Photochemical Reduction of *p*-Quinones with Hydrogen Donors Studied by CIDNP Technique[1,2]

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Photo-reduction of *p*-benzoquinone, 1,4-naphthoquinone, and their methyl- or chloro-derivatives has been investigated by means of CIDNP technique. Strongly polarized PMR signals due to unstable reaction intermediates, *p*-quinones, and hydroquinones were observed during the course of reaction. Structures of the unstable reaction intermediates, none of which accumulated as reaction products, were determined, their polarized PMR signals being compared with those of the unstable reaction intermediates resulting from the deuterated substrates. From these results, a reaction scheme for these photo-reduction was proposed.

Photo-reduction of *p*-benzoquinone or chloranil in the presence of hydrogen donors is well known.[3–5] However, no systematic studies or details of the reaction mechanism have been published.

According to Moore and Waters,[3] chloranil reacted with *p*-xylene to form 2,3,5,6-tetrachloro-4-(4-methylbenzyloxy)-phenol. A similar compound was isolated in the photochemical reaction of chloranil with tetralin.[6] Chemically induced dynamic nuclear polarization (CIDNP) technique affords an effective method for investigating unstable active intermediates as well as stable products produced through radical mechanism even in a very small amount.

A preliminary examination revealed that *p*-benzoquinone and its methyl- or chloro-derivatives dissolved in a suitable solvent are photochemically reduced in the presence of hydrogen donors; *i.e.*, xanthene, 9,10-dihydroanthracene, fluorene, or diphenylmethane, to give hydroquinone, quinhydrone, and/or their methyl- and chloro-derivatives. During the course of photoreductions, strongly polarized PMR signals due to stable reaction products; *i.e.*, hydroquinones, unstable reaction intermediates, as well as *p*-benzoquinones could be observed.

Photo-reduction of *p*-benzoquinone, 1,4-naphthoquinone, and their methyl- or chloro-derivatives by several types of hydrogen donors was investigated by means of CIDNP technique, and stable photo-reduction products were also investigated in macro scale in the photochemical reaction. Emphasis is laid on the photochemical reaction of *p*-quinones with xanthene.

Results and Discussion

Using the NMR probe shown in Fig. 1 we examined the process of photochemical reaction of *p*-quinones with hydrogen donors *in situ* by NMR spectrometer. Carbon tetrachloride and acetone-d_6 were used as solvents. Light was introduced into the probe from the upper side through a hole, reflected by a mirror. A 500 W high-pressure mercury arc lamp was used.

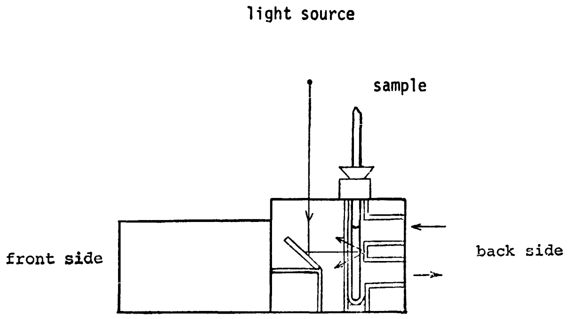
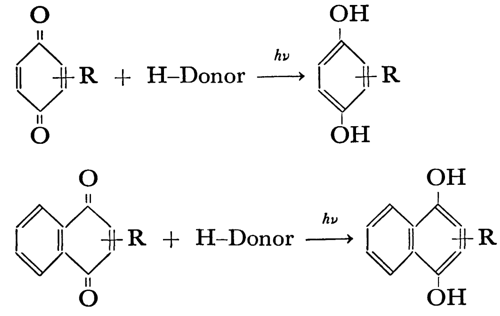


Fig. 1. NMR probe for irradiation.

Structures of the *p*-quinones and types of hydrogen donors are shown in the following.



R: H, CH_3, $(CH_3)_2$, $(CH_3)_3$, $(CH_3)_4$, Cl, $(Cl)_2$, $(Cl)_3$ *etc.*

H–Donor: Xanthene, 9,10-Dihydroanthracene, Fluorene, Ether, Alkylaromatics.

