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Photochemical Reaction of 9,10-Phenanthrenequinone with Hydrogen Donors.[1] Behavior of Radicals in Solution as Studied by CIDNP

Kazuhiro MARUYAMA, Tetsuo OTSUKI, and Yoshinori NARUTA
Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606

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Behavior of radicals produced in the photochemical reaction of 9,10-phenanthrenequinone was investigated by use of CIDNP and ESR technique. By comparison of the sign of CIDNP signals in formation of and in decomposition (photochemical or thermal) of adducts, the rearrangement of adducts, *e.g.*, from the 1,2-adduct to 1,4-adduct and *vice versa*, was proposed. Although the adducts are stable enough to isolate in general, they decomposed photochemically or thermally to give the mixture of 9,10-phenanthrenediol (or its quinhydrone), the dehydrogenated dimer of hydrogen donor, and others as minor product.

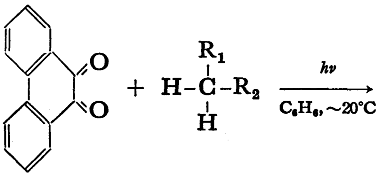
Photochemical reactions of 9,10-phenanthrenequinone with hydrogen donors were reinvestigated by means of CIDNP technique.[2] Although the results are rather qualitative, investigation by means of CIDNP technique is quite informative for study of the radical reaction mechanism.

Results and Discussion

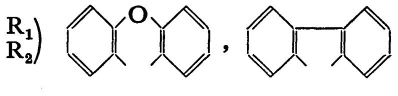
The photochemical reaction of 9,10-phenanthrenequinone with hydrogen donors in preparative scale can be classified in the following three types on the basis of the resulting major products. The inspection of the CIDNP spectra, however, reveals that the formation of both 1,2- and 1,4-photoadducts is essential but their stabilities are dependent on the nature of hydrogen donors, solvents used, and reaction temperature. Polarized PMR signals of the protons indicated by Gothic letter were the indices of formations of 1,2- and 1,4-photoadducts. The assignments of polarized signals were straightforward by comparison of the chemical shifts with those of isolated products, and the results could be substantiated by reaction of 9,10-phenanthrenequinone with the corresponding deuterated hydrogen donors.

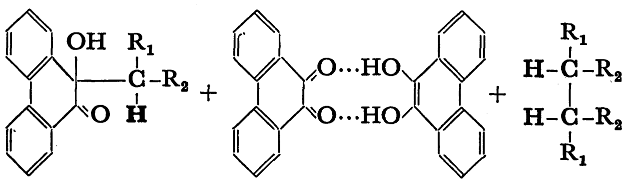
Photochemical Reaction of 9,10-phenanthrenequinone with Hydrogen Donors at 15—20°C.

Type 1



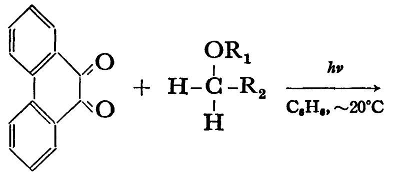
R_1: Aryl
R_2: Aryl or Alkyl



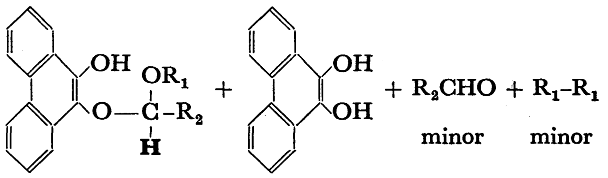


"1,2-adduct"
ν_{OH}: 3510 cm^{-1} (sharp)
$\nu_{C=O}$: 1690 cm^{-1}

Type 2



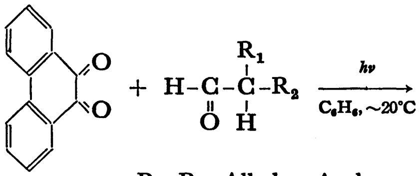
R_1: Alkyl or Aralkyl
R_2: Alkyl or Aryl



