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Photolysis of 2,2-Diethoxy-2,3-dihydrophenalene-1,3-dione

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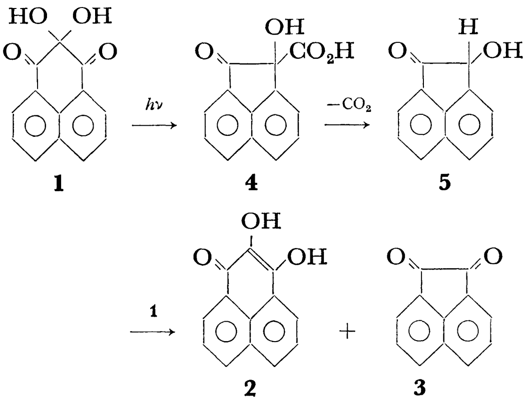
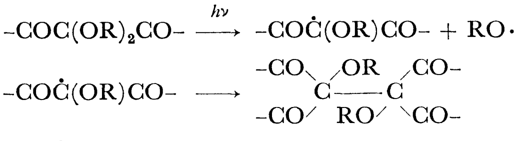
Irradiation of 2,2-diethoxy-2,3-dihydrophenalene-1,3-dione (**6**) with a pyrex-filtered high-pressure Hg arc lamp afforded acetaldehyde, 2-ethoxy-3-hydroxyphenalene-1-one (**7**) and bis-2-(2-ethoxy-1,3-dioxo-2,3-dihydro) phenalenyl (**8**). Mechanistic studies revealed that the first step of this photoreaction was a homolytic fission of the C–OC$_2$H$_5$ bond to 2-(2-ethoxy-1,3-dioxo-2,3-dihydro)phenalenyl radical (**9**) and ethoxyl radical. This homolytic fission occurred mostly from the triplet and in part from the singlet excited state of **6**. Dimerization of **9** gave **8** and the disproportionation between **9** and ethoxyl radical gave acetaldehyde and **7**. The photochemical behaviors of a variety of triketone derivatives were discussed.

In a separate paper,[1] we have reported that 2,2-dihydroxy-2,3-dihydrophenalene-1,3-dione (**1**) undergoes the redox disproportionation with elimination of CO$_2$ to 2,3-dihydroxyphenalene-1-one (**2**) and acenaphthene-1,2-dione (**3**) upon irradiation in organic solvents. A key step of this reaction was a rearrangement of **1** to 2-carboxy-2-hydroxyacenaphthene-1-one (**4**) from the singlet excited state of **1** (see Scheme 1).



Scheme 1

However, we have previously presented evidence supporting that 2,2-dihydroxy- or 2,2-dialkoxy-1,3-diketones such as alloxan monohydrate,[2] ninhydrin[2] or 5,5-dialkoxybarbituric acids[3] undergo the photoreaction involving an α-cleavage as illustrated in Scheme 2.



$$\text{-COC(OR)}_2\text{CO-} \xrightarrow{h\nu} \text{-CO}\dot{\text{C}}\text{(OR)CO-} + \text{RO}\cdot$$

$$\text{-CO}\dot{\text{C}}\text{(OR)CO-} \longrightarrow \begin{matrix} \text{-CO} & & \text{OR} & \text{CO-} \\ & \text{C} & \text{——} & \text{C} \\ \text{-CO} & & \text{RO} & \text{CO-} \end{matrix}$$

$$\text{-CO}\dot{\text{C}}\text{(OR)CO-} \longrightarrow \text{-COCOCO-} + \text{R}\cdot$$

where R represents H or alkyl.

Scheme 2.

These diverse photochemical behaviors of triketone derivatives prompted us to study the photochemistry of 2,2-diethoxy-2,3-dihydrophenalene-1,3-dione (**6**). The specific effect such as an intramolecular hydrogen bonding, which is present between the hydroxyl and carbonyl groups of **1**, is absent in **6**. We observed that **6** undergoes the α-cleavage reaction upon irradiation, but the radical produced behaves differently from those represented in Scheme 2. In this paper, the results so far obtained are summarized and the mechanism of the photoreaction is discussed.

