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The Addition Reaction of Acyl Radicals to 9,10-Phenanthrenequinone in the Presence of the Corresponding Aldehydes. A Support for the In-Cage Mechanism of the Photochemical Reaction of 9,10-Phenanthrenequinone with Aldehydes

Kazuhiro MARUYAMA, Hiroshi SAKURAI, and Tetsuo OTSUKI
Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606

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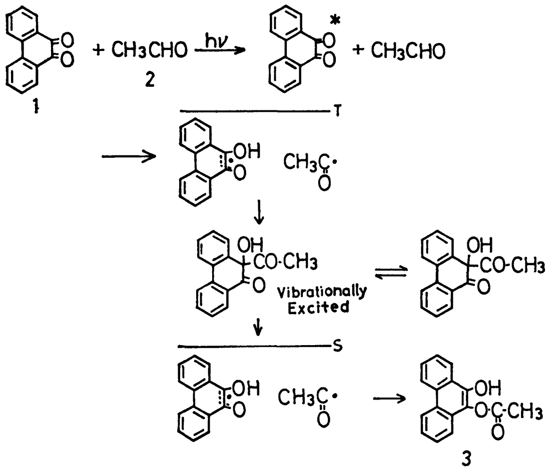
Regarding the photochemical reaction of 9,10-phenanthrenequinone, **1**, with acetaldehyde, **2**, two reaction mechanisms have been proposed: the in-cage mechanism (Eq. 1) and the radical chain mechanism involving an acyl radical as the chain carrier (Eq. 2). For the establishment of the true reaction mechanism, the thermal addition reaction of an acyl radical to 9,10-phenanthrenequinone was investigated. The products in the thermal reaction were the dimeric isomers of the aryloxyl radical, **6**, *i.e.*, **4** and **5**, which were quite different from the product of the photochemical reaction of 9,10-phenanthrenequinone with acetaldehyde, *i.e.*, 9-acetoxy-10-hydroxyphenanthrene, **3**. These results, as well as the estimation of the quantum efficiency for the photochemical reaction, exclude the radical chain mechanism (Eq. 2) and strongly support the in-cage mechanism (Eq. 1) for the photochemical reaction of 9,10-phenanthrenequinone with aldehyde.

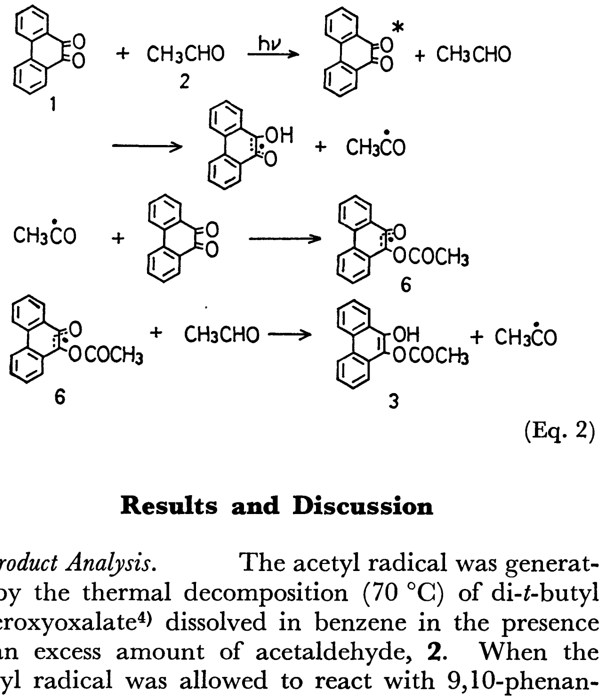
The photochemical reactions of quinone have been of great practical significance, providing a method of synthesizing complex organic molecules.[1] The mechanistic elucidation of these reactions are essential to ensure further success in preparative organic photochemistry.

