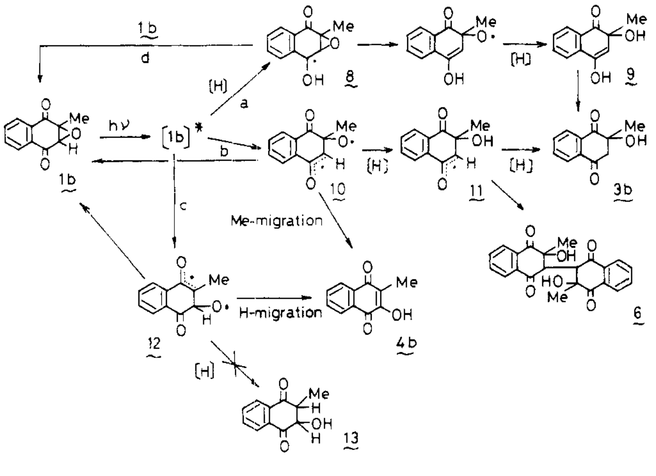


(3)

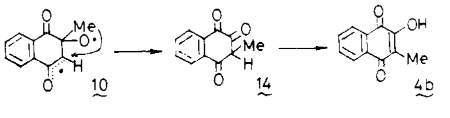
After electron promotion, the n → π^* excited state of a carbonyl group has two electrons in the bonding π orbital, one in the antibonding π^* orbital, and the remaining 2p (i.e., n) electron still localized on the oxygen atom. This last electron exhibits the characteristic behavior of reactive alkoxy radicals, one example being hydrogen abstraction. On the other hand, the carbonyl carbon of the excited state has odd electron capabilities, and hence a greater probability for β elimination, one example being the C_α–O bond cleavage for α,β-epoxy ketones (eq 3).

Our results can be explained using this concept. A possible reaction mechanism for the photochemical reaction of 2-methyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone (**16**) with xanthene is presented in Scheme I. The formation of the product **3b** can be interpreted by considering two reaction routes a and b. The reaction route a involves initial hydrogen abstraction and subsequent ring-opening rearrangement of the resulting radical **8.** The reaction route b involves initial C-3–O bond cleavage of the oxirane ring and subsequent hydrogen abstraction of the resulting diradical **10.** In route b, the

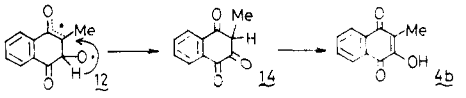
Scheme I



diradical intermediate **10** abstracts a hydrogen atom to afford the radical **11.** At the low concentrations of the hydrogen donor, the radical intermediate **11** will undergo self-coupling to give the product **6.** At the high concentrations of the hydrogen donor radical **11** will abstract a hydrogen atom to give product **3b.** Actually, the ratio of product **6** to product **3b** was dependent upon the concentrations of xanthene (Table III), supporting the assumption described above. The yield of **4b** (phthicol) showed no isotope effects, and was not affected by the molar ratio of reactants (Tables II and III). Therefore, **4b** might be formed by photoisomerization of **1b.** Possible reaction routes for this photoisomerization are shown in eq 4 and 5. Each reaction route is in analogy to the photoisomerization of α,β-epoxy ketones to β-diketones.[2] Equation 4 shows methyl migration in diradical intermediate **10** formed from the C-3–O bond cleavage of **1b.** On the other hand, eq 5 shows



(4)



(5)

hydrogen migration in diradical intermediate **12** resulting from the C-2–O bond cleavage of **1b.** Markos and Reusch reported the following order for the migration aptitude of β substituents in the photoisomerization of α,β-epoxy ketones to β-diketones: H > Me.[7] As a result, we may reasonably conclude that methyl migration (eq 4) is less favorable than hydrogen migration (eq 5). Thus, **4b** could be formed by reaction route c in Scheme I, involving intramolecular hydrogen migration in diradical intermediate **12.**

The ratio of products **3b** and **4b** is dependent upon the nature of hydrogen donors. In the reaction with xanthene, the major product is the compound **3b** rather than **4b.** In contrast, the photochemical reaction in 2-propanol gave **4b** as the major product. In the reaction with xanthene, a good hydrogen-donor–hydrogen-abstraction reaction predominates, while photoisomerization is preferred in 2-propanol, a poor hydrogen donor.

The effect of adding naphthalene to the reacting system was examined for characterization of the excited state. Naphthalene was often used as a triplet quencher.[8] The results were tabulated in Table V. As shown from the last two columns in Table V, with increasing amounts of naphthalene the total rate of reaction diminished, and the yields of **4b** and **6** also decreased, but those of **3b** appeared to remain rather unchanged. The apparent absence of a quenching effect with naphthalene for **3b** formation is difficult to explain at present. However, it seems to indicate that the excited triplet state[9] of **1b** is complexed with the naphthalene molecule. If it was, the relative ratio of routes a, b, and c in Scheme I could alter. In addition, such complexing may result in a change in the reaction course, for example, by inhibiting dimerization and