Results

Products. A Pyrex-filtered irradiation of a solution of **6** in benzene with a high-pressure Hg arc lamp under nitrogen at room temperature afforded acetaldehyde, 2-ethoxy-3-hydroxyphenalene-1-one (**7**) and bis-2-(2-ethoxy-1,3-dioxo-2,3-dihydro)phenalenyl (**8**). Acetaldehyde, which distilled out upon passing nitrogen into the reaction mixture, was identified as its 2,4-dinitrophenylhydrazone. The dimer **8** deposited on the bottom of the reaction vessel and it was easily separated from other products by filtration. The unreacted starting material and **7** were satisfactorily separated by a column-chromatography on silica gel.

The structure of **7** was confirmed by the analytical and spectral data. The NMR spectrum (CDCl$_3$) showed a triplet (J=7.5 Hz, 3H) at 1.40 ppm (–CH$_2$-CH_3), a quartet (J=7.5 Hz, 2H) at 4.42 ppm (–CH_2-CH$_3$), a broad singlet (1H) at 6.96 ppm (–OH), and the multiplet signal (6H) due to the aromatic protons from 7.28 to 8.47 ppm. The IR spectrum (KBr) exhibited a band at 3520 cm^{-1} due to the hydroxyl group and at 1630 cm^{-1} attributable to the carbonyl group. The mass spectrum displayed prominent peaks at m/e 240 (M$^+$), 212 (M$^+$—CO), and 196 (M$^+$—CH$_3$–CHO).

In support of the structure assignment of **8**, we observed the molecular weight to be 474 (calcd 478) by the Rast method. The IR spectrum (KBr) indicated a band at 1679 cm^{-1} due to the carbonyl group. The analytical data showed the molecular formula to be C$_{30}$H$_{22}$O$_6$.

The same sort of the products was also obtained when irradiation was carried out in acetonitrile and 2-propanol. The isolated yields are shown in Table 1. A ratio of the yield of the dimer **8** to that of **7** was higher in the non-polar solvent, benzene, than in the polar solvents such as acetonitrile and 2-propanol.

Quantum Yields for the Formation of **7**. The photolysis of **6** was conducted in three solvents in a 1 cm optical cell under anaerobic conditions by irradiation of 313 nm light. As the reaction proceeded, an absorption of 320 nm band due to **6** decayed with

TABLE 1. PHOTOLYSES OF **6**

Solvent	Recovered starting material %	Yields of products %[a)]	
		7	**8**
C_6H_6[b)]	36	21	14
CH_3CN[b)]	28	61	1.5
2-PrOH[c)]	20	66	5.0

a) The yields are based on the total amount of the starting material initially used.

b) A solution of 200 mg of **6** in 50 ml of the solvent in a quartz vessel was irradiated for 48 hr externally from the outside of the reaction vessel.

c) A solution of 200 mg of **6** in 200 ml of the solvent was irradiated for 6 hr employing an immersion-type apparatus.

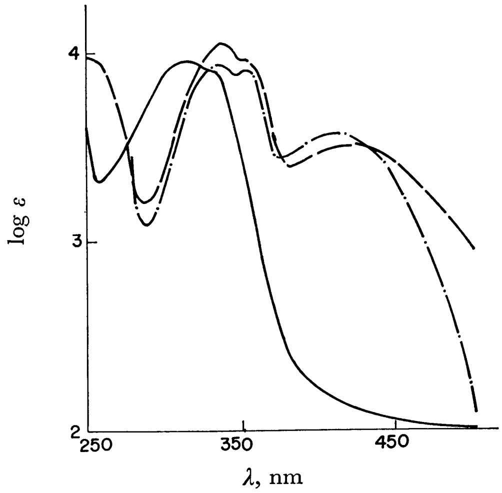


Fig. 1. Absorption spectra of 2,2-diethoxy-2,3-dihydrophenalene-1,3-dione (**6**) and 2-ethoxy-3-hydroxyphenalen-1,-one (**7**)
——, **6** in 2-PrOH; ——, **7** in 2-PrOH; —•—, **7** in C_6H_6 and CH_3CN. The stectra of **6** in C_6H_6 and CH_3CN were almost identical with that in 2-PrOH.

