Photochemical Reactions of Phenanthraquinone with Hydrogen Donors. An Investigation of the Reaction by CIDNP Method

Kazuhiro MARUYAMA, Heisaburo SHINDO,* and Tetsuo MARUYAMA*
Department of Chemistry, College of Liberal Arts and Science, Kyoto University, Kyoto
**Japan Electron Optics Laboratory, Akishima, Tokyo*

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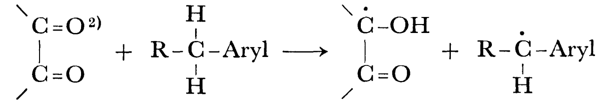
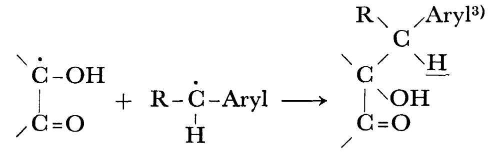
The rate of hydrogen abstraction by α-dicarbonyl compounds in triplet state is usually too fast for the observation of intermediate radicals by means of ESR technique. In order to make direct confirmation of the contribution of radicals in the photochemical reaction between phenanthraquinone and hydrogen donors, CIDNP (chemically induced dynamic nuclear polarization) technique[1] was applied. During the course of irradiation a strongly enhanced proton NMR absorption signal was observed at the methylene group region of photo-adduct. This is due to the secondary recombination process of two different intermediate radicals resulting from the primary hydrogen abstraction reaction by photo-excited phenanthraquinone triplet state as shown in the following:



(primary hydrogen abstraction process)



(secondary recombination process)

Phenomena of such an enhanced NMR absorption signal were observed during the course of irradiation in the following systems: phenanthraquinone and toluene (enhanced signal at τ: 7.10), phenanthraquinone and ethylbenzene (enhanced signal at τ: 7.10), and phenanthraquinone and diphenylmethane (enhanced signal at τ: 5.92). When irradiation was stopped, the enhanced signal disappeared immediately. Thus, the contribution of radical species in the hydrogen abstraction reaction of photo-excited α-dicarbonyl compounds was directly confirmed.

General procedures: Phenanthraquinone, dissolved into a hydrogen donor as solvent, was irradiated in a rotating NMR sample tube fitted with a light guide with a 500 W high pressure Hg lamp from above. Light was collected by a quartz lens before irradiation, and focused at the light guide. The light guide is a simple quartz tube coated on the in ner side with an aluminum metal. Oxygen dissolved into a sample was expelled by passing nitrogen. Assignment of a signal observed to the photo-adduct was carried out by comparison with that of the authentic sample, prepared by photochemical reaction of phenanthraquinone with a hydrogen donor on a larger scale. 60 MHz NMR spectrometer manufactured by JEOL was used.

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1) G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **91**, 4549 (1969); G. L. Closs, *ibid.*, **91**, 4550, 4552 (1969); G. L. Closs and A. D. Trifunac, *ibid.*, **91**, 4554 (1969); *ibid.*, **92**, 2183, 2186 (1970); G. L. Closs, C. E. Doubleday, and D. R. Paulson, *ibid.*, **92**, 2185 (1970); R. Kaptein and J. L. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195, 214 (1969).

2) Photo-excited triplet state.

3) Enhanced signal is due to the underlined proton.