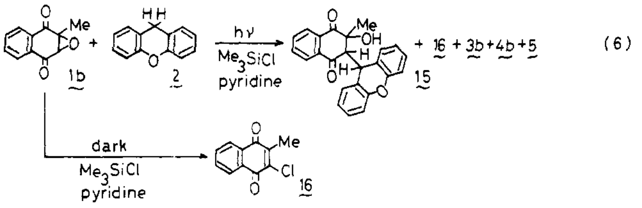
Table V. Photoreduction of the Epoxyquinone **1b** with Xanthene. Effect of the Addition of Naphthalene[a]

Added naphthalene, M	Products, %				Recovery, %	
	3b	**4b**	**6**	**5**	**1b**	**2**
0	48	20	15	65	17	35
0.1	51	9	6	47	34	53
0.2	51	3	4	49	42	51
0.3	48	3	3	44	46	56
0.4	51			45	49	55

[a] [**1b**] = 0.1 M, [xanthene] = 0.2 M, solvent, benzene. Yields of products were determined by NMR, after 6 h irradiation. Yields were based on the amounts of the epoxyquinone **1b** and xanthene used.

isomerization of radical **10**, and permitting only hyodrgen abstraction from xanthene, which is a good hydrogen donor. In fact, it has been reported that alkoxy radicals as well as peroxy radicals are complexed by the aromatic ring, and subsequently their reactivities and the selectivities of the reactions are altered.[10] Thus the results shown in Table V may be tentatively explained in terms of the complexing of the excited triplet state of **1b** with naphthalene. Addition of piperylene, a triplet quencher, in the reacting system reduced the formation of **3b**, **4b**, and **6**, but it also reacted with **1b**. Therefore, further examination was abandoned.

Photolysis of 2-Methyl-2-hydroxy-3-(9′-xanthenyl)-2,3-dihydro-1,4-naphthoquinone (15). In an attempt to trap the enol intermediate **9** shown in Scheme I, we examined the photochemical reaction in the presence of trimethylsilyl chloride and pyridine. No silyl enol ethers were obtained. However, two compounds, **16** (4%) and **17** (6%), in addition to the usual photoproducts **3b**, **4b**, and **5** were obtained in low yields (eq 6). 2-Methyl-3-chloro-1,4-naphthoquinone (**16**)[11] was also obtained by allowing a pyridine solution of epoxyquinone **1b** and trimethylsilyl chloride to stand overnight in the dark. The structure of product **15** was assigned as 2-methyl-2-hydroxy-3-(9′-xanthenyl)-2,3-dihydro-1,4-naphthoquinone on the basis of the spectral data outlined below [IR (KBr) 3470 (OH), 1683, 1672 (CO) cm^{-1}; NMR (CDCl$_3$) δ 1.35 (s, CH$_3$) 3.45 (d, H$_a$), 4.21 (s, OH), 4.84 (d, H$_b$) 6.8–8.0 (m aromatic H, 12 H); mass spectra m/e 370 (M$^+$), 352, 181]. Compound **15** underwent photodecomposition upon further irradiation. The results gave important information about the reaction mechanism for the reaction of **1b** with xanthene.



(6)

When a benzene solution of compound **15** was irradiated with a high-pressure mercury lamp, photodecomposition readily occurred, and the dimeric products **6** and 9,9′-bixanthenyl were obtained as the main products. On the other hand, the photodecomposition of **15** in the presence of xanthene gave the reduction products **3b** and 9,9′-bixanthenyl. These results suggest initial cleavage of the C-3–C-9 bond to produce a radical pair composed of radical **11** and xanthenyl radical **17** (Scheme II).

Figure 1 shows the CIDNP spectrum observed in the photolysis of **15** in deuteriochloroform. The methine proton H$_a$ of the quinone moiety appeared as enhanced emission, and the methine proton H$_b$ of the xanthenyl moiety as enhanced absorption (Figure 1). On the basis of the radical pair theory,[12] the observed CIDNP may be interpreted by considering initial decomposition of **15** to give rise to the radicals **11** and **17**, and recombination of **11** and **17** via radical pair to reproduce **15**. Thus, the photolysis of the compound **15** in the absence or presence of xanthene gave the dimeric product **6** or the reduction product **3b**, respectively, both of which were also obtained in the photochemical reaction of epoxyquinone **1b** with xanthene. From these data, we concluded that **6** and **3b** were formed via the same radical intermediate **11**, supporting the reaction route b in Scheme I.

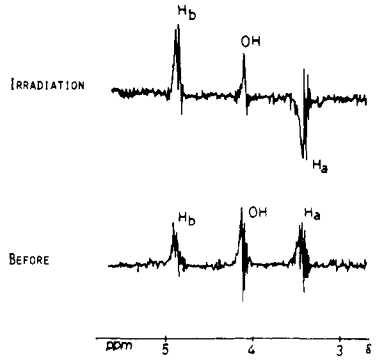
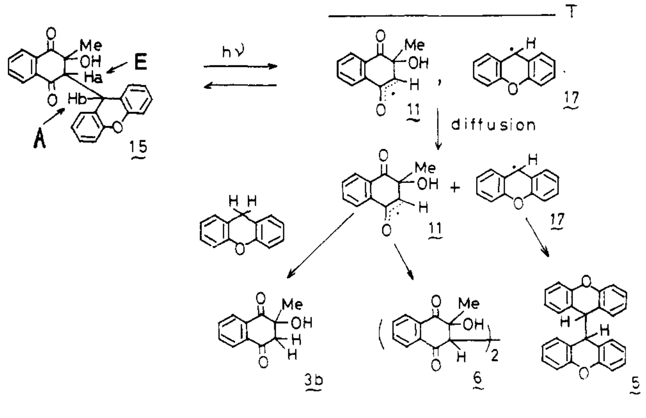


Figure 1. CIDNP spectrum observed in the photolysis of compound **15** in CDCl$_3$.