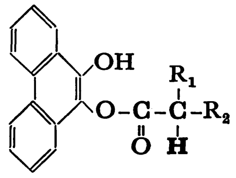
major
"1,4-adduct"
ν_{OH}: 3280 cm^{-1}
$\nu_{C=O}$: none

minor

Type 3



R_1, R_2: Alkyl or Aryl



(nearly quantitative)

"1,4-adduct"
ν_{OH}: 3380 cm^{-1}
$\nu_{C=O}$: 1730 cm^{-1} (ester)

According to the accepted simple rule for the polarized signal by Kaptein,[3] the absorption polarized signal of methine proton of xanthyl moiety (or methine proton of diphenylmethyl moiety) due to the 1,2-photoadduct (Fig. 1) is reasonable (see Eq. (1)). By the same reason the emission polarized signal due to methyl protons of acetyl moiety of 1,2-adduct (Fig. 2) is con-

$$\mathrm{PQ} \xrightarrow{h\nu} \mathrm{PQ}^{\mathrm{T}} \xrightarrow{\mathrm{RH}} \overline{\mathrm{PQH}\cdot\ \cdot\mathrm{R}}^{\mathrm{T}} \longrightarrow \text{1,2-photoadduct} \qquad (1)$$

PQ: 9,10-phenanthrenequinone
RH: hydrogen donor
$\overline{\mathrm{PQH}\cdot\ \cdot\mathrm{R}}^{\mathrm{T}}$: radical pair derived from triplet precursor

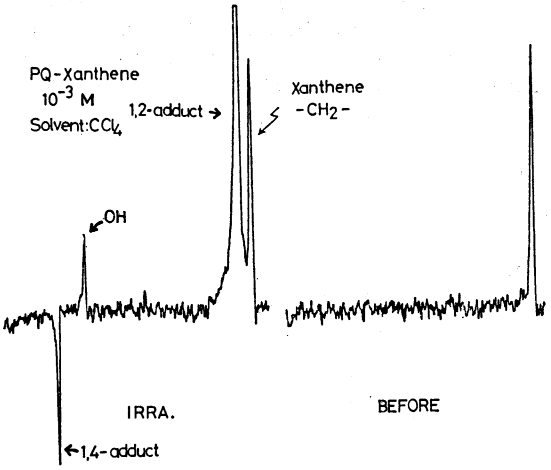


Fig. 1. Polarized PMR spectra observed in the course of the photochemical reaction of PQ with xanthene (Solvent: CCl_4 at room temperature).

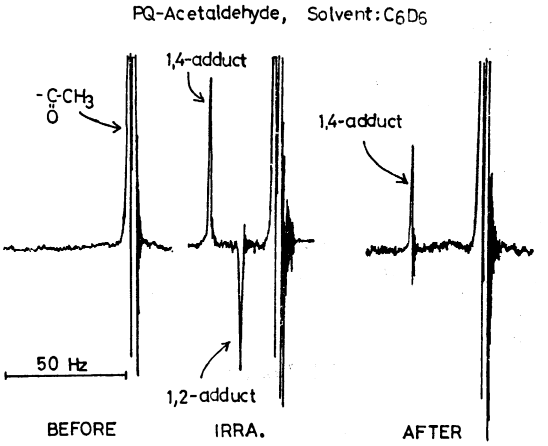


Fig. 2. Polarized PMR spectra observed in the course of the photochemical reaction of PQ with acetaldehyde (Solvent: C_6D_6 at room temperature).

vincible according to the following considerations.

$$\Gamma = \Delta g \varepsilon \mu \alpha \qquad (2)$$

if $\Gamma = +$, then absorption polarized signal,
$\Gamma = -$, then emission polarized signal

These parameters have their usual meaning.3) In the case of the reaction of 9,10-phenanthrenequinone with alkyl aromatics, $\Delta g = -$,4) $\varepsilon = +$, $\mu = +$, and $\alpha = -$5) are to be considered on the basis of the preceding reaction mechanism for methine-H and then, $\Gamma = -++- = +$, that is, the absorption polarized signal is expected.