Figure 2 shows PMR spectra observed in the reaction of *p*-benzoquinone with xanthene. Spectra (a), (b), and (c) correspond respectively to the PMR spectra observed before irradiation, during the course of irradiation, and after a longer irradiation. Comparing (b) with (a) we find newly appearing strong polarized signals (indicated by arrows). However, when irradiation is stopped they disappear completely with the exception of signal 1 within a few seconds. Since spectrum (c) is obtained after a long photochemical reaction, signal 1 is due to benzene ring protons of hydroquinone which is a stable product. Thus, emission polarized signal 1 in (b) can be assigned to benzene ring protons of hydroquinone. Actually, hydroquinone and bixanthyl are the only stable reaction

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[1] This work was presented at the International Symposium "Organic Chemistry in Excited State," held at Reading, England, July 24th, 1972.

[2] Photochemical Reaction of Quinones X. Previous report of this series; *Chem. Lett.*, **1972**, 131.

[3] A. Schönberg and A. Mustafa, *J. Chem. Soc.*, **1945**, 657.

[4] A. Schönberg and A. Mustafa, *ibid.*, **1944**, 67.

[5] R. F. Moore and W. A. Waters, *ibid.*, **1953**, 3405.

[6] A. Schönberg, G. O. Schenck, and D–A. Neumüller "Preparative Organic Photochemistry," Springer (1968), p. 182.

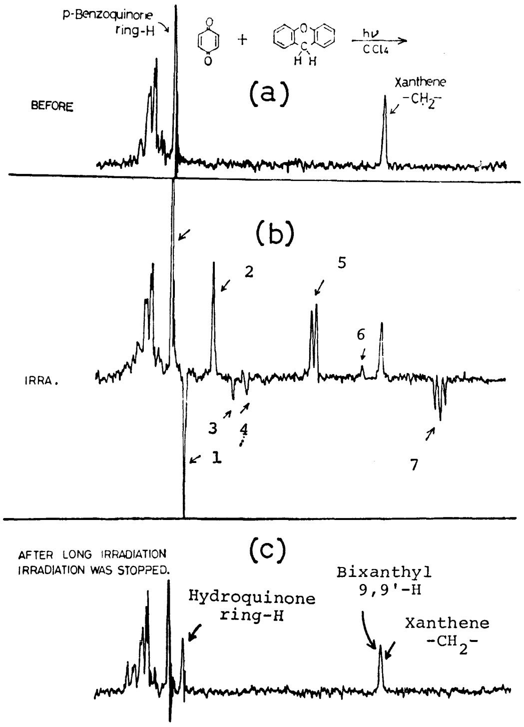

Fig. 2. PMR spectra observed in the photochemical reaction of p-benzoquinone with xanthene (solvent: CCl_4, 22 °C). (a): before irradiation, (b): during irradiation, (c): after long irradiation (in this case irradiation was stopped)

products. Bixanthyl gives no polarized PMR signal.[7] None of the unstable intermediates giving the polarized PMR signals [signals 2,3,4,5,6, and 7 in (b)] accumulate in the reaction system.

For the purpose of obtaining information on their structure we have used deuterated xanthene in 9-methylene group and deuterated p-benzoquinone (Fig. 3). Spectrum (b) is observed in the reaction of non-deuterated p-benzoquinone with xanthene, (d) in that of non-deuterated p-benzoquinone with deuterated xanthene, and (e) in that of deuterated p-benzoquinone with non-deuterated xanthene. Three absorption polarized signals 2, 5, and 6 appearing in (b) disappear in (d). Thus, we can conclude that they are based on methine proton of xanthene moiety of the active intermediates. On the other hand, signal 7 changes to doublet from triplet (double doublet). Further, comparing (e) with (b), three emission polarized signals 3, 4, and 7 disappear and the absorption polarized signal 5 changes to singlet from doublet. From the results we may assign three structures ([I], [II], and [III]) to the unstable intermediates. Absorption polarized signal 2 might be due to methine proton of xanthene moiety in [I] and emission polarized signals 3 and 4 to two pair protons of hydroquinone moiety in [I]. These two emission polarized signals might be the right half of the AX-type signal and we can not observe the left half hidden behind the other larger signals of aromatic ring protons. Ab-

