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# PHOTOCHEMICAL REACTION OF 9,10-PHENANTHRAQUINONE WITH GLYOXALS[1)]

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A novel type of photochemical reaction between 9,10-phenanthraquinone and glyoxal was discovered and extended to several glyoxals, i,e., methyl-, ethyl-, n-propyl-, i-propyl-, t-butyl-, cyclohexyl-, and phenyl-glyoxals. In these reactions, monoesters of 9,10-dihydroxyphenanthrene could be obtained accompanying with the vigorous evolution of carbon monoxide. The dynamic aspect of these photochemical reactions was investigated using CIDNP technique, and the reverse hydrogen abstraction reaction between two radical species which were resulted from glyoxal and photo-excited 9,10-phenanthraquinone was found to occur.

9,10-Phenanthraquinone and freshly prepared glyoxal dissolved in benzene reacted photochemically to give the monoester of 9,10-dihydroxyphenanthrene accompanying with vigorous evolution of carbon monoxide. The glyoxals examined were methyl-, ethyl-, n-propyl-, i-propyl-, t-butyl-, cyclohexyl-, and phenyl-glyoxal. These monoesters of 9,10-dihydroxyphenanthrene also can be obtained by the photochemical reactions of 9,10-phenanthraquinone with the corresponding aldehydes.[2)] After 10-20 hours irradiation of samples through 5cm thick water layer by 400 W high pressure mercury arc lamp, the yields of these monoesters were 35-50% (after recrystallization, based on the amount of 9,10-phenanthraquinone used). These monoesters, were identified by IR, PMR, and mixed melting point determination with the authentic samples which were obtained by photochemical reaction of 9,10-phenanthraquinone with the corresponding aldehydes. Physical constants of the monoesters are tabulated in Table 1.

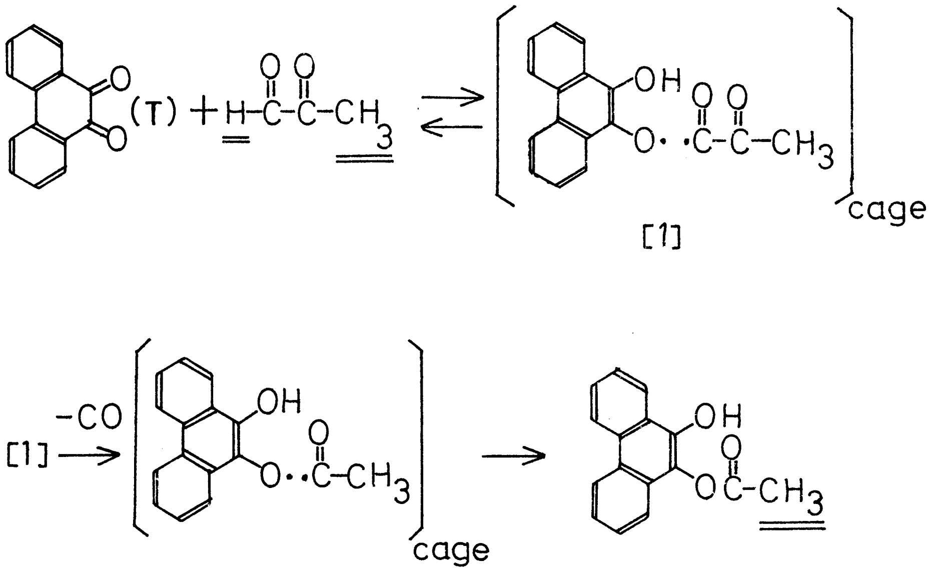
Table 1. Physical Constants of the Monoesters of 9,10-Dihydroxyphenanthrene, $C_{14}H_8(OH)(O\overset{O}{\overset{\|}{C}}-R)$