Scheme II



Reaction of 2-Methyl-2,3-epoxy-3,4-dihydro-4-hydroxynaphthalen-1(2*H*)-one (18) with Di-*tert*-butyl Peroxalate. In an attempt to verify the participation of route a described in Scheme I we examined the reaction of 2-methyl-2,3-epoxy-3,4-dihydro-4-hydroxynaphthalen-1(2*H*)-one (**18**) with di-*tert*-butyl peroxalate (DBPO). The reaction of **18** with DBPO in benzene at 60–70 °C gave **3b** and **1b** as readily identified products. The relative yields of these products were dependent upon the amount of DBPO used. The results are summarized in Table VI. At higher peroxalate concentration the ratio of [**1b**]/[**3b**] was relatively high, but it decreased with decreasing concentrations of DBPO. Such a phenomenon was also observed in the reaction of cyclopropylphenylcarbinol with di-*tert*-butyl peroxide previously reported.[13] Therefore, these data suggest the intermediacy of α-hydroxyalkyl radical **8** generated via hydrogen atom abstraction from **18** in the photochemical reaction. At higher concentrations of DBPO the oxidation process via **8** will mainly proceed to give **1b**, the starting epoxyquinone. At lower concentrations of DBPO the ring-opening rearrangement of radical **8** to enolate radical **19** might occur concomitantly with the oxidation process. The resulting enolate radical **19** might abstract a hydrogen atom to give **3b**. Thus, participation of route a could not be ruled out. In other words, **3b** is probably formed via both routes a and b (Scheme III).

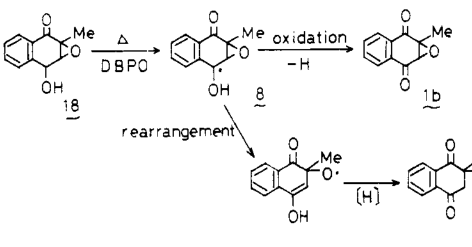
CIDNP Examination. In general, CIDNP gives useful

Table VI. The Reaction of the Alcohol 18 with Di-*tert*-butyl Peroxalate (DBPO)

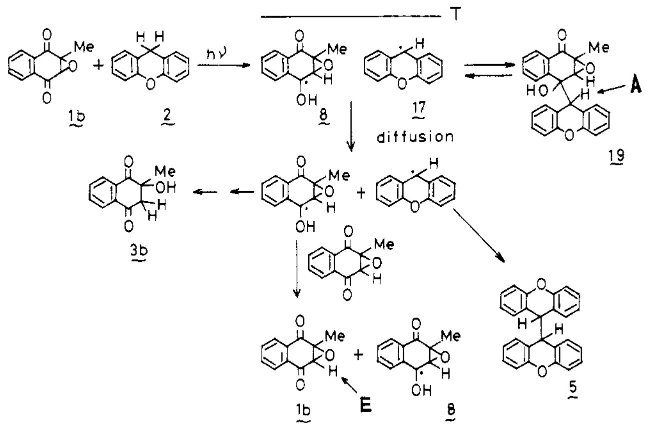
[Alcohol 18]/[DBPO]	[1b]/[3b][a]
0.25	~4
1.21	2.8
2.43	1.3

[a] The ratio of products was determined by NMR. The initial concentration of 18 was kept constant for these runs.

Scheme III



Scheme IV



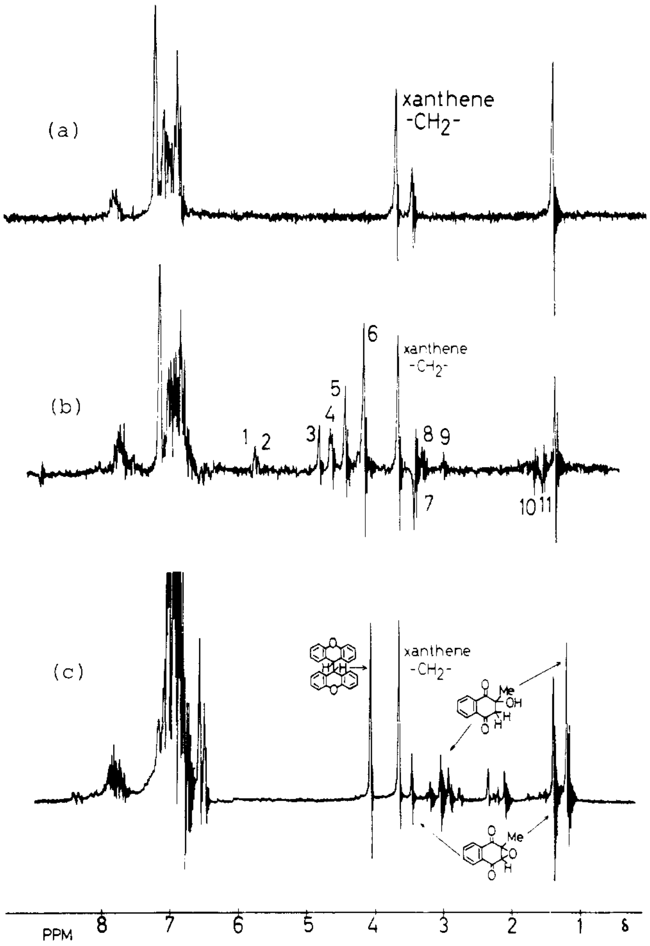


Figure 2. NMR spectra observed in the photochemical reaction of the epoxyquinone **1b** with xanthene in C_6D_6: (a) before irradiation; (b) during irradiation for 8 h.