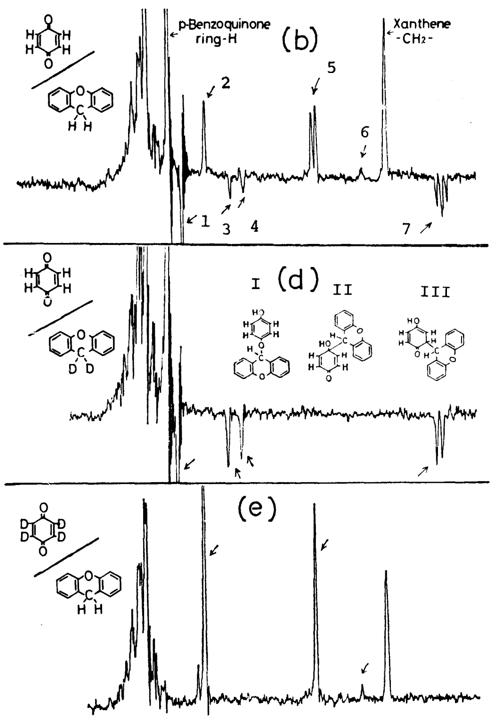

Fig. 3. PMR spectra observed in the photochemical reaction of p-benzoquinone with xanthene (solvent: CCl_4, 22 °C).
(b): during irradiation, reaction of p-benzoquinone with xanthene
(d): during irradiation, reaction of p-benzoquinone with deuterated xanthene
(e): during irradiation, reaction of deuterated p-benzoquinone with xanthene

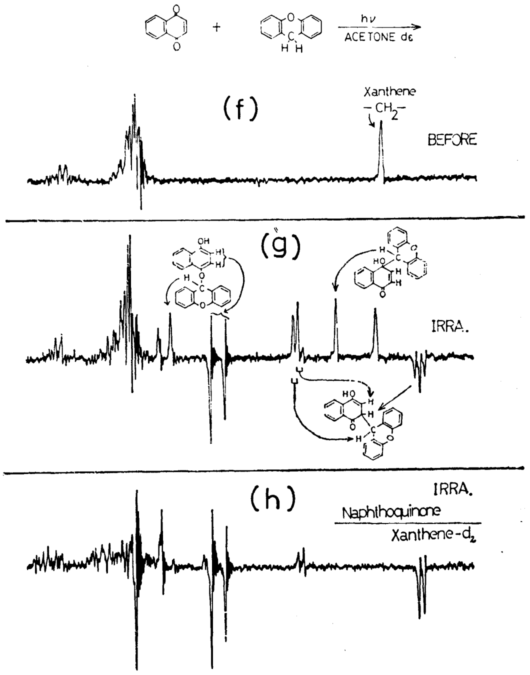

Fig. 4. PMR spectra observed in the photochemical reaction of 1,4-naphthoquinone with xanthene (solvent: CCl_4, 22 °C).
(f): before irradiation, (g): during irradiation,
(h): during irradiation, but with use of deuterated xanthene

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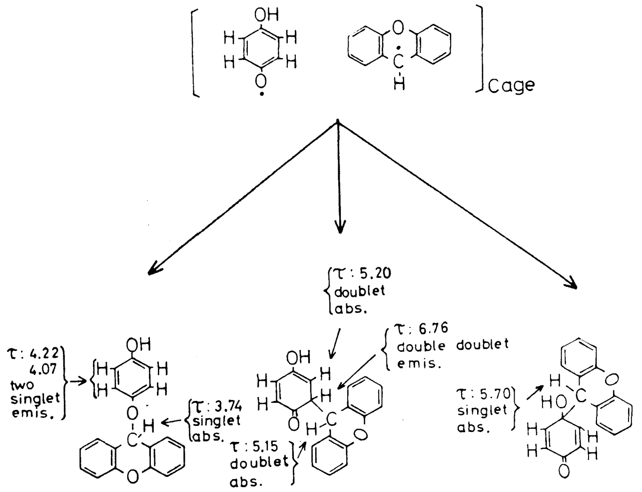
[7] We could not observe the polarized PMR signal in the combination reaction of two symmetrical radicals. G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, **92**, 2183, 2186 (1970); R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195, 214 (1969).