The irradiation of a benzene solution of 9,10-phenanthrenequinone, **1**, and acetaldehyde, **2**, for example, gives 9-acetoxy-10-hydroxyphenanthrene, **3**, in a quantitative yield. The other aldehydes, aliphatic and aromatic, behave similarly to give the corresponding 9-acyloxy-10-hydroxyphenanthrenes in good yields. Recently for the above reaction the present authors proposed the intervening contribution of a radical pair, *i.e.*, the in-cage mechanism, mainly on the basis of an investigation using the ^{1}H-CIDNP technique (Eq. 1).[2] In contrast, Moore and Waters suggested about twenty years ago a radical-chain mechanism involving the acetyl radical as a chain carrier (Eq. 2)[3]

In the present investigation the acetyl radical generated from the hydrogen abstraction of acetaldehyde by the *t*-butoxyl radical was allowed to react with 9,10-phenanthrenequinone, **1**, and the products were compared with those of the photochemical reaction of 9,10-phenanthrenequinone, **1**, with acetaldehyde, **2**.



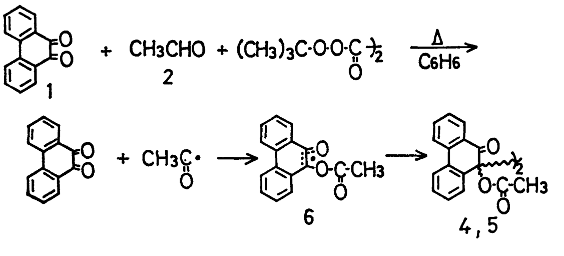
(Eq. 1)



(Eq. 2)

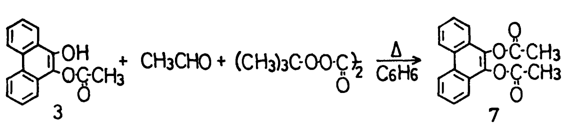
Results and Discussion

Product Analysis. The acetyl radical was generated by the thermal decomposition (70 °C) of di-*t*-butyl diperoxyoxalate[4] dissolved in benzene in the presence of an excess amount of acetaldehyde, **2**. When the acetyl radical was allowed to react with 9,10-phenanthrenequinone, **1**, the yellow color due to **1** disappeared. After the evaporation of the solvent, column chromatography on silica gel gave two white crystals in nearly equal amounts (total yield: 90%). Their molecular weights, as determined by the vapor-pressure method, indicated that both of them are dimers of the aryloxy radical, **6**. The aryloxy radical, **6**, is to be yielded by the addition of an acetyl radical to 9,10-phenan-



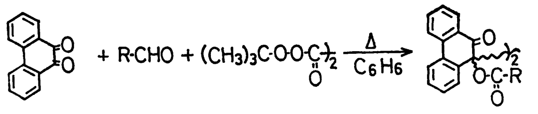
(Eq. 3)

threnequinone. On the basis of their mass analysis and spectral data, the two products were concluded to be configurational isomers with each other and were identified as **4** ("*dl*-form") and **5** ("*meso*-form") respectively[5] (see Eq. 3). The other products were quite small in their amounts, but different from 9-acetoxy-10-hydroxyphenanthrene, **3**, which was the sole product in the photolysis of a solution of **1** and **2**.[2] Further, the possible formation of **4** and **5** *via* **3** was examined by treating **3** with di-*t*-butyl diperoxyoxalate in the presence of acetaldehyde, but no **4** or **5** was found. The exclusive product in this reaction was 9,10-diacetoxyphenanthrene, **7** (Eq. 4). Thus, we can exclude the intermediacy of **3** in the formation of **4** and **5**. As will be described in the following section, the time-dependent parallelism of the amount of **4** relative to **5** also supports the above consideration. In the reaction with other acyl radicals 9,10-phenanthrenequinone gives dimeric mixtures analogous to that of **4** and **5**. The total yields of the isomeric dimers are summerized in Table 1.



