

Syntheses of 9-Acyloxy-10-hydroxyphenanthrenes by Photochemical Reaction

Kazuhiro MARUYAMA*, Akio TAKUWA**, Tetsuo OTSUKI** and Saburo KAKO**

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Synthetic use of the photochemical reaction between phenanthraquinone and aldehydes to give 9-acyloxy-10-hydroxyphenanthrenes was extended. The reactions are in general very clean and the yields are nearly quantitative in all cases examined. The dynamic aspect of the reactions was also examined using the CIDNP technique. The photochemical reaction between phenanthraquinone and phenylglyoxal is investigated to result 9-benzoyloxy-10-hydroxyphenanthrene in a nearly quantitative yield. The same compound is also obtained in a quantitative yield by the photochemical reaction of phenanthraquinone with benzaldehyde.

I. INTRODUCTION

Photochemical reactions of phenanthraquinone with aldehydes to give 9-acyloxy-10-hydroxyphenanthrenes have been investigated by several investigators.¹⁻⁶⁾ The reactions reported so far are in general fairly clean and the yields are high. 9-Acyloxy-10-hydroxyphenanthrene can be prepared by the mono-acylation of 9,10-dihydroxyphenanthrene which is extremely vulnerable to the air-oxidation and the yield is not so satisfactory. Phenanthraquinone has $n \rightarrow \pi^*$ absorption band in the visible region (λ_{max} : ~ 500 nm) and in the triplet state resulted by the intersystem crossing from the excited singlet state, phenanthraquinone indicates a strong hydrogen abstracting character. Thus, alkylaromatics, alcohols, ethers, and aldehydes can act as hydrogen donors for the photochemical reaction. The products are 1,2-adduct, 1,4-adduct, 9,10-dihydroxyphenanthrene, quinhydrone and the dimer of the radical moiety resulting from a hydrogen abstraction.⁷⁾ The reactions with twelve of aldehydes and phenylglyoxal were investigated in this work.

II. EXPERIMENTAL

Materials. Phenanthraquinone Phenanthraquinone was prepared by the oxidation of phenanthrene with potassium dichromate. mp 202–204°C.

Aldehydes All aldehydes used were commercially available and they were purified by distillation before use.

Photochemical Reaction A typical photo-reaction was accomplished as the following: 1 mmole of phenanthraquinone, 1.5 mmoles of an aldehyde and 20 ml of benzene were

* 丸山和博: Department of Chemistry, Faculty of Science, Kyoto University, Kyoto.

** 宅和暁男, 大槻哲夫, 加古三郎: Department of Chemistry, College of Liberal Arts and Science, Kyoto University.

mixed in a usual glass tube. The mixture contained some undissolved phenanthraquinone was irradiated under occasional shaking with 400 W high pressure mercury arc lamp through 3 cm thick water layer. Needles were crystallized out after a suitable irradiation time which is dependent on the reactivity of an aldehyde and the solubility of the resulting photo-adduct. After the color of phenanthraquinone in the mixture was completely faded (in general, after irradiation for 10–15 hrs), benzene was distilled out of the mixture until a half of the volume, and then 10 ml of petroleum-ether was poured into the mixture. Again, the volume of the mixture was concentrated to a suitable volume. After standing on the mixture for about one hour at room temperature, photo-adduct crystallized as needles was filtered. The photo-adduct thus obtained was, in general, in highly pure state, and the yield was nearly quantitative based on the amount of phenanthraquinone used.

Identification of Photo-adduct.

9-Ethanoyloxy-10-hydroxyphenanthrene: white needles, mp 182–183°C (yield, quantitative). ν_{OH} : 3330 cm^{-1} , $\nu_{\text{C=O}}$: 1724 cm^{-1} , τ : 1.30 (OH), τ : 1.35–2.90 (aromatic-H), τ : 6.38 (CH_3), (IR spectrum was measured with KBr disk and PMR spectrum was measured in acetone- d_6 unless otherwise stated). Elemental analysis; found, C: 75.92, H: 4.72%; calculated for $\text{C}_{16}\text{H}_{12}\text{O}_3$, C: 76.18, H: 4.08%.

9-Propanoyloxy-10-hydroxyphenanthrene: white needles, mp 158–159°C (yield, quantitative). ν_{OH} : 3350 cm^{-1} , $\nu_{\text{C=O}}$: 1730 cm^{-1} , τ : 1.20 (OH), τ : 1.30–2.90 (aromatic-H), τ : 7.20 ($-\text{CH}_2-$), τ : 8.78 (CH_3). Elemental analysis; found, C: 76.52, H: 5.25%; calculated for $\text{C}_{17}\text{H}_{14}\text{O}_3$, C: 76.68, H: 5.30%.

