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Photochemical Reaction of 3,3-Dimethyl-1,2-indanedione with Xanthene

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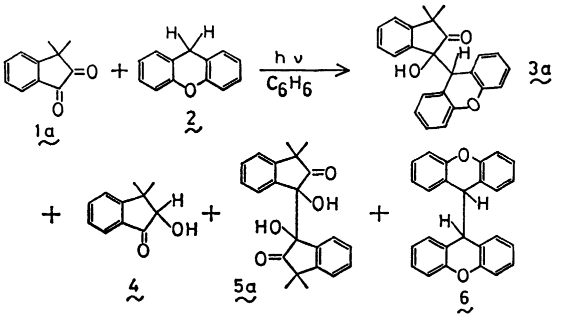
The photochemical reaction of 3,3-dimethyl-1,2-indanedione (DMID) with xanthene was investigated in detail. The products are 1-hydroxy-3,3-dimethyl-1-(9-xanthenyl)-2-indanone (**3a**) (49%), 2-hydroxy-3,3-dimethyl-1-indanone (13%), 1,1'-dihydroxy-3,3,3',3'-tetramethyl-1,1'-biindan-2,2'-dione (**5a**) (23%), and 9,9'-bixanthenyl (**6**) (49%). The reaction proceeds *via* hydrogen abstraction by $^3(n\pi)^*$ of DMID leading to triplet radical pair composed of its semidione radical and 9-xanthenyl radical. The product **3a** is a combination product from the radical pair, while **5a** and **6** are escaping products from it. The hydrogen abstraction occurs at C-1 carbonyl group of DMID in a fairly efficient quantum yield ($\Phi=0.71$). Behavior of the DMID semidione radical is rather resemble those of open-chain semidione radicals than those of sterically hindered semidione radicals.

The photochemical reactions of a number of α-diketones in which the carbonyl groups are held in a somewhat rigid *cis*-configuration have been studied under various conditions.[1] *s-cis*-α-Diketone has been shown to undergo photo-hydrogen abstraction reaction in the presence of a hydrogen donor, and the resulting products can almost invariably be rationalized by taking into consideration a mechanistic pathway involving the initial hydrogen abstraction by photoexcited α-diketone *via* $^3(n\pi)^*$ excitation. For example, camphorquinone in methanol or in 2-propanol gives products derived from the initial hydrogen abstraction reaction from the solvent.[2] When 9,10-phenanthrenequinone is irradiated in hydrogen donating solvents, it yields 1,2-adduct or 1,4-adduct corresponding to the structures of the solvents.[3] In these light-induced reactions of camphorquinone and 9,10-phenanthrenequinone, intermediate radical pairs have been successfully detected by using CIDNP technique.[4] The light-induced hydrogen abstraction reactions of 3,3-dimethyl-1,2-indanedione (DMID), which is a nonenolizable aromatic α-diketone, have been investigated from the standpoint of comparing the photoreactivity with those of open-chain α-diketones.[5] The qualitative behaviors of photoexcited DMID in 2-propanol, diethyl ether, and toluene were reported by Rigaudy,[6] but the quantitative investigation has not been accomplished yet. In this investigation we have found that photoexcited DMID shows such a high reactivity to hydrogen donors as that of benzil.