sorption polarized signal 5 may be assigned to methine proton of xanthene moiety in [III] and emission polarized signal 7 to methine proton of *p*-benzoquinone moiety in [III]. Rather weak absorption polarized signal 6 may be due to methine proton of xanthene moiety in [II]. Assignment of signal 6 to [II] can be deduced from a comparison of the polarized PMR signal observed in the photochemical reaction of anthraquinone with xanthene. In this case a sole strongly polarized absorption signal in the corresponding chemical shift region to signal 6 could be observed.8) The assignments can be further supported by comparison of these results with those observed in the reaction of 1,4-naphthoquinone with xanthene (Fig. 4). PMR spectra (f), (g), and (h) were obtained in the photochemical reaction of 1,4-naphthoquinone with xanthene, (f) being observed before irradiation, and (g) during the course of irradiation. (h) was also observed during the course of irradiation, but in the reaction of 1,4-naphthoquinone with deuterated xanthene in the 9-methylene group. We see that (g) has quite the same pattern of signals as (b) (Fig. 2). Thus, we may assign the three structures described in (g) to the unstable intermediates. As in the photochemical reaction of *p*-benzoquinone, none of these intermediates accumulates in the reaction system, and we obtain only 1,4-dihydroxynaphthalene and bixanthyl as stable products.

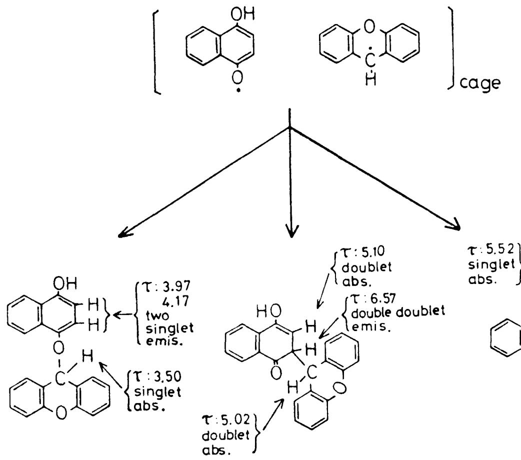
Since only the products which are produced through radical mechanism can give such a polarized PMR signal, photochemical reduction process of *p*-quinones by xanthene can be summarized as follows. Photoexcited *p*-benzoquinone, probably in the triplet state, abstracts hydrogen atom from xanthene and forms semiquinone radical and xanthyl radical in a solvent cage. These two radicals may combine in the solvent cage to form three unstable intermediates which finally decompose to solvent separated semiquinone radical and xanthyl radical (Reaction Schemes 1 and 2). Analogous examples which can be observed in photochemical reactions of methyl- or chloro-substituted *p*-quinones are shown in Figs. 5—8. From the PMR spectra observed in the reaction of 2,5-dimethyl-*p*-benzoquinone with xanthene (Fig. 5), we see that PMR signals in the chemical shift region of methyl proton undergo a strong nuclear spin polarization also. When the sample was irradiated in a NMR probe the corresponding numbers of polarized PMR signals 5, 6, 7, and 9 (Fig. 5 (b)) to methyl groups of stable or unstable products could be observed. Thus, the emission polarized signal 5 corresponds to methyl protons of 2,5-dimethylhydroquinone. Methyl protons of quinone themselves also show emission polarized signal. A more typical example of similar phenomena can be found in Fig. 6 (b) (signal 8) and Fig. 7 (b) (signal 8). The other three or more absorption polarized PMR signals 6, 7, and 9 (Fig. 5 (b)) can be observed in the

Possible structure of unstable intermediates



Reaction Scheme 1.

Possible structure of unstable intermediates



Reaction Scheme 2.

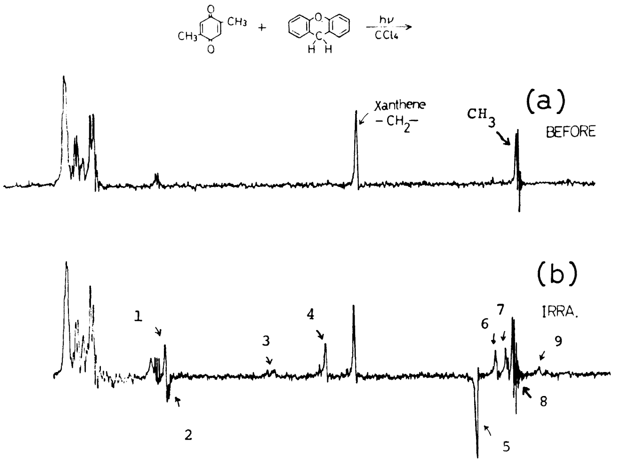


Fig. 5. PMR spectra observed in the photochemical reaction of 2,5-dimethyl-*p*-benzoquinone with xanthene (solvent; CCl_4, 22 °C).
(a): before irradiation, (b): during irradiation

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8) From a consideration of their structures, [I], [II], and [III] should be so stable as to be isolated, but none of them accumulated in the photochemical reaction examined. Because of the higher polarity of the solvents used the unstable intermediates might be forced to decompose giving two radicals. In fact we were able to isolate the adducts which might be derived from similar reaction intermediates in the photochemical reaction of 2,3-dichloro- or 2,3-dibromo-1,4-naphthoquinone with xanthene dissolved in cold benzene.