| R : | melting point*) (°C) | IR. ($cm^{-1}$) | | |
|---|---|---|---|---|
| $CH_3$ | 180~183 | $\nu_{OH}$ : 3450, | $\nu_{CH}$ : 2940, | $\nu_{C=O}$ : 1725 |
| $C_2H_5$ | 157~159 | $\nu_{OH}$ : 3460,<br>(3430) | $\nu_{CH}$ : 2970,<br>(2950) | $\nu_{C=O}$ : 1718 |
| $n-C_3H_7$ | 150~151.5 | $\nu_{OH}$ : 3360, | $\nu_{CH}$ : 2950,<br>(2925) | $\nu_{C=O}$ : 1730 |
| $i-C_3H_7$ | 158.5~159 | $\nu_{OH}$ : 3400, | $\nu_{CH}$ : 2960,<br>(2925) | $\nu_{C=O}$ : 1720 |
| $t-C_4H_9$ | 145~146 | $\nu_{OH}$ : 3425, | $\nu_{CH}$ : 2950, | $\nu_{C=O}$ : 1720 |
| cyclo-$C_6H_{11}$ | 185.5~186.3 | $\nu_{OH}$ : 3400, | $\nu_{CH}$ : 2920,<br>(2850) | $\nu_{C=O}$ : 1722 |
| phenyl | 185~187 | $\nu_{OH}$ : 3460, | $\nu_{C=O}$ : 1720 | |

*) All of these monoesters were white needles.

However, in the reaction of t-butylglyoxal with 9,10-phenanthraquinone t-butylmonoether was another major product (yield : ca 12%); monoether : mp 102.7~103.2°C, $\nu_{OH}$ : 3300, $\nu_{\phi H}$ : 3050, $\nu_{CH}$ : 2960, mass analysis : $M^+$= 266.

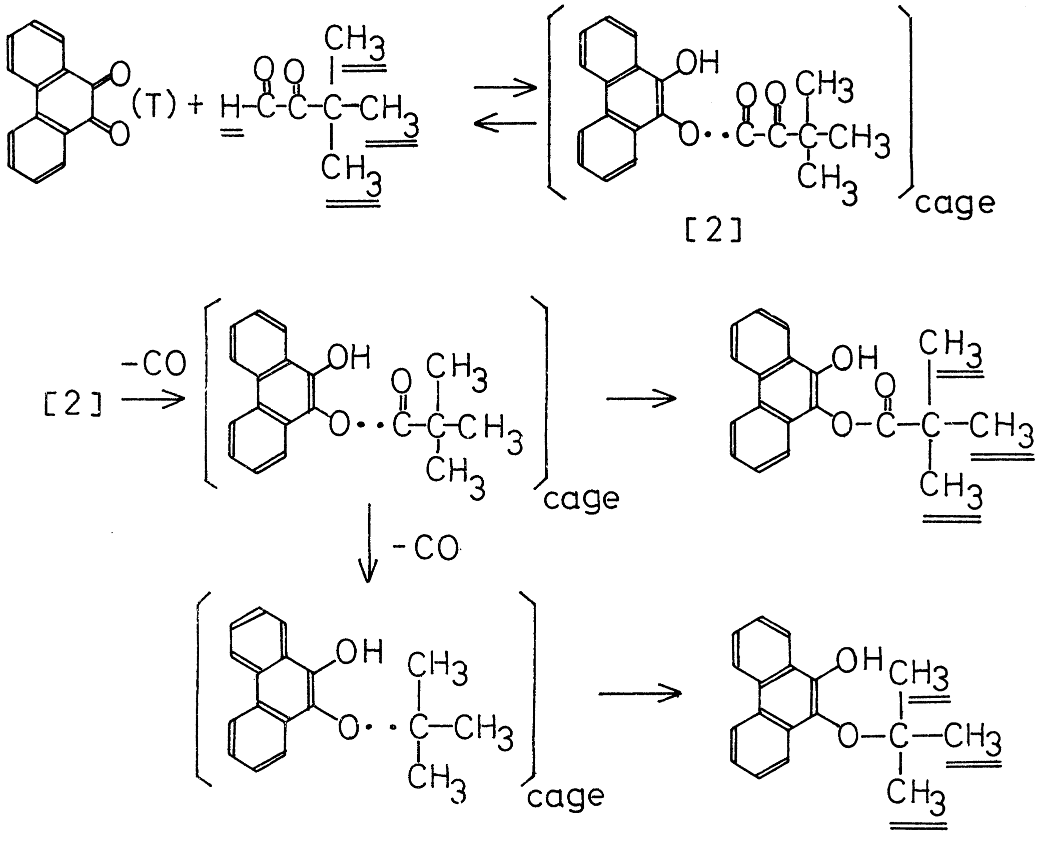
The photochemical reactions described above were examined by CIDNP technique using 60 MHz PMR spectrometer equipped with a modified probe for photo-irradiation. As Fig. 1 shows, during the course of irradiation the strong polarized PMR signals due to alkyl protons and/or aromatic ring protons of the monoester produced can be



The under-lined protons show the strongly polarized PMR signal.