In the case of the reaction of 9,10-phenanthrenequinone with acetaldehyde, for acetyl-H $\Gamma = -+++ = -$, then the emission polarized signal is expected. However, the reversely polarized signals due to 1,4-photoadducts compared to those of 1,2-adducts are hard to be explained by the simple route given in Eq. (1) (see Figs. 1 and 2). Since the radical components of the pair for 1,2- and 1,4-adducts are the same, Δg, ε, and α for the formation of 1,4-adducts have the same sign for those of 1,2-adduct. If we postulate the preceding formation of a radical pair which may result from vibrationally excited but singlet molecule of 1,2-adduct in advance of the formation of 1,4-adduct, all of the observed polarized signals for 1,4-adducts may be explicable, because the sign of μ is to be reverse. Further, we can explain the polarized signals due to methine-H of 1,2- and 1,4-adducts (Fig. 3) observed during the course of photochemical reaction of 9,10-phenanthrenequinone with dibenzyl ether (in general, with ethers) taking into consideration of the similar concept described above.

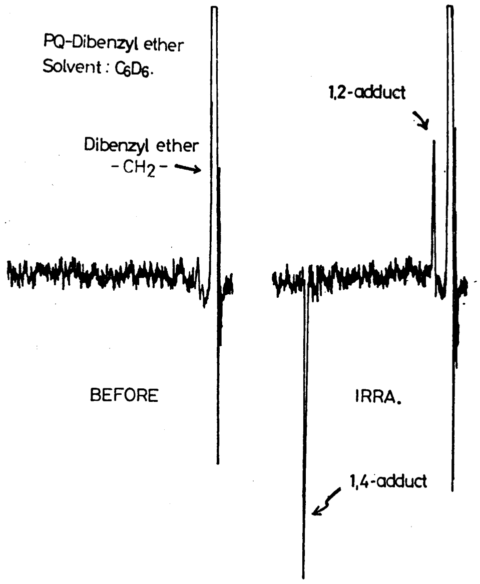


Fig. 3. Polarized PMR spectra observed in the course of the photochemical reaction of PQ with dibenzyl ether (Solvent: C_6D_6 at room temperature).

In fact, the concept was confirmed experimentally. Thermal and/or photo-induced decomposition of the purely isolated 1,2-adducts in suitable solvents was inspected by means of CIDNP. When at slightly elevated temperature (32 °C) isolated pure 1,2-adduct from 9,10-phenanthrenequinone (PQ) and an alkyl aromatic (PQ–*p*-xylene, PQ–*m*-xylene, PQ–*o*-xylene, PQ–mesitylene, PQ–diphenylmethane and PQ–xanthene system), was activated in carbon tetrachloride or benzene-d_6 by light of high pressure mercury arc lamp, two polarized signals due to methine or methylene proton corresponding to 1,2-(absorption in region of δ: 4.0) and 1,4-adducts (emission in region of δ: 6.0) are observed. Although the 1,4-adduct thus derived is too unstable to be isolated in this condition, this is the unambiguous evidence for the rearrangement from 1,2-adduct to 1,4-adduct *via* the radical pair derived from singlet precursor (Fig. 4). ESR inspection of the decomposing system at the same condition in the region of g-value=2.00 reveals the presence of no appreciable