9-n-Butanoyloxy-10-hydroxyphenanthrene: white needles, mp 142–143°C (yield, quantitative). ν_{OH} : 3350 cm^{-1} , $\nu_{\text{C=O}}$: 1730 cm^{-1} , τ : 0.98 (OH), τ : 1.00–2.90 (aromatic-H), τ : 7.20, 8.30 ($-\text{CH}_2-$), τ : 8.93 (CH_3). Elemental analysis; found, C: 76.93, H: 5.79%; calculated for $\text{C}_{18}\text{H}_{16}\text{O}_3$, C: 77.12, H: 5.75%.

9-[2'-Methyl]-propanoyloxy-10-hydroxyphenanthrene: white needles, mp 152–154°C (yield, quantitative). ν_{OH} : 3400 cm^{-1} , $\nu_{\text{C=O}}$: 1725 cm^{-1} , τ : 4.00 (OH), τ : 1.50–2.90 (aromatic-H), τ : 7.45 ($-\text{CH}-$), τ : 8.90 (CH_3). Elemental analysis; found, C: 77.95, H: 5.87%; calculated for $\text{C}_{18}\text{H}_{16}\text{O}_3$, C: 77.12, H: 5.75%.

9-n-Pentanoyloxy-10-hydroxyphenanthrene: white needles, mp 123°C (yield, quantitative). ν_{OH} : 3350 cm^{-1} , $\nu_{\text{C=O}}$: 1715 cm^{-1} , τ : 1.15 (OH), τ : 1.20–2.90 (aromatic-H), τ : 7.20, 8.00–8.80 ($-\text{CH}_2-$), τ : 9.00 (CH_3). Elemental analysis; found, C: 77.17, H: 6.22%; calculated for $\text{C}_{19}\text{H}_{18}\text{O}_3$, C: 77.53, H: 6.16%.

9-[3'-Methyl]-butanoyloxy-10-hydroxyphenanthrene: white needles, mp 142–144°C (yield, quantitative). ν_{OH} : 3400 cm^{-1} , $\nu_{\text{C=O}}$: 1715 cm^{-1} , τ : 1.20 (OH), τ : 1.10–2.80 (aromatic-H), τ : 7.20, 7.90 ($-\text{CH}_2-$), τ : 8.90 (CH_3). Elemental analysis; found, C: 77.08, H: 6.14%; calculated for $\text{C}_{19}\text{H}_{18}\text{O}_3$, C: 77.53, H: 6.16%.

9-Benzoyloxy-10-hydroxyphenanthrene; white needles, mp 182–184°C (yield, quantitative). ν_{OH} : 3350 cm^{-1} , $\nu_{\text{C=O}}$: 1710 cm^{-1} , τ : 1.12 (OH), τ : 1.30–2.80 (aromatic-H). Elemental analysis; found, C: 80.28, H: 4.36%; calculated for $\text{C}_{21}\text{H}_{14}\text{O}_3$, C: 80.24, H: 4.49%.

9-[4'-Methoxy]-benzoyloxy-10-hydroxyphenanthrene: white needles, mp 223–226°C (yield, quantitative). ν_{OH} : 3300 cm^{-1} , $\nu_{\text{C=O}}$: 1710 cm^{-1} , τ : 6.08 (OCH_3), τ : 1.30–

3.10 (aromatic-H) overlapped with OH proton. Elemental analysis; found, C: 76.23, H: 4.52%; calculated for $C_{22}H_{16}O_4$, C: 76.73, H: 4.68%.

9-[4'-Nitro]-benzoyloxy-10-hydroxyphenanthrene: small orange needles, mp 224–225°C (yield, nearly quantitative). ν_{OH} : 3350 cm^{-1} , $\nu_{C=O}$: 1710 cm^{-1} , τ : 1.50 (OH), τ : 1.00–2.70 (aromatic-H). Elemental analysis, found, C: 70.17, H: 3.70, N: 3.63%; calculated for $C_{21}H_{13}O_5N$, C: 70.19, H: 3.65, N: 3.90%.

9-[3'-Nitro]-benzoyloxy-10-hydroxyphenanthrene: small pale-yellow needles, mp 208–210°C (yield, nearly quantitative). ν_{OH} : 3400 cm^{-1} , $\nu_{C=O}$: 1710 cm^{-1} , τ : 1.00 (OH), τ : 1.10–2.80 (aromatic-H). Elemental analysis; found, C: 70.35, H: 3.56, N: 3.77%; calculated for $C_{21}H_{13}O_5N$, C: 70.19, H: 3.65, N: 3.90%.