(Eq. 4)

TABLE 1. THE THERMAL REACTION OF 9,10-PHENANTHRENEQUINONE WITH THE ACYL RADICAL



R	Yields of dimers (%)
CH_3-	90
C_3H_7-	83
p-CH_3-C_6H_4-	88
p-CH_3O-C_6H_4-	66

The Yield of 4 Relative to that of 5 versus *the Reaction Time.* With the progress of the reaction the amount of **4** relative to **5** was followed; the amounts of **4** and **5** increased monotonously with the time. As was concluded from Fig. 1, the relative yield, **4**/**5**, was invariably constant throughout the reaction. Thus, both **4** and **5** must be primary products in the reaction; hence, **3** cannot be a precursor of **4** and **5**.

Concluding Remarks. Without doubt the acetyl radical adds to 9,10-phenanthrenequinone, **1**, to form the **6** radical in the primary step of the reaction. Subsequently, the **6** radical could undergo dimerization, resulting in the formation of **4** and **5** in nearly comparable amounts. Thus, the *free* acetyl radical adds to **1** even in the presence of a large excess of acetaldehyde, as summarized in Eq. 3.

Contrary to the present reaction, the photochemical reaction of 9,10-phenanthrenequinone, **1**, with acetaldehyde gives **3** in a quantitative yield without **4** or **5**. Therefore, in the photochemical reaction of 9,10-phenanthrenequinone with acetaldehyde the intervention of the *free* acetyl radical, and thus the intermediacy of the aryloxyl radical, **6**, can be excluded completely. That is, the photochemical reaction of 9,10-phenanthrenequinone with acetaldehyde may proceed *via* the in-cage radical pair, *i.e.*, the in-cage mechanism, resulting in the quantitative formation of **3** (Eq. 1). The exclusion of the radical-chain mechanism (Eq. 2) was further supported by the disappearance of 9,10-phenanthrenequinone in the presence of a 10-fold molar quantity of acetaldehyde. Its quantum efficiency was about 0.21.

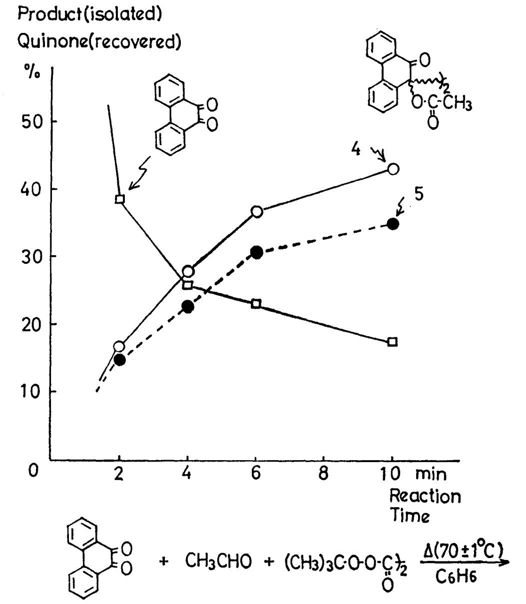


Fig. 1. The effect of the reaction time.

Experimental

Materials. The 9,10-phenanthrenequinone was prepared by the oxidation of phenanthrene with potassium dichromate; mp 202—204 °C. The di-*t*-butyl diperoxyoxalate was prepared according to the method in the literature.[4] All the aldehydes examined here were commercially available and were submitted to the thermal reactions after purification by distillation.

General Procedures. 9,10-Phenanthrenequinone (7.2 mmol) and aldehyde (26.8 mmol) were dissolved in dry benzene (30 ml), while the temperature of the solution was kept at 70 °C. To the solution di-*t*-butyl diperoxyoxalate (10.2 mmol) was added in portions. After an appropriate reaction time, the reaction was quenched by cooling and the reaction mixture was purified by chromatography on silica gel.