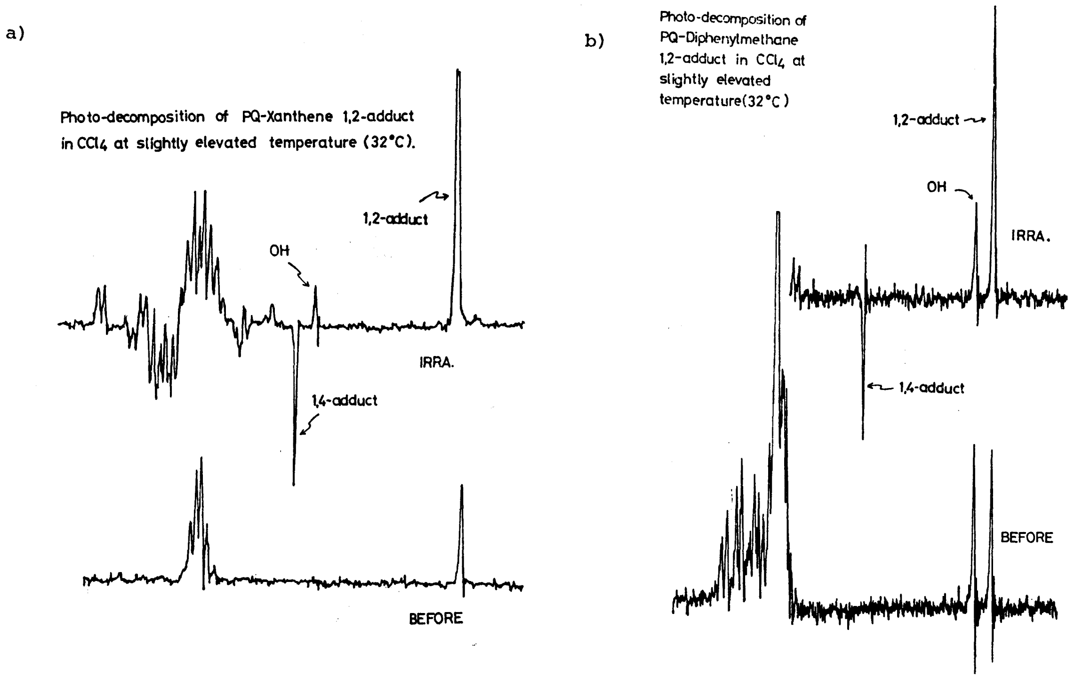


Fig. 4. Polarized PMR spectra observed in the course of the photodecomposition of a) PQ-xanthene 1,2-adduct, b) PQ-diphenylmethane 1,2-adduct (Solvent: CCl_4 32 °C).

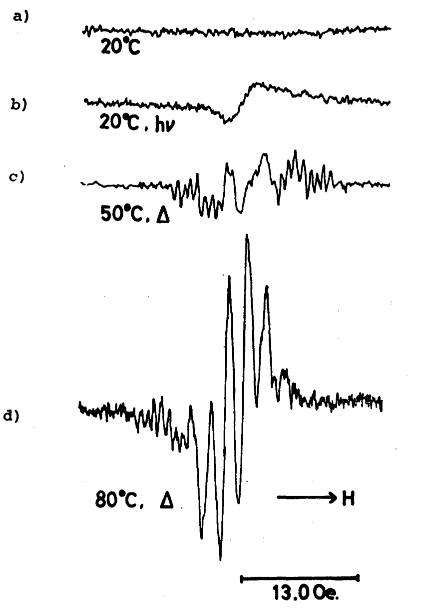


Fig. 5. ESR signals observed in the course of the decomposition of PQ-xanthene 1,2-adduct, a) 20 °C, b) 20 °C, *hν*, c) 50 °C, d) 80 °C (Solvent: CCl_4). Non symmetry of signals indicates that signals are composed of a mixture of radicals.

free radical in solution (Fig. 5). On the other hand, when we decomposed 1,2-adduct (from PQ-xanthene and PQ-diphenylmethane) at 80 °C or higher temperature, an absorption polarized and an emission polarized signal each corresponding to 1,4- and 1,2-adducts were observed (Fig. 6). In the decomposing systems of 1,2-adduct at these temperatures were observed, in actual, strong ESR.signals indicating the appearence of *free radicals* in solution (see Fig. 5). We can recognize the polarized signals which were observed during the course of decompositions taking into consideration of the following reaction scheme;