information on the photoreduction of the carbonyl compound.[14] Photoreduction of **1b** with xanthene was examined by means of CIDNP. CIDNP spectra were taken using a 100-MHz NMR spectrometer, equipped with a modified NMR probe for photolysis at 22 °C. The observed CIDNP spectrum was presented in Figure 2. Figure 2a–c show the observed spectra before irradiation, during irradiation, and after irradiation for 8 h, respectively. As shown in Figure 2b the methine proton at C-3 of epoxyquinone **1b** appears at δ 3.55 as enhanced emission signal 7. Many polarized signals were observed during irradiation of a solution of **1b** and xanthene in hexadeuteriobenzene. Polarized signals 1–6 appeared in the region between δ 4.0 and 6.0. However, no compounds corresponding to these polarized signals were produced after long irradiation (Figure 2c). This fact suggests the transient formation of unstable reaction intermediates or the formation of the minor products due to side reactions. In addition signals 1–6 disappeared when the reaction was carried out using xanthene-9-d_2. The observation of CIDNP signals unequivocally shows the radical nature of the photochemical reaction of **1b** with xanthene. The emission polarization indicated as signal 7 in Figure 2b is due to the methine proton at C-3 of **1b**. We can rationalize this emission signal by taking into consideration the initial formation of a triplet geminate pair composed of α-hydroxyepoxycarbinyl radical **8** and xanthenyl radical **17** (Scheme IV). The triplet character of reactive species was also supported by the effect of added naphthalene. CIDNP signal intensity decreased with addition of naphthalene to the reacting system. Thus, in the proposed Scheme IV, the radical **8** escaping from the initial triplet radical pair may reproduce the starting epoxyquinone **1b**, donating a hydrogen to another epoxyquinone **1b**. The Kaptein equation allow us to predict the net effect of polarization, Γ_{ne}.[15]

$$\Gamma_{ne} = \mu\epsilon\Delta g A_i \qquad (7)$$

In the application of the Kaptein equation (eq 7) to Scheme IV the parameters μ and ϵ will be positive and negative, respectively, because the reproduced **1b** is an escaping product from the initial triplet radical pair. The parameter Δg will be positive because the g value of the radical **8** with an α-hydroxy group is higher than that of the xanthenyl radical **17**. The hyperfine coupling constant A_i for the methine proton at C-3 of **1b** will be positive, because the proton occupies the β position to the radical center in the radical **8**. Thus in eq 7 $\Gamma_{ne} = +-++ = -$, and then an emission signal is predicted, in good agreement with the observed polarization. Furthermore, geminate combination must be considered in the initial triplet radical pair. If the combination occurred, the adduct **19** might be produced, although we could not isolate this adduct. It is not improbable that the most strongly polarized absorption signal 6 at δ 4.32 may be attributed to the methine proton of a xanthenyl moiety in the adduct **19**. Actually this signal disappears in the reaction with xanthene-9-d_2, and the observed absorption polarized signal is consistent with that predicted by the Kaptein equation.

The reaction mechanism as presented in Scheme IV was also proposed for the photolysis of benzaldehyde[16] or the photochemical reaction of benzophenone in 2-propanol.[21] Thus, the examination of CIDNP revealed the process of the

Table VII. Epoxynaphthoquinones 1a–g

1	Mp, °C	Found C	Found H	Calcd C	Calcd H	Formula
a, R = H	133–134			68.96	3.47	$C_{10}H_6O_3$
b, R = Me	96–96.5			70.21	4.29	$C_{11}H_8O_3$
c, R = Et	50.5–51	71.52	4.94	71.28	4.99	$C_{12}H_{10}O_3$
d, R = Pr	34–35	72.44	5.53	72.21	5.59	$C_{13}H_{12}O_3$
e, R = *i*-Pr	Oil	72.73	5.75	72.21	5.59	$C_{13}H_{12}O_3$
f, R = CH_2Ph	110–111	72.22	4.58	77.26	4.58	$C_{17}H_{12}O_3$
g, R = *t*-Bu	65–66	73.14	6.32	73.02	6.13	$C_{14}H_{14}O_3$

reproduction of **1b** from the radical intermediate **8** (route d in Scheme I).

In addition to signals **6** and **7**, other polarized signals remain unassignable, indicating that these photochemical reactions are more complex than those described above.