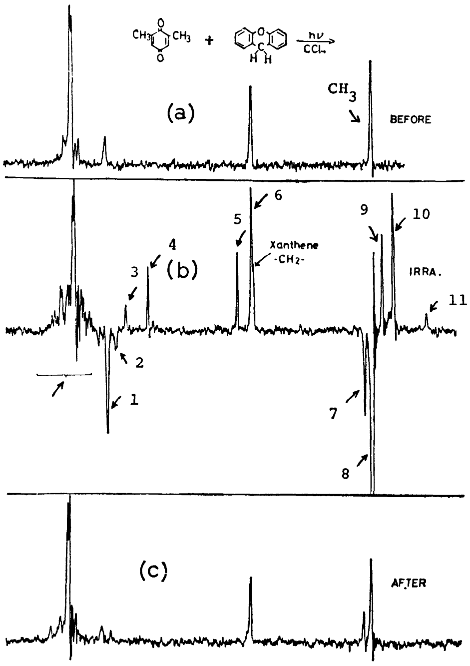


Fig. 6, PMR spectra observed in the photochemical reaction of 2,6-dimethyl-*p*-benzoquinone with xanthene (solvent; CCl_4, 22 °C).
(a): before irradiation, (b): during irradiation,
(c): after long irradiation (in this case irradiation was stopped)

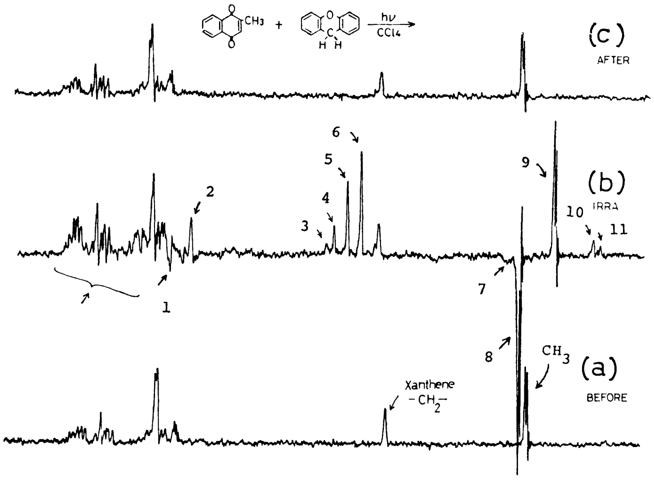


Fig. 7. PMR spectra observed in the photochemical reaction of 2-methyl-1,4-naphthoquinone with xanthene (solvent; CCl_4, 22 °C).
(a): before irradiation, (b): during irradiation,
(c): soon after irradiation (in this case irradiation was stopped)