Photodecomposition at lower temperature:

$$\begin{tikzcd}
\text{1,2-adduct} \arrow[r, "h\nu\ (400\text{—}500\ \mathrm{nm})"] & \overline{\mathrm{PQH}\cdot\ \cdot\mathrm{R}}^{\mathrm{T}} \arrow[d] & \\
\text{1,2-adduct} & \text{1,2-adduct}_{\textit{vibrationally excited}} \arrow[l] \arrow[d] & \\
 & \overline{\mathrm{PQH}\cdot\ \cdot\mathrm{R}}^{\mathrm{S}} \arrow[r] & \text{1,4-adduct}
\end{tikzcd}$$

Thermal decomposition at higher temperature:

$$\begin{tikzcd}
 & \text{1,2-adduct} \arrow[r, shift left, "\Delta"] & \overline{\mathrm{PQH}\cdot\ \cdot\mathrm{R}}^{\mathrm{S}} \arrow[l, shift left] \arrow[r] & \mathrm{PQH}\cdot + \cdot\mathrm{R} \arrow[d] \\
\mathrm{PQ}\cdots\mathrm{PQH}_2 + \mathrm{R\text{-}R} & & \text{1,4-adduct} \arrow[ll] & \overline{\mathrm{PQH}\cdot\ \cdot\mathrm{R}}^{\mathrm{F}} \arrow[l]
\end{tikzcd}$$

$\overline{\mathrm{PQH}\cdot\ \cdot\mathrm{R}}^{\mathrm{T}}$: radical pair derived from triplet precursor
$\overline{\mathrm{PQH}\cdot\ \cdot\mathrm{R}}^{\mathrm{S}}$: radical pair derived from singlet precursor
$\overline{\mathrm{PQH}\cdot\ \cdot\mathrm{R}}^{\mathrm{F}}$: radical pair derived from free radical precursor

Thus, the absorption polarized PMR signal corresponding to 1,4-adduct observed in thermally decomposing system of 1,2-adduct at the higher temperature indicates the recombination of the two component radicals *via free radical* state.

On irradiation of 9,10-phenanthrenequinone with ethers by visible light in benzene-d_6 or carbon tetrachloride at about 20 °C, 1,4-adducts (methine-H: in region of δ: 5.7—6.4, emission polarized) are accumu-

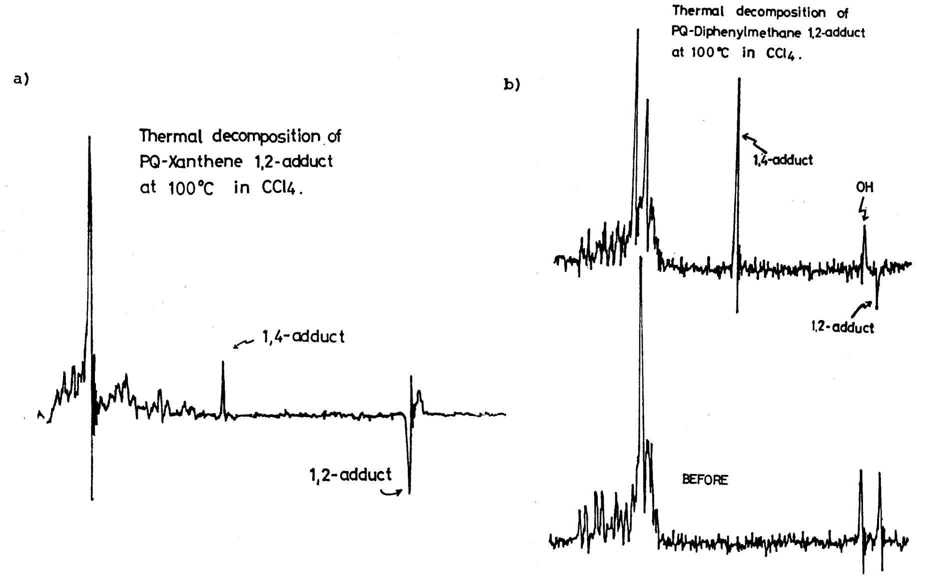


Fig. 6. Polarized PMR spectra observed in the course of the thermal decomposition of a) PQ-xanthene 1,2-adduct, b) PQ-diphenylmethane 1,2-adduct (Solvent: CCl_4 at 100 °C).