Experimental Section

The melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. Microanalyses were performed by the Microanalytical Laboratory of Kyoto University. IR spectra were recorded with a Jasco IR-G spectrophotometer, and NMR spectra were taken with a JEOL PS-100 spectrometer with the use of tetramethylsilane as an internal standard and chemical shifts expressed in δ values. UV spectra were recorded with a Shimadzu UV-200 spectrometer. Mass spectra were taken with a Hitachi M-52 mass spectrometer. Preparative TLC was carried out on Merk Kieselgel PF_{254}. UV irradiation was carried out in a Pyrex vessel at room temperature, using an Eikosha 300-W high-pressure mercury lamp.

Preparation of Epoxyquinones. 2,3-Epoxy-2,3-dihydro-1,4-naphthoquinone was prepared by the method of Marmor.[16] 2-Methyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone was prepared by the method of Fieser.[4] 2-Ethyl-, 2-propyl-, 2-isopropyl- 2-*tert*-butyl- and 2-benzyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone were prepared by the epoxidation of the corresponding 1,4-naphthoquinones prepared by the method by Jacobsen and Torssell[17] with 30% aqueous hydrogen peroxide in alkaline medium. The data of melting points and elemental analyses are summarized in Table VII.

The UV absorption spectrum of 2,3-epoxy-2,3-dihydro-14-naphthoquinone (**1a**) in cyclohexane exhibited four absorption bands at 227 (ϵ 25 000), 263 (7500), 303 (2100), and 341 nm (230). The last weak band at 341 nm is attributed to the $n \rightarrow \pi^*$ transition. The UV absorption spectra of other epoxyquinones exhibited similar absorption bands to that of the epoxyquinone **1a.**

Photochemical Reaction of 2,3-Epoxy-2,3-dihydro-1,4-naphthoquinone (1a) with Xanthene. A degassed solution of **1a** (300 mg, 1.72 mmol) and xanthene (628 mg, 3.44 mmol) in 20 mL of benzene was irradiated for 10 h in a Pyrex tube using a 300-W high-pressure mercury lamp. Evaporation of solvent gave the semisolid residue, which was crystallized upon addition of methanol. Filtration of the crystals and recrystallization from benzene–methanol gave 9,9′-bixanthenyl as colorless needles (364 mg, 58%). The filtrate was evaporated and the products were separated by preparative TLC to give 2-hydroxy-2,3-dihydro-1,4-naphthoquinone (**3a**) as the main product (88 mg, 29%). 2-Hydroxy-2,3-dihydro-1,4-naphthoquinone (**3a**) was purified by sublimation and recrystallization from benzene–hexane: colorless needles; mp 122–123 °C; IR (KBr) 3400 (OH), 1685 ($C{=}O$) 1590, 1420 cm^{-1}; NMR ($CDCl_3$) δ 3.00 (dd, 1 H, C-3 CH_2, $J_{3,3} = 16$, $J_{2,3} = 12$ Hz), 3.51 (dd, 1 H, C-3 CH_2, $J_{3,3} = 16$, $J_{2,3} = 7$ Hz), 3.85 (d, 1 H, OH, $J_{2OH} = 2$ Hz) 4.80 (octet, H-2, $J_{2,3} = 12$, $J_{2,3} = 7$, $J_{2OH} = 2$ Hz), 7.70–8.20 (m, 4 H, aromatic H); UV ($CHCl_3$) λ_{max} 254, 296 nm (log ϵ 4.01 and 3.29). Anal. Calcd for $C_{10}H_8O_3$: C, 68.18; H, 4.58. Found: C, 67.93; H, 4.69.

Photochemical Reaction of 2-Methyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone (1b) with Xanthene. A degassed solution of **1b** (300 mg, 1.60 mmol) and xanthene (582 mg, 3.20 mmol) in 20 mL of benzene was irradiated for 13 h. Colorless crystals were deposited and then filtered off. Recrystallization of the crystals from chloroform or benzene gave the product **6** as colorless needles (13 mg, 4%). The filterate was evaporated under the reduced pressure and the residue was crystallized on the addition of methanol. Filtration of the crystals and recrystallization from benzene–methanol gave 9,9′-bixanthenyl (333 mg, 57%). The mother liquors from the filtration of 9,9′-bixanthenyl were evaporated and the resulting residue was chromatographed on silica gel. Elution with petroleum ether gave unreacted xanthene (168 mg 29%). The elution with 10:1 petroleum ether–ether gave a small amount of 9,9′-bixanthenyl and starting epoxyquinone **1b.** Elution with 5:1 petroleum ether–ether gave the product **4b** (49 mg, 16%). Elution with 3:1 petroleum ether–ether gave the product **3b** (129 mg, 42%). 2-Methyl-2-hydroxy-2,3-dihydro-1,4-naphthoquinone (**3b**): colorless needles from hexane; mp 108–109 °C; IR (KBr) 3390 (OH), 1680 ($C{=}O$), 1593, 1450, 1410 cm^{-1}; NMR ($CDCl_3$) δ 1.44 (s, 3 H, CH_3), 3.09, 3.29 (AB quartet, 2 H, C-3 CH_2, $J = 16$ Hz), 3.90 (s, 1 H, OH), 7.6–8.2 (m, 4 H, aromatic H); UV ($CHCl_3$) λ_{max} 254 and 296 nm (log ϵ 4.04 and 3.32). Anal. Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.41; H, 5.26.