9-[3'-Phenyl]-propenoyloxy-10-hydroxyphenanthrene: yellowish needles, mp 191–192°C (yield, nearly quantitative). ν_{OH} : 3350 cm^{-1} , $\nu_{C=O}$: 1705 cm^{-1} , τ : 0.80 (OH), τ : 1.00–2.70 (aromatic-H), τ : 2.70 (–CH=). Elemental analysis; found, C: 81.62, H: 4.66%; calculated for $C_{23}H_{16}O_3$, C: 81.16, H: 4.74%.

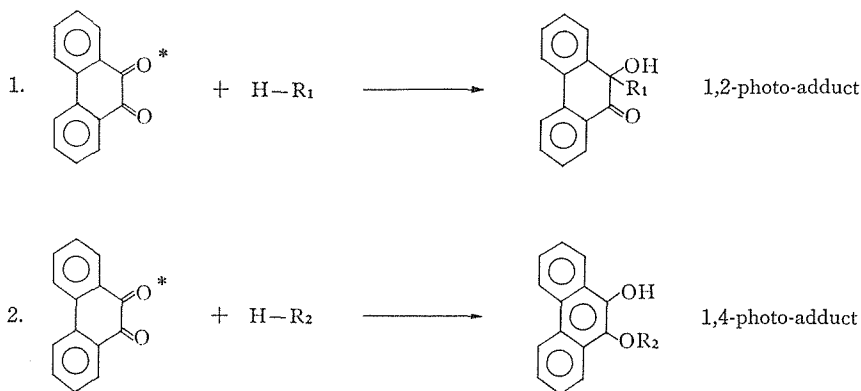
9-[3',4'-Methylenedioxy]-benzoyloxy-10-hydroxyphenanthrene: white powder, mp 182–184°C (decom.) (yield, nearly quantitative). ν_{OH} : 3350 cm^{-1} , $\nu_{C=O}$: 1705 cm^{-1} , τ : 1.12 (OH), τ : 1.10–2.90 (aromatic-H), τ : 2.40 (–CH₂–).

9-Benzoyloxy-10-hydroxyphenanthrene: resulted from the reaction of phenanthraquinone with phenylglyoxal, white needles, mp 182–184°C (yield, 85%). ν_{OH} : 3350 cm^{-1} , $\nu_{C=O}$: 1710 cm^{-1} . No depression of melting point was confirmed by the mixed melting point determination with the photo-adduct resulted from the reaction of phenanthraquinone with benzaldehyde. IR spectrum was completely coincided with that of the latter.

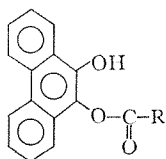
CIDNP Examinations. Investigation of these photochemical reactions by CIDNP technique was performed using 60 Mc NMR spectrometer, equipped with the modified NMR probe for the photo-irradiation. The spectrometer and the modified NMR probe were manufactured by JEOL Co. LTD.

III. RESULTS AND DISCUSSION

In the photochemical reaction of phenanthraquinone with the hydrogen donors, 1,2-photo-adduct or 1,4-photo-adduct can be produced depending on the nature of the hydrogen donor.



Photochemical reactions of phenanthraquinone with alkyl aromatics, *e. g.* toluene, fluorene, or xanthene, give in general 1,2-photo-adducts as the main product⁷⁾. However, in the photochemical reactions of phenanthraquinone with aldehydes, 1,4-photo-adducts are exclusively produced as they are described in the experimental section (see Structure 1).



Structure 1

R: CH₃, C₂H₅, *n*-C₃H₇, *iso*-C₃H₇, *n*-C₄H₉, *iso*-C₄H₉, C₆H₅, *p*-CH₃OC₆H₄, *p*-NO₂C₆H₄, *m*-NO₂C₆H₄, C₆H₅CH=CH, 3,4-Methylenedioxy-C₆H₃,

Each of the photo-adducts can be easily differentiated by comparison of their IR or PMR spectra. The 1,2-photo-adduct has characteristic IR bands; ν_{OH} : 3510 cm⁻¹, $\nu_{\text{C=O}}$: 1690 cm⁻¹, or PMR signal; τ_{OH} : 6.30 (in CCl₄), but the 1,4-photo-adduct has characteristic IR bands; ν_{OH} : \sim 3350 cm⁻¹, $\nu_{\text{C=O}}$: \sim 1710 cm⁻¹, or PMR signal; τ_{OH} : \sim 1.0 (in acetone-d₆).