lated products in spite that the CIDNP signals indicate the transient formation of 1,2-adducts (methine-H: in region of δ: 4.4—5.1, absorption polarized) accompanying with 1,4-adducts. Irradiation of a 1,4-adduct, for example, 1,4-adduct derived from 9,10-phenanthrenequinone and dibenzyl ether, by UV-light[6] *in situ* exhibits an absorption polarization of methine-H (δ: 5.8) due to 1,4-adduct and an absorption polarization of methine-H (δ: 4.6) due to 1,2-adduct[7] (Fig. 7). This is an indication of rearrangement from 1,4-adduct to 1,2-adduct *via* radical pair produced from triplet precursor. It may be formularized as the followings;

$$\begin{array}{l} PQ^T + R'H \longrightarrow \overline{PQH\cdot\ \cdot R'}^T \\ \qquad\qquad\qquad \downarrow \\ \qquad\quad \text{1,2-adduct}_{\substack{\textit{vibrationally} \\ \textit{excited}}} \longrightarrow \begin{array}{c}\text{1,2-adduct}\\ \text{(H-A)}\end{array} \\ \qquad\qquad\qquad \downarrow \\ \qquad\quad \overline{PQH\cdot\ \cdot R'}^S \longrightarrow \begin{array}{c}\text{1,4-adduct}\\ \text{(H-E)}\end{array} \end{array} \qquad (3)$$

$$\text{1,4-adduct} \xrightarrow{\text{UV-light}} \overline{PQH\cdot\ \cdot R'}^T \begin{array}{l} \nearrow \begin{array}{c}\text{1,4-adduct}\\ \text{(H-A)}\end{array} \\ \searrow \begin{array}{c}\text{1,2-adduct}\\ \text{(H-A)}\end{array} \end{array} \qquad (4)$$

H-A: polarized absorption signal of methine-H
H-E: polarized emission signal of methine-H

Similarly, the absorption polarized PMR signal due to acyl proton of stable 1,4-adduct (9-acyloxy-10-hydroxyphenanthrene) is comprehensive by assuming the preceding formation of unstable 1,2-adduct, and the subsequent rearrangement to 1,4-adduct *via* singlet radical pair. This is obviously confirmed in the photo-

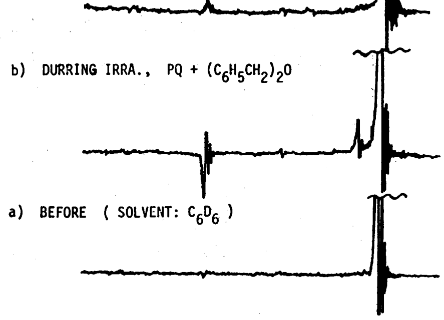
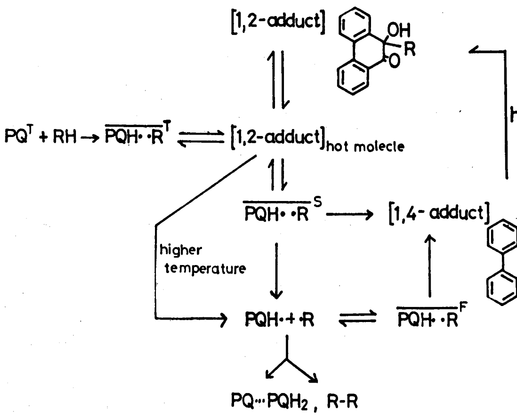


Fig. 7. Polarized PMR spectra observed in the course of the photodecomposition reaction of PQ-dibenzyl ether (Solvent: C_6D_6 at room temperature).