2-Methyl-3-hydroxy-1,4-naphthoquinone (phithiocol, **4b**) was readily prepared by treatment of 2-methyl-2,3-epoxy-2,3-dihydro-14-naphthoquinone with sulfuric acid:[4] yellow needles from hexane; mp 173–174 °C; IR (KBr) 3330 (OH), 1655 ($C{=}O$) cm^{-1}; NMR ($CDCl_3$) δ 2.08 (s, 3 H, CH_3), 7.28 (s, 1 H, OH), 7.5–8.1 (m, 4 H, aromatic H).

3,3′-Dimethyl-3,3′-dihydroxy-1,1′,4,4′-tetraoxo-1,1′,2,2′,3,3′,-4,4′-octahydro-2,2′-binaphthalene (**6**): mp 180–181 °C dec; IR (KBr) 3450 (OH), 1690 ($C{=}O$), 1600, 1420 cm^{-1}; NMR (CD_3SOCD_3) δ 1.12 (s, 6 H, CH_3), 2.83 (s, 2 H, C-2 C-2′CH), 6.83 (s, 2 H, OH), 7.4–7.9 (m, 8 H, aromatic H); mass *m/e* 360 ($M^+ - 18$), 342, 327, 318 (base) 300, 271, 243, 215. Anal. Calcd for $C_{22}H_{18}O{\cdot}H_2O$: C, 66.66; H, 5.09. Found: C, 66.59; H, 5.19.

Dehydration of Products 3b and 6 with Sodium Acetate. When a solution of 45 mg of **3b** or **6** in 15 mL of acetic acid in the presence of sodium acetate (75 mg) was refluxed for 1 h, dehydration readily occurred and 2-methyl-1,4-naphthoquinone or a biquinone **7,** respectively, was produced in 50–60% yield. 3,3′-Dimethyl-2,2′-binaphthoquinone (**7**): yellow needles from ethanol; mp 246–247 °C (lit.[5] mp 242–245 °C); IR (KBr) 1655 cm^{-1} ($C{=}O$); ^1H NMR ($CDCl_3$) δ 2.02 (s, 6 H, CH_3) and 7.6–8.2 (m, 8 H, aromatic H); UV ($CHCl_3$) λ_{max} 245 (sh) 250, 260 (sh) and 334 nm (log ϵ 4.59, 4.63, 4.50 and 3.81); mass spectrum *m/e* 342 (M^+, base). Anal. Calcd for $C_{22}H_{14}O_4$: C, 77.18; H, 4.12. Found: C, 77.25; H, 3.85.

Photochemical Reactions of Other Epoxyquinones 1c–g with Xanthene. The degassed solutions of other epoxyquinones **1c–g** (300 mg) and 2 equiv of xanthene in 20 mL of benzene were irradiated for a suitable time. The products were separated by the same procedures as those of epoxyquinones **1a** and **1b.** The products obtained were purified by TLC, sublimation, and recrystallizations. The results are summarized in Table I.

The products obtained were identified by the following physical data. 2-Ethyl-2-hydroxy-2,3-dihydro-1,4-naphthoquinone (**3c**): colorless crystals from hexane; mp 56–56.5 °C; IR (KBr) 3490 (OH) 2995, 2985 (alkane), 1680 ($C{=}O$) 1590, 1445, 1425 cm^{-1}; NMR ($CDCl_3$) δ 0.83 (t, 3 H, CH_3), 1.70 (m, 2 H, CH_2, CH_3), 3.04. 3.28 (AB quartet, 2 H, C-3 CH_2, $J = 16$ Hz), 3.94 (s, 1 H, OH), 7.56–8.12 (m, 4 H, aromatic H). The dehydration of **3c** with sodium acetate gave 2-ethyl-1,4-naphthoquinone. Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.39; H, 5.90.

2-Ethyl-3-hydroxy-1,4-naphthoquinone (**4c**) was also obtained by treatment of the epoxyquinone **1c** with sulfuric acid: yellow needles from hexane; mp 141–142 °C; IR (KBr) 3250 (OH), 1665 (sh), 1636 ($C{=}O$), 1590, 1460 cm^{-1}; NMR ($CDCl_3$) δ 1.15 (t, 3 H, $CH_2C\mathbf{H}_3$), 2.64 (quartet, 2 H, $C\mathbf{H}_2CH_3$), 7.50 (s, 1 H, OH), and 7.64–8.30 (m, 4 H, aromatic H). Anal. Calcd for $C_{12}H_{10}O_3$: C, 71.28; H, 4.99. Found: C, 70.56; H, 5.03.

2-Propyl-2-hydroxy-2,3-dihydro-1,4-naphthoquinone (**3d**): colorless needles from hexane; mp 56–57 °C; IR (KBr) 3380 (OH), 2940 (alkane), 1675 ($C{=}O$), 1592, 1455 cm^{-1}; NMR ($CDCl_3$) δ 0.78 (t, 3 H, $CH_2CH_2C\mathbf{H}_3$), 1.04–1.90 (m, 4 H, $C\mathbf{H}_2C\mathbf{H}_2CH_3$), 3.01, 3.06 (AB quartet, 2 H, C-3 CH_2, $J = 16$ Hz), 3.94 (s, 1 H, OH), 7.52–8.06 (m, 4 H, aromatic H). Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.39; H, 6.32.