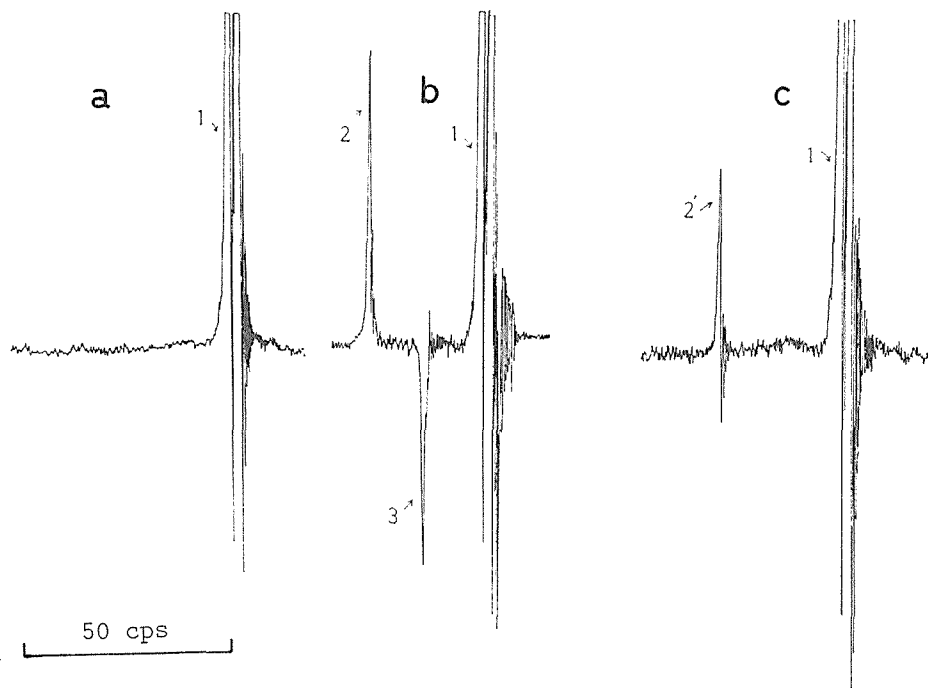


Fig. 1-A. PMR Spectra observed in the Reaction of Phenanthraquinone with Acetaldehyde in Benzene Solution.

- Before irradiation. Signal 1: methyl protons of acetaldehyde.
- During the course of irradiation. Signal 1: methyl protons of acetaldehyde. Signal 2: absorption polarized signal, which corresponds to 1,4-adduct. Signal 3: emission polarized signal, which is not accumulated in the reaction system after a long irradiation.
- After a long irradiation. Signal 2': normal signal, which corresponds to 1,4-photo-adduct accumulated in the reaction system.

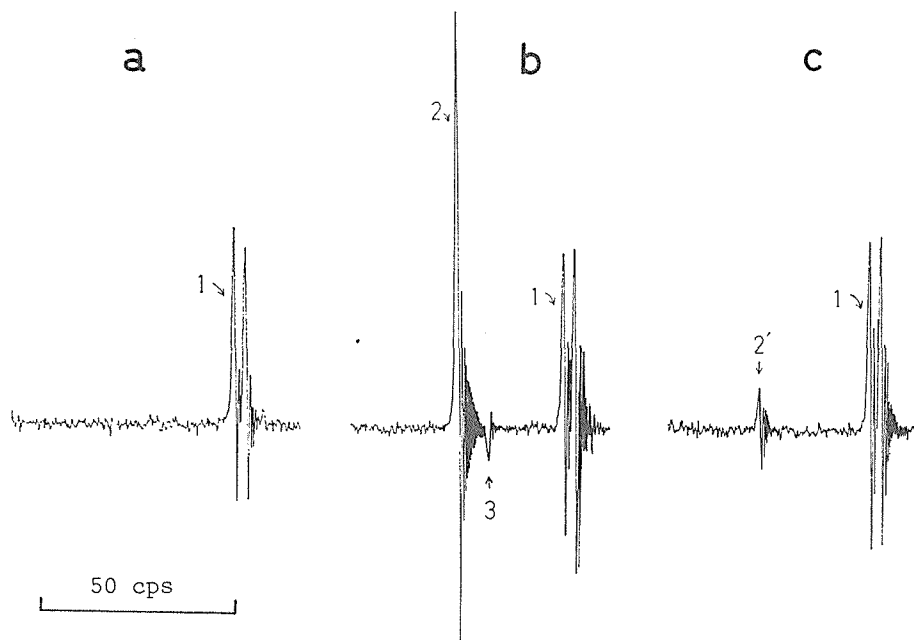


Fig. 1-B. PMR Spectra observed in the Reaction of Phenanthraquinone with Acetaldehyde in Carbon Tetrachloride Solution.