Identification of Products. *9,9′-Diacetoxy-9,9′,10,10′-tetrahydro[9,9′-biphenanthrene]-10,10′-dione*: yield, 90%. dl-*9,9′-Diacetoxy-9,9′,10,10′-tetrahydro[9.9′-biphenanthrene]-10,10′-dione (4)*: white crystals; mp 200.2—201.2 °C. Found; C, 76.76; H, 4.21%. Calcd for $C_{32}H_{22}O_6$; C, 76.48; H, 4.41%. Molecular weight (vapor-pressure method); $m/e=502$ (Calcd for $C_{32}H_{22}O_6$; $m/e=502$). Mass; $m/e=251$ (monomer$^+$), 209, 207, 180, 179. IR (KBr); 1750, 1690 cm^{-1}. ^{1}H-NMR ($CDCl_3$); δ: 1.55 (6H,s), 6.40 (2H,d,$J=8$Hz), 6.9—8.0 ppm (14H,m). UV max ($CHCl_3$); 339 nm (log ε: 3.68), 252 (4.64), 216 (4.57).

meso-*9,9′-Diacetoxy-9,9′,10,10′-tetrahydro[9,9′-biphenanthrene]-10,10′-dione (5)*: white crystals; mp 216—217 °C. Molecular weight (vapor-pressure method); $m/e=553$ (Calcd for $C_{32}H_{22}O_6$; $m/e=502$), Mass; $m/e=251$ (monomer$^+$), 209, 207, 180, 179. IR (KBr); 1770, 1690 cm^{-1}. ^{1}H-NMR ($CDCl_3$); δ: 2.10 (6H,s), 7.0—7.9 ppm (16H,m). UV max ($CHCl_3$); 339 nm (log ε: 3.56), 227 (4.47), 216 (4.58).

9′9′-Bis(butyryloxy)-9,9′,10,10′-tetrahydro[9,9′-biphenanthrene]-10,10′-dione: yield, 83%.

dl-*9,9′-Bis(butyryloxy)-9,9′,10,10′-tetrahydro[9,9′-biphenanthrene]-10,10′-dione*: white crystals; mp 190—191 °C. Mass; $m/e=279$ (monomer$^+$). IR (KBr); 1750, 1695 cm^{-1}. ^{1}H-NMR ($CDCl_3$); δ: 0.70 (6H,t,$J=6$ Hz), 1.32 (4H, sextet, $J=6$ Hz), 1.84 (4H,t,$J=6$ Hz), 6.44 (2H,d,$J=8$ Hz), 7.0—8.1 ppm (14H, m). UV max (CH_2Cl_2); 337, 256, 248 (sh)nm.

meso-*9,9′-Bis(butyryloxy)-9,9′,10,10′-tetrahydro[9,9′-biphenanthrene]-10,10′-dione*: white crystals; mp 176—177 °C. Mass; $m/e=279$ (monomer$^+$). IR (KBr); 1750, 1695 cm^{-1}. ^{1}H-NMR ($CDCl_3$); δ: 0.92 (6H,t, $J=6$ Hz), 1.56 (4H, sextet, $J=6$ Hz), 2.30 (4H), 2.30 (4H, t, $J=6$ Hz), 6.8—7.8 ppm (16H,m). UV max (CH_2Cl_2): 337, 255 (sh), 248 nm.

*9,9′-Bis(*p*-toluoyloxy)-9,9′,10,10′-tetrahydro[9,9′-biphenanthrene]-10,10′-dione*: yield, 88%; white crystals, mp 195 °C (dec) as a mixture of nearly equal amounts of two isomers. Mass; $m/e=327$ (monomer$^+$). IR (KBr); 1740, 1690 cm^{-1}. ^{1}H-NMR ($CDCl_3$); δ: 2.35 (s,CH_3(*dl*-form)), 2.42 (s, CH_3 (*meso*-form)), 6.42 (d, $J=8$ Hz, aromatic-H (*dl*-form)), 6.8—8.2 ppm (m). UV max (CH_2Cl_2); 338, 248 nm.