2-Propyl-3-hydroxy-1,4-naphthoquinone (**4d**) was also prepared by treatment of the epoxyquinone **1d** with sulfuric acid: yellow needles; mp 98–100 °C; IR (KBr) 3320 (OH), 2940, 2880 (alkane), 1660 (sh), 1632 ($C{=}O$), 1590, 1456 cm^{-1}; NMR ($CDCl_3$) δ 0.96 (t, 3 H, $CH_2CH_2C\mathbf{H}_3$), 1.59 (sextet, 2 H, $CH_2C\mathbf{H}_2CH_3$), 2.56 (t, 2 H, $C\mathbf{H}_2CH_2CH_3$), 7.28 (s, 1 H, OH), 7.52–8.20 (m, 4 H, aromatic H). Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 72.50; H, 5.47.

2-Isopropyl-2-hydroxy-2,3-dihydro-1,4-naphthoquinone (**3e**): colorless crystals from benzene–hexane; mp 129 °C; IR (KBr) 3430 (OH), 2995, 2888 (alkane), 1680 ($C{=}O$), 1590, 1450, 1425 cm^{-1}; NMR ($CDCl_3$) δ 0.74 (d, 1 H, CH_3, $J = 7$ Hz), 1.08 (d, 1 H, CH_3, $J = 8$ Hz), 1.85 [septet 1 H, $C\mathbf{H}(CH_3)_2$], 3.02, 3.49 (AB quartet, 2 H, C-3 CH_2, $J = 16$ Hz), 3.96 (s, 1 H, OH), 7.74–8.25 (m, 4 H, aromatic H). Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.74; H, 6.51.

2-Benzyl-2-hydroxy-2,3-dihydro-1,4-naphthoquinone (**3f**): colorless crystals from benzene–hexane; mp 110–111 °C; IR (KBr) 3480 (OH), 1676 (C=O), 1592 cm^{-1}; NMR ($CDCl_3$) δ 2.82, 2.97 (AB quartet, 2 H, CH_2Ph, $J = 12$ Hz), 3.05, 3.31 (AB quartet, 2 H, C-3 CH_2, $J = 16$ Hz), 3.79 (s, 1 H, OH), 6.70–8.20 (m, 5 H aromatic H), 7.55–8.01 (m, 4 H, aromatic H). Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.40; H, 5.32.

2-Benzyl-3-hydroxy-1,4-naphthoquinone (**4f**): yellow plates; mp 181–182 °C; IR (KBr) 3330 (OH), 1665 (sh), 1645 (C=O), and 1590 cm^{-1}; NMR ($CDCl_3$) δ 3.90 (s, 2 H, CH_2Ph), 7.10–7.40 (m, 5 H, aromatic H), 7.40 (s, 1 H, OH), 7.60–8.20 (m, 4 H, aromatic H). Anal. Calcd for $C_{17}H_{12}O_3$: C, 77.26; H, 4.58. Found: C, 76.91; H, 4.48.

Photochemical Reactions of 1b with Xanthene in the Presence of Trimethylsilyl Chloride and Pyridine. A solution of **1b** (300 mg) and xanthene (600 mg) in 30 mL of benzene in the presence of trimethylsilyl chloride (350 mg) and pyridine (500 mg) was irradiated for 15 h. The products were separated by the same procedure used in the photochemical reaction of **1b** with xanthene. In addition to the usual photoproducts **3b, 4b,** and **5,** two new products, i.e., the product **15** (25 mg, 4%) and 2-methyl-3-chloro-1,4-naphthoquinone (**16**) (20 mg, 6%), were obtained.

2-Methyl-2-hydroxy-3-(9′-xanthenyl)-2,3-dihydro-1,4-naphthoquinone **15**: colorless needles; mp 180–181 °C; IR (KBr) 3470 (OH), 1683 1672 (C=O), 1590, 1480, 1460 cm^{-1}; NMR ($CDCl_3$) δ 1.35 (s, 3 H, CH_3) 3.45 (d, H_a, 1 H), 4.21 (s, OH, 1 H), 4.84 (d, H_b, 1 H), 6.8–8.0 (m, 12 H, aromatic H); mass spectrum m/e 370 (M^+), 352, 181 (base), 168, 167. Anal. Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90. Found: C, 77.52; H, 5.05.

2-Methyl-3-chloro-1,4-naphthoquinone (**16**) was also obtained by the reaction of the epoxyquinone **1b** with trimethylsilyl chloride in pyridine in the dark. A mixture of the epoxyquinone **1b** (300 mg) and trimethylsilyl chloride (300 mL) in 5 mL of pyridine was allowed to stand in the dark overnight. Solvent was removed and the crystallization from ethanol gave 2-methyl-3-chloro-1,4-naphthoquinone (161 mg, 49%), mp 158–159 °C.[11]

Photolysis of 15. A solution of **15** (20 mg) in hexadeuteriobenzene (0.5 mL) was irradiated in an NMR tube for 15 h using a high-pressure mercury lamp. Crystals were deposited in the NMR tube. The crystals were identified as dimeric product **6** by the melting point. The NMR analysis showed the formation of 9,9′-bixanthenyl and the presence of unreacted starting material **15**. 9,9′-Bixanthenyl was also isolated from the reaction mixture and confirmed by its melting point. The starting material **15** was also recovered (12 mg, 60%).