[ Scheme 1 ]

observed. Surprisingly, in addition to the polarized PMR signals due to protons of reaction product, formyl proton and alkyl protons of glyoxal itself also show strongly polarized PMR signals during the course of irradiation; that is, formyl proton shows emission polarized signal and methyl protons show absorption polarized one. This is an obvious evidence of the reproduction of glyoxal through the corresponding radical precursor, and is the first example which showed unambiguously the co-occurrence of hydrogen abstraction reaction and the reverse reaction.3) Although the usual pattern of the photochemical reaction between 9,10-phenanthraquinone and glyoxal can be summarized in Scheme 1, the reaction of t-butylglyoxal indicates the other aspect of the photochemical reaction. That is; in some parts the other one mole of carbon monoxide can be liberated during the course of the reaction to result monoether of 9,10-dihydroxyphenanthrene. Thus, we can recognize the corresponding polarized PMR signal of monoether. Such a reaction can be summarized in Scheme 2.



The under-lined protons show the strongly polarized PMR signal.

[ Scheme 2 ]

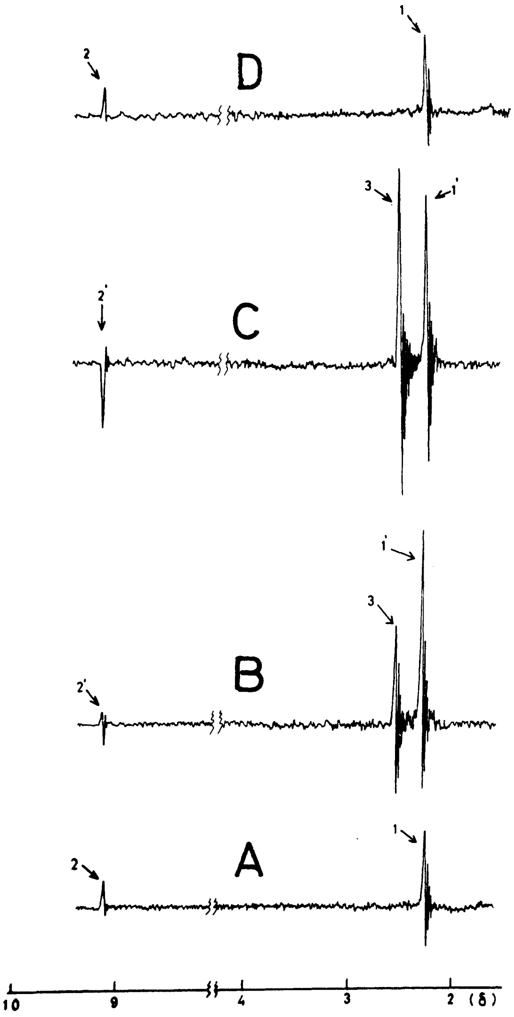


Fig. 1 PMR signals observed in the photochemical reaction of phenanthraquinone and methylglyoxal(MG)

A: before irradiation. Signal 1; methyl proton of MG. signal 2; formyl proton of MG.

B: during irradiation. Signal 1; methyl protons of MG(absorption polarized). signal 3; methyl protons of the monoester of 9,10-dihydroxyphenanthrene(absorption polarized). Signal 2; formyl proton of MG(emission polarized).

C: during irradiation, but observed in a later run of field sweep.

D: after irradiation.

In all the photochemical reactions described above, benzene was used as a solvent, but in the examination of the reaction by CIDNP technique carbon tetrachloride was a suitable solvent. The preliminary examination of the quantum yield in the photochemical reaction of phenanthraquinone with glyoxals is inclined to show the value of order of $10^{-1}$.

## REFERENCES

1) Photochemical Reaction of Quinones. XII.

2) K. Maruyama, A. Takuwa, T. Otsuki, and S. Kako, Bull. Inst, Chem. Res., Kyoto Univ., 50, No 4. 348(1972).

3) Irradiation of methylglyoxal dissolved in carbon tetrachloride does not show any polarized PMR signal. There may be another possibility to give the polarized PMR signal than the described in Scheme 1. That is; methylglyoxalyl radical ($CH_3$-CO-$\dot{C}$O) slipped out of solvent cage could abstract hydrogen from the other glyoxal molecule and might show the polarized PMR signal. However, this reaction does not occur through radical pair, and then if any, in this case we can't expect such strongly polarized PMR signals as those were observed.

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