- a) Before irradiation. Signal 1 : methyl protons of acetaldehyde.
- b) During the course of irradiation. Signal 1 : methyl protons of acetaldehyde. Signal 2 : absorption polarized signal, which corresponds to 1,4-adduct. Signal 3 : negligibly small emission polarized signal, which is not accumulated in the reaction system even after a long irradiation.
- c) After a long irradiation. Signal 2' : normal signal, which corresponds to 1,4-photo-adduct accumulated in the reaction system.

Thus, in the photochemical reaction of phenanthraquinone with aldehydes 1,4-photo-adducts, that is, 9-acyloxy-10-hydroxyphenanthrenes, are produced in quantitative or nearly quantitative yields. However, the dynamic feature of the reaction is not straightforward. Investigations by CIDNP technique revealed some aspects of the complexities of the reaction.

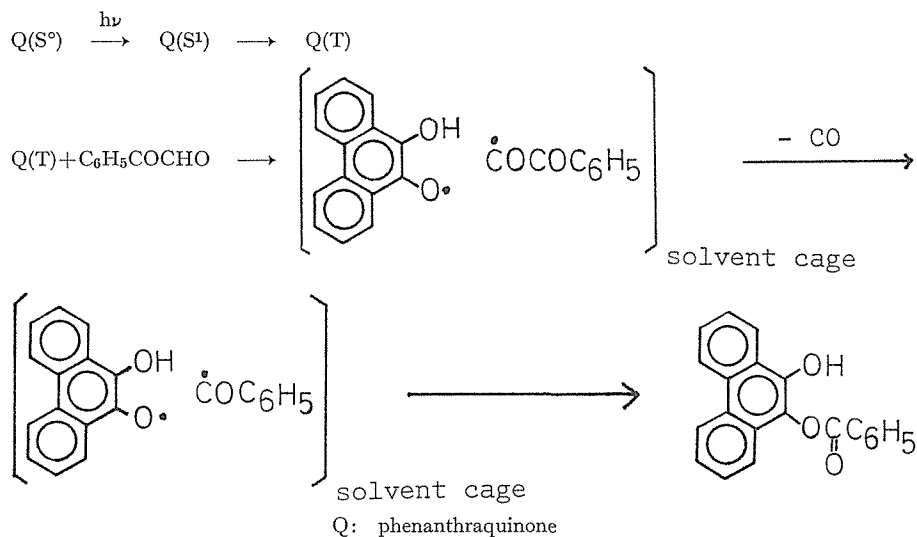
In benzene solution phenanthraquinone and acetaldehyde showed two strongly polarized PMR signals due to methyl protons during the course of irradiation, of which the one (absorption polarized, signal 2 in Fig 1-A-b) corresponds to that of the 1,4-photo-adduct. This can be confirmed by the accumulation of the adduct in the reaction system after a long irradiation. The other (emission polarized, signal 3 in Fig 1-A-b) corresponds to the meta-stable photo-adduct or exciplex, which is not accumulated in the reaction system even after a long irradiation.

On the other hand, in carbon tetrachloride solution of phenanthraquinone and acetaldehyde the extremely strong absorption polarized PMR signal (signal 2 in Fig 1-B-b) and the other negligibly small emission polarized (signal 3 in Fig 1-B-b) could be observed during the course of irradiation. The former corresponds to the stable 1,4-photo-

adduct accumulating in the reaction system, and the latter to the meta-stable photo-adduct which is not accumulated.

Since 1,2-photo-adducts resulted from the reaction of phenanthraquinone with alkyl aromatics decompose more easily in carbon tetrachloride than in benzene to give quinhydrone and the dimer of the alkylaromatic moiety, the results described above may be rationalized by assuming that the meta-stable photo-adduct must have the structure alike to the 1,2-photo-adduct, and this must be rearranged to the 1,4-photo-adduct finally. Thus, it is noticeable that the elemental processes of photochemical reaction are solvent-dependent.

At last, the photochemical reaction of phenanthraquinone with phenylglyoxal remains to be discussed. The reaction gives 9-benzoyloxy-10-hydroxyphenanthrene accompanying the evolution of carbon monoxide. The compound is the same to that resulting from the reaction of phenanthraquinone with benzaldehyde. Since the reaction is fairly clean and the yield of 9-benzoyloxy-10-hydroxyphenanthrene is nearly quantitative, the principal course of the reaction may be represented by the following scheme;



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- (8) The similar phenomena could be observed in the photochemical reaction of phenanthraquinone with propanal or butanal.