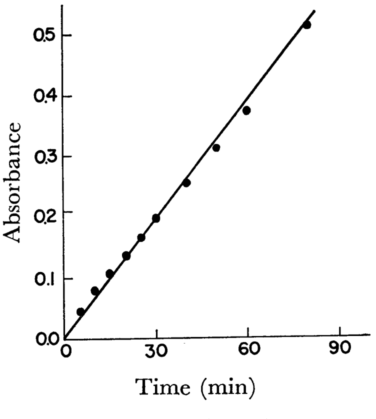


Fig. 2. Rate of appearance of the absorbance of 2-ethoxy-3-hydroxyphenalene-1-one (**7**) at 413 nm upon irradiation of 2,2-diethoxy-2,3-dihydrophenalene-1,3-dione (**6**) in C_6H_6.

appearance of 410—425 nm band due to **7** as shown in Fig. 1. The rates of the formation of **7** were followed by monitoring an appearance of the absorptions at 413 nm in benzene, at 410 nm in acetonitrile, and at 425 nm in 2-propanol. The amounts of **7** formed linearly increased with irradiation time in all solvents until more than 50% of **6** was consumed. In a typical example, the result of the photolysis of **2** in benzene is shown in Fig. 2. The rate data were then converted into the quantum yields by use of the ferric oxalate actinometer. The quantum yields obtained are summarized in Table 2.

TABLE 2. QUANTUM YIELDS FOR THE FORMATION OF **7** UPON IRRADIATION BY 313 nm LIGHT

Concn. of **6**, M	Solvent	Φ
1.01×10^{-3}	C_6H_6	0.040
1.04×10^{-4}	CH_3CN	0.035
1.00×10^{-3}	CH_3CN	0.046
9.97×10^{-3}	CH_3CN	0.059
1.00×10^{-3}	$2\text{-}C_3H_7OH$	0.043

The results of Table 2 indicate that the quantum yield for the formation of **7** is not so much affected by the concentration of **6** present and not at all by the nature of solvents used.

Stern-Volmer Plots. In order to gain information on the nature of the excited state involved, quenching experiments were carried out. A 1.00×10^{-3} M solution of **6** in benzene was irradiated in the presence of various concentrations (0—0.01 M) of cyclohexadiene, a triplet quencher, and the quantum yield for the formation of **7** was measured as described above. In Fig. 3, the reciprocals of the quantum yields were plotted against the concentrations of cyclohexadiene added (Stern-Volmer plot). From Fig. 3, it can be seen that the quantum yield for the formation of **7** is reduced strongly by the presence of lower concentrations of cyclohexadiene, but weakly by the presence of higher concentrations of cyclohexadiene. This phenomenon suggests that **7** is formed mostly from a triplet

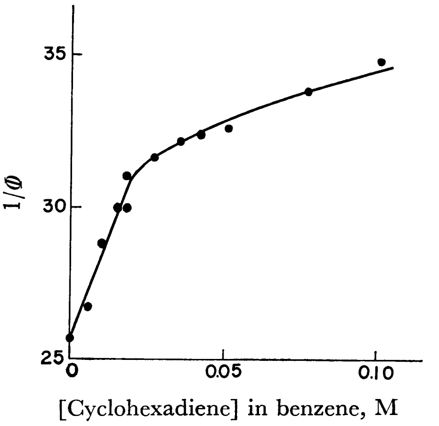
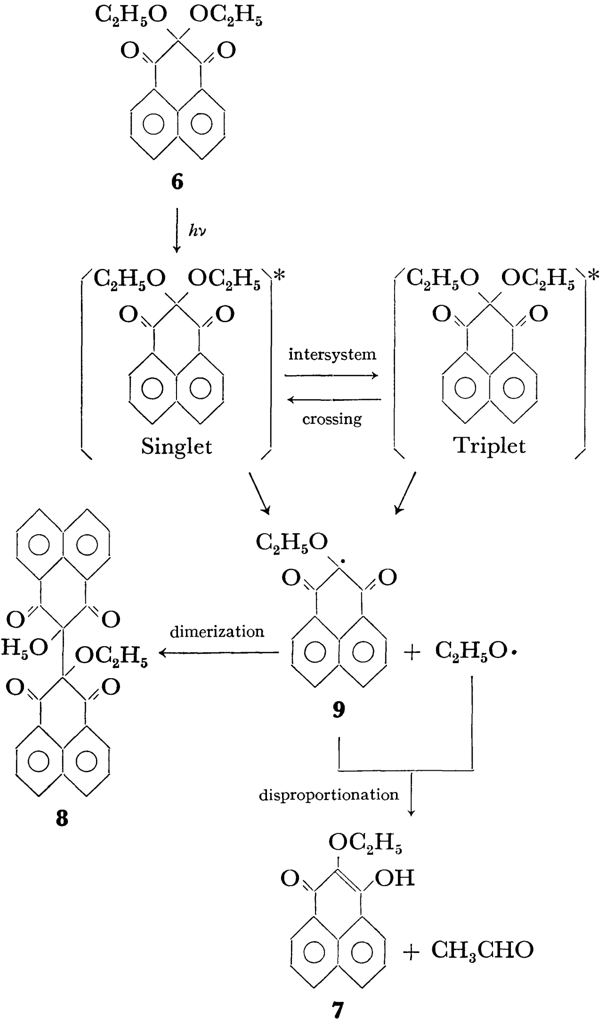