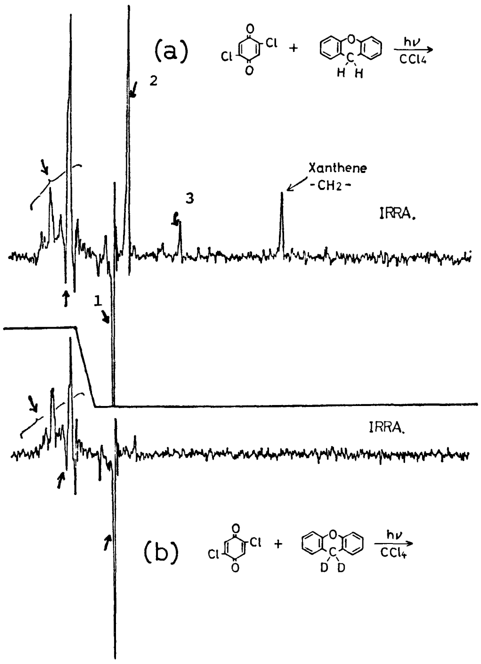


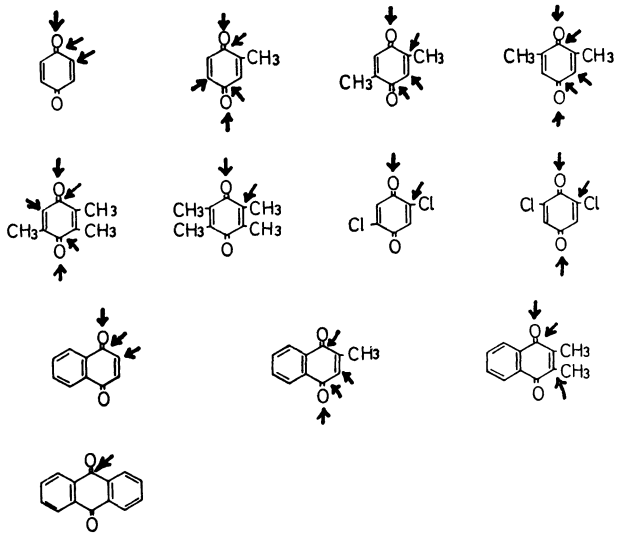
Fig. 8. PMR spectra observed in the photochemical reaction of 2,5-dichloro-*p*-benzoquinone with xanthene (solvent: CCl_4, 22 °C).
(a): during irradiation, (b): during irradiation, but with use of deuterated xanthene

methyl group region. The signals should be due to methyl protons of the unstable intermediates.

The emission polarized signal 1 in Fig. 6 (b) of the polarized PMR signals observed in the photochemical reaction of 2,6-dimethyl-*p*-benzoquinone with xanthene is due to the ring protons of quinone. The absorption polarized signals 3, 4, 5, and 6 in Fig. 6 (b) can be assigned to the unstable intermediates. They may be due to the methine proton of xanthene moiety having structures in which xanthene moiety attaches to the oxygen atom or carbonyl carbon. One of the two emission polarized signals (signal 7 in Fig. 6 (b)] in methyl proton region corresponds to methyl group of 2,6-dimethylhydroquinone and the other (signal 8) to the methyl groups of quinone itself. The other three or the more absorption polarized signals 9, 10, and 11 (Fig. 6 (b)) are due to the methyl protons of the unstable intermediates. In Fig. 7 we find a quite analogous example in the photochemical reaction of 2-methyl-1,4-naphthoquinone with xanthene. Several groups of strongly polarized PMR signals containing the strong emission polarized signal 8 due to methyl protons of quinone can be observed. They correspond to the ring proton, the methine proton, and the methyl proton of quinone or xanthene moieties in methyl substituted hydroquinone or in unstable intermediates [signal 7 to CH_3 of hydroquinone, and signals 9, 10, 11 to CH_3's of unstable intermediates]. PMR spectra observed in the photochemical reaction of 2,5-dichloro-*p*-benzoquinone with xanthene are shown in Fig. 8. Both spectra (a) and (b) are observed during the course of irradiation, (b) being of the deuterated xanthene case. Thus, absorption polarized signals in (a) (signals 2 and 3) are assigned to methine proton of xanthene moiety of unstable active intermediates. Emission polarized signal 1 is due to the ring proton of 2,5-dichlorohydroquinone produced as a stable product.

We can thus decide the attaching position of xanthene moiety to *p*-quinone moiety to form the unstable intermediates. The positions are indicated by arrows as follows.

For example, 2-methyl-*p*-benzoquinone forms five unstable intermediates. It is interesting that almost all the possible intermediates having a different structure can be found.



p-Quinone as a starting material, hydroquinone as stable product, and unstable intermediates can give the polarized PMR signal. However, no bixanthyl as the other stable reaction product and no xanthene as the other starting material in the photochemical reaction can give any polarized PMR signal. The photochemical reaction of *p*-quinones with xanthene in carbon tetrachloride or acetone is quite clean and gives only hydroquinones and bixanthyl as the stable reaction products. The photochemical reactions of *p*-quinones with xanthene can be formulated as follows.