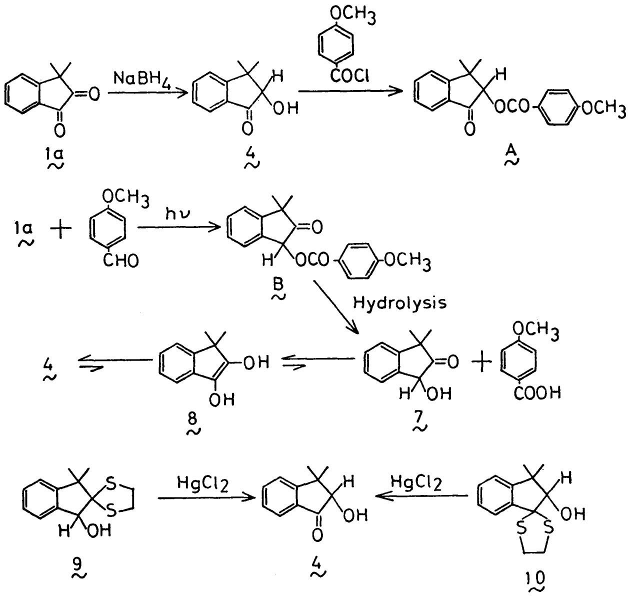
Scheme 1

Results and Discussion

a) Reaction Products. A degassed solution of DMID **1a** (0.04 M) and equimolar xanthene **2**, a good hydrogen donor, in benzene was irradiated for an hour, using a 300 W high-pressure mercury lamp. Separation of the products by column chromatography and preparative TLC gave 1-hydroxy-3,3-dimethyl-1-(9-xanthenyl)-2-indanone **3a** (49%), 2-hydroxy-3,3-dimethyl-1-indanone **4** (13%), and 9,9'-bixanthenyl **6** (46%). On the other hand, the ^{1}H NMR spectrum of this reaction mixture showed two characteristic signals at δ 0.92 and 1.26 corresponding to the dimethyl protons of 1,1'-dihydroxy-3,3,3',3'-tetramethyl-1,1'-biindan-2,2'-dione **5a** (pinacol), indicating its yield of 23% besides those of photoreaction products mentioned above (Scheme 1). When silica gel chromatography was applied for the product separation, **5a** was not isolated owing to its high susceptibility to autoxidation on silica gel. The structures of these products were determined by their IR, UV, ^{1}H NMR, elemental analyses and chemical reactions.

The IR spectrum of **3a** showed characteristic bands at 3420 (hydroxy) and 1746 cm^{-1} (nonconjugated five membered ring ketone), the ^{1}H NMR spectrum ($CDCl_2$) showed signals at δ 0.40 (s, 3H), 1.18 (s, 3H), 2.70 (broad, 1H), 4.40 (s, 1H) and 6.60—7.75 (m, 12H), in agreement with the structure of **3a**.

The IR spectrum of **4** showed two characteristic absorptions of a hydroxyl group (3500 cm^{-1}) and a conjugated five membered ring ketone (1726 cm^{-1}). The ^{1}H NMR spectrum (CCl_4) of **4** showed signals at δ 1.13 (s, 3H), 1.54 (s, 3H), 4.17 (s, 1H), 4.10 (broad 1H) and 7.20—7.26 (m, 4H). The hydroxy ketone **4** was independently prepared by reduction of DMID with sodium borohydride, and compared with the photoreduction product. It is an interesting problem which one of two carbonyl groups is reduced in the photoreaction or in the hydride reduction. The problem was solved in the following way. Esterification of **4** with *p*-anisoyl chloride gave ester **A**, and its IR spectrum showed two characteristic bands at 1721 and 1757 cm^{-1} corresponding to the ester of a five membered ring ketone. On the other hand, irradiation of DMID with *p*-anisaldehyde in benzene gave a small amount (4%) of ester **B** besides various other products. The IR spectrum of the ester **B** showed two characteristic bands at 1723 and 1774 cm^{-1} corresponding to the ester of a five membered ring ketone, but clearly different from **A**; the esters, **A** and **B**, are regioisomers each other. Comparison of the IR spectra of these two isomers led to a conclusion that **B** might have a nonconjugated carbonyl group and **A** a conjugated one. Surprisingly the alkaline hydrolysis of **B** gave a mixture of **4** and *p*-anisic acid as well as the hydrolysis of **A** (Scheme 2). The result observed in the hydrolysis of **B** was explained in terms of a series of equilibria involving a indenediol **8** as a common intermediate. The equilibria might favor rather **4** because of the stability of the conjugated ketone. This was confirmed in the oxidative hydrolysis of both 1-hydroxy-3,3-dimethylspiro(indan-2,2′-[1,3]-dithiolane) **9** and 2-hydroxy-3,3-dimethylspiro(indan-1,2′-[1,3]dithiolane) **10** with mercury(II) chloride; namely, both isomers gave only **4**.