A solution of **15** (20 mg) and xanthene (25 mg) in hexadeuteriobenzene (0.5 mL) was irradiated in a NMR tube for 15 h. The NMR analysis showed the formation of the product **3b** and 9,9′-bixanthenyl. These two products were each isolated from the reaction mixture and confirmed by their melting points. The starting material **15** was also recovered (10 mg, 50%).

Reaction of 2-Methyl-2,3-epoxy-3,4-dihydro-4-hydroxynaphthalen-1(2*H*)-one (18) with Di-*tert*-butyl Peroxalate. The alcohol **18** was prepared by reduction of the epoxyquinone **1b** with sodium borohydride.[18] 2-Methyl-2,3-epoxy-3,4-dihydro-4-hydroxynaphthalen-1(2*H*)-one (**18**): colorless needles; mp 164–165 °C; IR (KBr) 3230 (OH), 1688 (C=O), 1600 cm^{-1}; NMR ($CDCl_3$) δ 1.60 (s, 3 H, CH_3) 2.52 (d, 1 H, OH, $J_{4,OH} = 12$ Hz), 3.78 (d, 1 H, C-3 CH, $J = 2$ Hz), 5.03 (br d, 1 H, C-4 CH, $J_{4,OH} = 12$ Hz), 7.14–7.92 (m, 4 H, aromatic H). Anal. Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.38; H, 5.32.

Di-*tert*-butyl peroxalate was prepared by the method of Bartlett et al.[19]

The reactions of the alcohol **18** with di-*tert*-butyl peroxalate were carried out as follows. Three solutions of different relative concentration were prepared: (i) a mixture of **18** (80 mg, 0.42 mmol) and DBPO (400 mg, 1.71 mmol) in benzene (10 mL); (ii) a mixturg of **18** (100 mg, 0.53 mmol) and DBPO (100 mg, 0.42 mmol) in benzene (15 mL); and (iii) a mixture of **18** (100 mg, 0.53 mmol) and DBPO (50 mg, 0.21 mmol) in benzene (15 mL). Each of these three solutions was heated at 60–70 °C and reacted with liberation of carbon dioxide. After evolution of carbon dioxide stopped and the solution stood at 60–70 °C for an additional 30 min, the heating was discontinued and the sample allowed to cool. Solvent was removed and the residues were dissolved in deuteriochloroform, and the ratio of the products **1b** and **3b** was estimated by NMR. The results were tabulated in Table VI.

The Photochemical Reaction of 1b with Xanthene in the Presence of Naphthalene. Five specimens each containing the solution of **1b** (94 mg, 0.5 mmol) and xanthene (182 mg, 1 mmol) in 5 mL of benzene were prepared in the Pyrex test tubes. To each solution the given amount of naphthalene [0 mg, 64 mg (0.5 mmol), 128 mg (1.0 mmol), 192 mg (1.5 mmol) and 256 mg (2.0 mmol)] were added. These five tubes were degassed by four freeze–pump–thaw cycles and sealed, and irradiated from outside with a 300-W high-pressure mercury lamp using a merry-go-round apparatus for 6 h at room temperature. After evaporation of benzene, the residues were dissolved in chloroform-*d* and analyzed by NMR. The results were summarized in Table V.

The results presented in Table III and IV were also obtained by the same procedure as that described here.

Measurement of Quantum Yields. The 313-nm line of a 400-W high-pressure mercury lamp was isolated with a 1-cm path of 0.02 M potassium chromate in a 1% aqueous solution of sodium carbonate.

The degassed solutions of epoxyquinones (0.05 M) and xanthene (0.1 M) in benzene (4 mL) were irradiated at 313 nm for a suitable time. The products and recovered starting epoxyquinones were separated by TLC and the yields were determined by UV spectrometry. The quantum yields were determined by the potassium ferrioxalate actinometry.[20] The results are summarized in Table II.

CIDNP Examination. The investigation of these photochemical reactions by CIDNP was performed using a JEOL PS-100 NMR spectrometer, equipped with a modified NMR probe for photolysis. The modified NMR probe is a usual one in electromagnetic system, but has a hole (1 × 2 cm) in the back-side wall for direct irradiation. Through the hole a sample was irradiated by the light from 1-kW high-pressure mercury lamp. The solutions of 0.07–0.2 M of samples in hexadeuteriobenzene were irradiated in an NMR tube at 22 °C.

Registry No.—**3a,** 63534-43-0; **3b,** 53948-68-8; **3c,** 53948-75-7; **3d,** 63534-44-1; **3e,** 63534-45-2; **3f,** 63534-46-3; **4b,** 483-55-6; **4c,** 29366-44-7; **4d,** 29366-45-8; **4f,** 15451-41-9; **5,** 4381-14-0; **6,** 63534-47-4; **7,** 22693-07-8; **15,** 63534-48-5; **18,** 63534-49-6; 2-ethyl-1,4-naphthoquinone, 5409-32-5; 2-propyl-1,4-naphthoquinone, 34491-84-4; 2-isopropyl-1,4-naphthoquinone, 20175-89-7; 2-*tert*-butyl-1,4-naphthoquinone, 51595-06-3; 2-benzyl-1,4-naphthoquinone, 33440-68-5.

References and Notes

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