*9,9′-Bis(*p*-arisoyloxy)-9,9′,10,10′-tetrahydro[9,9′-biphenanthrene]-10,10′-dione*: yield, 66%; white crystals; mp 151—161 °C as a mixture of nearly equal amounts of isomers. Mass; $m/e=343$ (monomer$^+$). IR (KBr); 1720, 1690 cm^{-1}. ^{1}H-NMR ($CDCl_3$); δ: 2.34 (s, OCH_3(*dl*-form)), 2.40 (s, OCH_3-(*meso*-form)), 6.64 (s, $J=8$ Hz, aromatic-H(*dl*-form)), 6.8—8.1 (m, aromatic-H(*dl*-form)), 7.0—8.0 ppm (m, aromatic-H (*meso*-form)). UV max (CH_2Cl_2); 337, 255 nm.

9,10-Diacetoxyphenanthrene (**7**): white crystals; mp 196.0—197.5 °C. Mass; $m/e=294$ (M^+). IR (KBr); 1780 cm^{-1}. ^{1}H-NMR($CDCl_3$); δ: 2.52 (6H,s), 7.7—8.0 (6H,m), 8.6—8.8 ppm (2H,m). UV max (CH_2Cl_2); 295, 285, 275, 255, 245 nm. 9,10-Diacetoxyphenanthrene was also yielded by the reductive acetylation (Zn–Acetic anhydride) of 9,10-phenanthrenequinone.

The Estimation of the Quantum Efficiency. The light sourse was a high-pressure Hg arc lamp (300W); by the use of a filter (Toshiba KL-50), the irradiation was carried out by selected light (wavelength: 498±8 nm) at 15.0±0.5 °C. The quanta of light absorbed by the reaction mixture was calibrated using an aqueous solution of potassium tris(oxalo)ferrate-(III) as a chemical actinometer.$^{7)}$ The reaction mixture submitted to the measurement was a benzene solution of 1.92×10^{-3} M of 9,10-phenanthrenequinone and 2.3×10^{-2} M of acetaldehyde. The quantum efficiency, followed by the disappearance of 9,10-phenanthrenequinone, was estimated to be 0.21.

References

1) J. M. Bruce, "The Chemistry of Quinonoid Compounds," ed by S. Patai, John Wiley & Sons, London (1974), p. 465.

2) a) K. Maruyama, A. Takuwa, T. Otsuki, and S. Kako, *Bull. Inst. Chem. Res., Kyoto Univ.*, **50**, 348 (1972; b) K. Maruyama, T. Otsuki, and Y. Naruta, *Bull. Chem. Soc. Jpn.*, **49**, 791 (1976).

3) R. F. Moore and W. A. Water, *J. Chem. Soc.*, **1953**, 238.

4) P. D. Bartlett, E. P. Benzing, and R. E. Pincok, *J. Am. Chem. Soc.*, **82**, 1762 (1960).

5) By inspecting their ^{1}H-NMR spectra and their molecular models, we assigned the stereochemistry of the two isomers to those described in the text on the basis of the fact that the acetyl and the aromatic ring protons in the "*dl*-form," **4**, would be more largely shielded by the anisotropy effect attributable to the carbonyl group and the aromatic rings than those in the "*meso*-form," **5**.

6) The estimated value of the quantum efficiency was far below unity; this suggests that the photolysis did not proceed by the chain mechanism. Moreover, the value is reasonable compared with those observed in the photochemical reaction of quinones with aldehydes. *Cf.* K. Maruyama and Y. Miyagi, *Bull. Chem. Soc. Jpn.*, **47**, 1303 (1974).

7) C. A. Parker, *Proc. R. Soc. London, Ser. A*, **220**, 104 (1952); D. A. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).