Reaction scheme.

chemical reaction of PQ with acetaldehyde in benzene-d_6 by use of CIDNP technique (Fig. 2).

Summarizing the behavior of radicals in photochemical reaction of 9,10-phenanthrenequinone we may write schematically the whole reaction as in the preceding reaction scheme.

Experimental

1,2-Adducts. 1,2-Adducts were obtained in preparative scale on irradiation of mixtures of 9,10-phenanthrenequinone and suitable hydrogen donors in neat or in benzene solution. The reaction mixture was kept in a usual glass tube dipped into cool water, and irradiated by high pressure Hg-arc lamp from outside. All the 1,2-adducts of 9,10-phenanthrenequinone with alkyl aromatics have characteristic IR bands due to carbonyl and hydroxyl groups; $\nu_{C=O}$: 1690 cm^{-1}, and ν_{OH}: 3510 cm^{-1} (sharp). Their compositions were confirmed by elemental analysis. PQ–xanthene: mp 103 °C (decomp.), PQ–diphenylmethane: mp 129—132 °C (decomp.), PQ–fluorene: mp 165—167 °C (decomp.), PQ–mesitylene: mp 165—167 °C (decomp.), PQ–*p*-xylene: mp 128—128.5 °C (decomp.), PQ–*m*-xylene: mp 93—94 °C (decomp.), PQ–*o*-xylene: mp 146 °C (decomp.), PQ–anisole: mp 109—111 °C (decomp.). (PQ: 9,10-phenanthrenequinone)

1,4-Adducts. 1,4-Adducts were obtained by procedures analogous to those of 1,2-adducts. They show characteristic IR band due to hydroxyl group; ν_{OH}: 3280 cm^{-1}, and no carbonyl band. PQ–1,4-dioxane: mp 92—94 °C (decomp.), PQ–1,4-dibenzyloxybenzene: mp 143—144 °C (decomp.). Their compositions were confirmed by elemental analysis.

CIDNP. PS-100 type and MH-100 type NMR instruments equipped with PMR probe for irradiation (manufactured by JEOL) were used in CIDNP examinations. For irradiation 1 kW and 500 W high pressure Hg-arc lamps were applied with or without use of filter (Toshiba VY-42).

ESR. ME-3 type ESR machine manufactured by JEOL (X-band) was used in this experiment.

References

1) This work was presented at Magnetic Conference on CIDNP and CIDEP which was held at Grenoble, May 21—23, 1975.

2) K. Maruyama, H. Shindo, and T. Maruyama; This Bulletin, **44**, 585 (1971), K. Maruyama, T. Otsuki, H. Shindo, and T. Maruyama; *ibid.*, **44**, 2000, 2756, 2789 (1971), K. Maruyama, and T. Otsuki; *ibid.*, **44**, 2885 (1971), K. Maruyama, A. Takuwa, T. Otsuki, and S. Kako; *Bull. Inst. for Chem. Res., Kyoto Univ.*, **50**, 348 (1971), and references cited therein.

3) R. Kaptein; *Chem. Commun.*, **1971**, 732; *J. Amer. Chem. Soc.*, **94**, 6251 (1972).

4) *g*-Value of semiquinone radical is in general larger than that of carbon radical without exception.

5) Sign of hyperfine coupling constant (α) of α-hydrogen of carbon radicals is assumed to be negative. *cf.* H. Fischer; "Structure of Free Radicals by ESR Spectroscopy" (J. K. Kochi Ed., "Free Radicals") Vol. 2, p. 435, Wiley Interscience, New York (1973).

6) For decomposition of 1,4-adduct visible light in the region of 400—500 nm is not effective, but UV-light is only effective. The decomposition may be induced by π-π^* excitation of 1,4-adduct, because the adduct has no carbonyl group.

7) K. Maruyama and T. Otsuki; This Bulletin, **44**, 2885 (1971).