Fig. 3. Stern-Volmer plot for the formation of 2-ethoxy-3-hydroxyphenalene-1-one (**7**) by irradiation of 2,2-diethoxy-2,3-dihydrophenalene-1,3-dione (**6**) in C_6H_6.

excited state and in part from a singlet excited state of **6**.[4)]

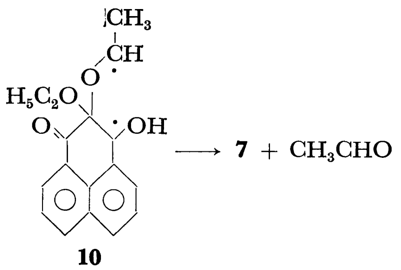
Discussion

A plausible mechanism which explains the results presented earlier is given in Scheme 3. The first step of the photoreaction is a homolytic cleavage of the C–OC_2H_5 bond in **6** to form the radical **9** and the ethoxyl radical. This cleavage reaction occurs mostly from a triplet excited state of **6** and in part from its singlet excited state. The radical **9** dimerizes to form the dimer **8**. On the other hand, the disproportionation between **9** and the ethoxyl radical gives **7** and acetaldehyde. The dimerization reaction is favored in non-polar solvent such as benzene, while the disproportionation reaction is favored in polar solvents such as acetonitrile and 2-propanol. The solvent effect of this sort in radical reactions has frequently been observed.[5)]



Scheme 3

The formation of **7** and acetaldehyde may also be explained by the other mechanism involving the 1,4-biradical intermediate **10** which can be formed *via* a γ-hydrogen abstraction by the excited carbonyl of **6**; a decomposition of **10** would lead to **7** and acetaldehyde. However, this possibility can be eliminated from the fact that the quantum yield for the formation of **7** was actually independent on the polarity of solvents used as shown in Table 2. If the biradical **10** participates as an intermediate of the photoreaction, then the quantum yield should become higher in the solvents of higher polarity, since the intermediate would be stabilized in polar solvents.[6)] However, this was not the case.



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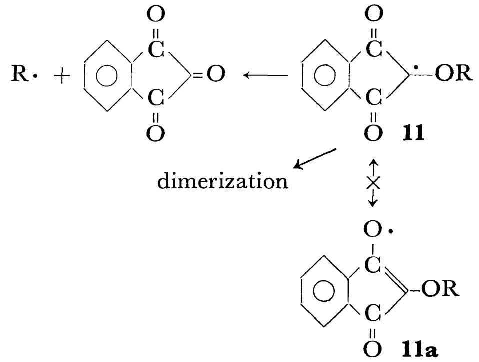
Unfortunately, the systematic understanding on the diversity of the photochemical behaviors of triketone derivatives is not attained at present. However, it would be important to note that the ionic-type reaction of **1** takes place from its singlet excited state,[1)] while the α-cleavage reaction of a radical-type as observed in **6** occurs mainly from a triplet excited state of the carbonyl group. An intramolecular hydrogen bonding between the hydroxyl and carbonyl groups of **1**, which was inferred from a broad hydroxyl band centered at 3200 cm^{-1} in the IR spectrum, may contribute at least in part to an exclusive formation of the singlet excited state.

A difference in the reactivity between the 1,3-dioxoradical generated from **6** and that from ninhydrin might be explained in terms of the stability of the radicals. The radical **9** generated from **6** can be stabilized by a conjugation with the vicinal carbonyl groups. In contrast, the radical **11** generated from ninhydrin would gain destabilization rather than stabilization by a conjugation with the vicinal carbonyl groups, since the structure of the type **11a** is of an anti-aromatic character.[7)]



An odd electron in the radical **11** thus become fixed to a greater extent at the 2-position, and hence the radical is forced to undergo dimerization or cleavage reaction to indanetrione and the radical R·. On the other hand, the resonance-stabilized radical **9** undergoes dimerization or disproportionation if other radicals are present in the reaction mixture.

