Reaction of Photo-excited Phenanthraquinone with Dibenzyl Ether. Formation of an Adduct and its Decomposition studied by CIDNP Method.

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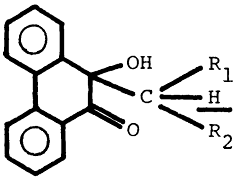
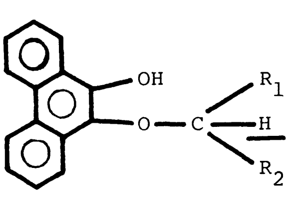
Whereas photo-excited phenanthraquinone reacts with alkyl aromatics showing enhanced PMR absorption signals for 1,2-adducts,[1] it reacts with dibenzyl ether showing an enhanced PMR emission signal for 1,4-adduct (Fig. 1-A). Dibenzyl glycol, phenyl benzyl ether, and hydroquinone dibenzyl ether undergo the same type of reaction showing all the enhanced PMR emission signals. Protons giving the enhanced signals are indicated in (1) and (2) (underlined). All these reactions are rationalized if we consider the hydrogen abstraction by photo-excited phenanthraquinone in n-π^* triplet state followed by recombination of the resulting radicals in a solvent cage, because none of the reactions are affected even if we use a UV-cut filter.[2] By comparing their PMR and/or IR spectra one can easily differentiate the 1,2-adduct and 1,4-adduct.[3]



1,2-adduct
(1)



1,4-adduct
(2)

1,4-Adduct which is transparent in visible region shows a slightly enhanced absorption signal (2 to 10 times) when it is irradiated with UV light and decomposes photochemically at an elevated temperature to give phenanthraquinhydrone, benzaldehyde, *sym*-diphenylethane, toluene and unidentified products.[4] During the course of photochemical decomposition we can observe the enhanced PMR absorption signal of the resulting benzaldehyde (due to formyl proton) (Fig. 1-B). When light was cut off, the enhanced signal decayed promptly. Thus, it is confirmed that the neutral molecule, *i.e.* benzaldehyde, produced by fragmentation of radical can take the nuclear spin polarized state. The photochemical decomposition is effective only with UV light. No such enhanced signal of benzaldehyde could be observed when we applied a UV-cut filter.[5]

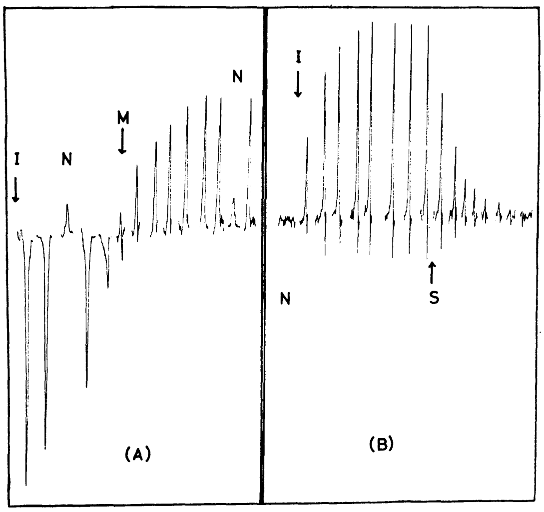


Fig. 1. (A) Enhanced PMR signals of 1,4-adduct (τ: 4.12) observed in the photochemical reaction of phenanthraquinone with dibenzyl ether (70°C). I: Irradiation initiated. N: The normal signal of the accumulated adduct under no irradiation. I→M: Enhanced emission signals. M: Enhanced emission and absorption signals balance, and nearly all of the phenanthraquinone in the reaction system is consumed.
(B) Enhanced PMR signals of benzaldehyde (τ: 0.35) observed in the photochemical decomposition of the 1,4-adduct (90°C). N: No irradiation. I: Irradiation initiated. I→S: enhanced absorption signals of benzaldehyde. S: Irradiation stopped.

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[1] K. Maruyama, H. Shindo, and T. Maruyama, This Bulletin, **44**, 585 (1971); K. Maruyama, T. Otsuki, H. Shindo, and T. Maruyama, *ibid.*, **44**, 2000 (1971).

[2] A 500 W high pressure Hg lamp as a light source and a Toshiba V-Y 42 filter were used. A 60 MHz C-60HL NMR spectrometer manufactured by JEOL was used.

[3] 1,2-Adducts show the following characteristic spectra;
IR, ν_{OH}: sharp ~3500 cm^{-1}, $\nu_{C=O}$: 1690 cm^{-1}
PMR, τ_{OH}: ~6.0 region, $\tau_{\text{methine or methylene}}$: ~7.0 region
1,4-Adducts show the following characteristic spectra;
IR, ν_{OH}: broad ~3300 cm^{-1}, $\nu_{C=O}$: none
PMR, τ_{OH}: in phenolic OH region, $\tau_{\text{methine or methylene}}$: 4.0—5.0 region

[4] These decomposition products were identified by PMR, TLC, GLC, and chemical analyses.

[5] 1,4-Adduct can decompose also thermally very slowly without any light. However, no PMR enhanced signal could be observed during the course of the reaction.