$$
\begin{aligned}
&\mathrm{Q[{}^0S]} \xrightarrow{h\nu} \mathrm{Q[{}^1S]} \longrightarrow \mathrm{Q[T]}\\
&\mathrm{Q[T]} + \text{R-H} \longrightarrow [\text{R-H}\cdots\mathrm{Q}] \longrightarrow [\mathrm{R}\cdot,\cdot\mathrm{QH}]_{\mathrm{cage}}\\
&\text{R-H} + \mathrm{Q} \longleftarrow\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!\rfloor\\
&[\mathrm{R}\cdot,\cdot\mathrm{QH}]_{\mathrm{cage}} \rightarrow \underline{[\text{Unstable Intermediates}]} \rightarrow \cdot\mathrm{QH} + \mathrm{R}\cdot\\
&2\cdot\mathrm{QH} \longrightarrow \underline{\mathrm{Q}} + \underline{\mathrm{QH_2}} \qquad\qquad \downarrow\\
&\qquad\qquad\qquad\qquad\qquad\qquad \mathrm{R-R}
\end{aligned}
$$

Q: *p*-Benzoquinones.
R-H···Q: Transition state.
·QH: Semiquinone Radicals.
QH_2: Hydroquinones.
The compounds underlined show the polarized signals.

The compounds underlined can show the polarized PMR signals. We can observe analogous polarized PMR signals in the photochemical reaction of *p*-quinones with the other hydrogen donors described above.

Experimental

Materials. Commercial *p*-quinones of guaranteed grade were purified by recrystallization or by sublimation. When not available, they were synthesized by oxidation of the corresponding phenols with Fremy's salt.[9]

TABLE 1. MELTING POINTS OF *p*-QUINONES

p-Quinones	Mp (°C)
p-Benzoquinone	111
2-Methyl-*p*-benzoquinone	66[a]
2,5-Dimethyl-*p*-benzoquinone	123—124[a]
2,6-Dimethyl-*p*-benzoquinone	71[a]
2,3,5-Trimethyl-*p*-benzoquinone	28[a]
2,3,5,6-Tetramethyl-*p*-benzoquinone	111—112
2,5-Dichloro-*p*-benzoquinone	161—162
2,6-Dichloro-*p*-benzoquinone	119
1,4-Naphthoquinone	125—126
2-Methylnaphthoquinone	104—105
Anthraquinone	286 (sub)[b]

a) Synthesized. b) Sublimed.

CIDNP Examination. A typical CINDP examination of the photochemical reaction is as follows: a suitable amount of *p*-quinone (~10^{-2}—10^{-3} M) and xanthene were dissolved (or suspended) in suitable solvents such as carbon tetrachloride, acetone-d_6, or benzene-d_6[10] in a NMR sample tube made of usual glass.

The sample was irradiated by a 500 W high pressure mercury arc lamp and PMR spectra were observed before, during, and after irradiation. A 60 MHz NMR spectrometer manufactured by JEOL was used.

Products. Photochemical reactions of *p*-quinones with xanthene are so smooth and clean that hydroquinones produced are in general separated out in the sample tube within a few minutes. The same photochemical reactions were examined in a macro scale using a test tube as reaction vessel. The sample was irradiated by a 400W high pressure mercury arc lamp through 10 cm thick of water layer. When the color of *p*-quinone had faded completely, the volume of the sample was reduced to 2~3 ml, and hydroquinone and bixanthyl were separated by short Florisil (100~200 mesh) column. Melting points of hydroquinones produced were: hydroquinone, 170 °C; 2-methylhydroquinone, 126—127 °C; 2,5-dimethylhydroquinone, 217 °C; 2,6-dimethylhydroquinone, 149—151 °C; 2,3,5-trimethylhydroquinone, 168—170 °C; 2,3,5,6-tetramethylhydroquinone, 233 °C; 2,5-dichlorohydroquinone, 170 °C; 2,6-dichlorohydroquinone, 164 °C; 1,4-dihydroxynaphthalene, 173 °C; 2-methyl-1,4-dihydroxynaphthalene, (decn. $<$100 °C). Melting point of bixanthyl, 208—209 °C.

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[9] H. J. Teuber and G. Staiger, *Chem. Ber.*, **88**, 802 (1955); H. J. Teuber and H. H. Dietz, *Angew. Chem. Internat. Edn.*, **4**, 871 (1965).

[10] Photochemical reactions of *p*-quinone with xanthene are so fast that the solvents do not interfere with the photochemical reactions.