Experimental

All melting points are uncorrected. Electronic absorption spectra were recorded with a Hitachi EPS-3T recording spectrophotometer or a Hitachi Perkin-Elmer 139 spectrophotometer. IR spectra were obtained with a Hitachi 215 infrared spectrophotometer. NMR spectra were obtained on a Hitachi H-60 high resolution NMR spectrometer with tetramethylsilane as an internal standard. Microanalyses were performed with a Hitachi 026 CHN analyzer. Irradiations were carried out with a 100 W Ushio UM-102 high-pressure Hg arc lamp equipped with a Pyrex water-cooling jacket.

Materials. 2,2-Diethoxy-2,3-dihydrophenalene-1,3-dione (**6**) was prepared by the method of Regitz and Adolph[8] and purified by recrystallization from ethanol; mp 137—138 °C (lit,[8] mp 138—139 °C). Cyclohexadiene was prepared by the method of Blomquist and Kwiatek[9] and purified by distillation; bp 79—81 °C (lit,[9] bp 79—81 °C).

*Photoreaction of **6**.* *(a) In Benzene*: A solution of 200 mg (0.704 mmol) of **6** in 50 ml of benzene was placed in a cylindrical quartz vessel. An outlet of the vessel was connected with a vinyl tubing to a flask containing a solution of 2,4-dinitrophenylhydrazine in an aqueous HCl. Nitrogen was introduced into the reactant solution for 30 min and then irradiation was carried out externally from the outside of the vessel at room temperature under bubbling nitrogen in the solution. After irradiation for 8 hr, nitrogen-bubbling was stopped and the outlet of the reaction vessel was sealed with a glass stopper. During this period, red precipitates appeared in the flask containing 2,4-dinitrophenylhydrazine. The precipitates, 20 mg, were separated by filtration. They melted at 146—147 °C and were identical with the authentic sample of 2,4-dinitrophenylhydrazone of acetaldehyde in every respect.

On the other hand, when the irradiation was continued for 48 hr, brown crystals appeared on the bottom of the reaction vessel. They were removed by filtration, and washed thoroughly with dioxane and then with chloroform. The crystals thus obtained were found to be 47 mg (14%) of **8**: mp 236—237 °C (decomp.). Found: C, 75.29; H, 4.65%. Calcd for $C_{30}H_{22}O_6$: C, 75.30; H, 4.63%.

Evaporation of the solvent from the filtrate, which was obtained after removal of **8**, under reduced pressure gave a brown oil. The oil was dissolved in benzene–chloroform (1: 1) and chromatographed on a silica gel column using the same solvent as an eluent. Evaporation of the first eluent gave 73 mg (36%) of the unreacted starting material as light yellow crystals of mp 134—137 °C, which melted at 138—139 °C after recrystallization from ethanol.

Further elution with benzene–chloroform and evaporation of the eluent gave 35 mg (21%) of **7**. Recrystallization from methanol gave orange crystals: mp 125—126 °C. Found: C, 75.05; H, 4.94%. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03%.

(b) In Acetonitrile: A solution 200 mg (0.704 mmol) of **6** in 50 ml of acetonitrile was irradiated for 48 hr as described above. After irradiation, the reaction mixture was worked up in the manner similar to that described above. From the reaction mixture, 5 mg (1.5%) of **8**, 56 mg (28%) of the unreacted starting material and 103 mg (61%) of **7** were obtained. 2,4-Dinitrophenylhydrazone of acetaldehyde was also isolated.

(c) In 2-Propanol: A solution of 200 mg (0.704 mmol) of **6** in 200 ml of 2-propanol was placed in an immersion-type apparatus, and nitrogen was bubbled for 30 min. Irradiation was then carried out in a stream of nitrogen at room temperature for 6 hr. Treatment of the reaction mixture afforded 17 mg (5.0%) of **8**, 41 mg (21%) of the starting material and 111 mg (66%) of **7**. 2,4-Dinitrophenylhydrazone of acetaldehyde was also isolated in this photolysis.

Determination of Quantum Yields. The same apparatus and procedure as those described separately[1] were employed for determination of the quantum yields. The rates of the formation of **7** were followed by monitoring the absorbances at 413 nm in benzene, at 410 nm in acetonitrile and at 425 nm in 2-propanol. In quenching experiments, the rates of the formation of **7** were measured by monitoring the absorbances at the same wavelengths as described above.

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