Scheme 2.

Irradiation of a degassed solution of 3,3-dimethyl-6-nitro-1,2-indanedione **1b** (NO_2-DMID) and xanthene for 6 h gave 1-hydroxy-3,3-dimethyl-6-nitro-1-(9-xanthenyl)-2-indanone **3b** in 70% yield and 1,1′-dihydroxy-3,3,3′,3′-tetramethyl-6-nitro-1,1′-biindan-2,2′-dione **5b** in 13% yield.

b) Reaction Mechanism. To investigate the reaction mechanism, we examined the photochemical reactions of DMID with xanthene in detail, changing the reaction conditions (Table 1).

Run 3 reveals that the pinacol **5a** photochemically decomposes to give two semidione radicals, which would regenerate **5a** by coupling or give DMID and hydroxy ketone by disproportionation. On irradiation, DMID thus formed would abstract a hydrogen atom from xanthene, giving **3a** and **6**. Run 4 shows obviously an occurrence of homolytic cleavage of photoexcited **3a**, yielding a semidione radical and 9-xanthenyl radical. However, exposure of a degassed solution of **5a** and **3a** in benzene to light of wavelength longer than 400 nm resulted in the nearly complete recovery of the starting materials (run 5 in the Table 1). When a solution of DMID and xanthene in benzene was irradiated with light of wavelength longer than 400 nm, DMID changed to give only **3a** and **5a** in yields of 13 and 27%, respectively, and **6** was formed in a yield of 29% (Run 2 in the Table 1).

The absence of hydroxy ketone in the reaction mixture of Run 2 might be ascribed to the much slower rate of disproportionation of the semidione radical than that of coupling of it. If **7** once would be produced from the semidione radical by disproportionation, **4** could be formed *via* the equilibria between **7** and **4** (Scheme 2).

In their stabilizing modes, the semidione radicals derived from α-diketones can be classified into two groups;$^{7)}$ namely those derived from rigidly cis, sterically hindered α-diketones, which decay by disproportionation, and those derived from flexible α-diketones such as benzil or anisil, which terminate by coupling in rather faster decay rates. It is noteworthy that the *free* DMID semidione radical decays predominantly by coupling, resulting in the formation of **5a** in spite of its rigidly *cis*-fixed configuration.

c) Radical Pair as an Intermediate. The fact that DMID changes to give only **3a** and **5a** upon irradiation with light of wavelength longer than 400 nm is of value for examining the behaviors of the radical pair. That is, **3a** is a combination product of the semidione radical and 9-xanthenyl radical, whereas **5a** and **6** are escaping products from the initial solvent cage. We examined the effects of the concentration of xanthene and reaction temperature on the product distribution (Table 2). At three different temperature the ratio of **5a** to **3a** was

TABLE 1. PHOTOCHEMICAL REACTION OF DMID **1a**, XANTHENE ADDUCT **3a** AND PINACOL **5a** WITH XANTHENE IN BENZENE. PHOTOREACTION PRODUCT DISTRIBUTION UNDER VARIOUS CONDITIONS

Run	Starting material	Irradiation condition	Products (%)				
			1	**3a**	**4**	**5a**	**6**
1	**1a**+**2**	A(1)	12	43	11	20	41
2	**1a**+**2**	B(3)	52	13	—	27	29
3	**5a**+**2**	A(6)	8	22	57	2	35
4	**3a**	A(6)	16	42	23	4	50
5	**3a**+**5a**	B(6)	—	98	—	96	—

A; usual irradiation, using high-pressure Hg lamp from outside. B; irradiation with light of wavelength longer than 400 nm. Yields were determined by ^{1}H NMR using durene as an internal standard.

TABLE 2. PHOTOCHEMICAL REACTION OF DMID **1a** AND XANTHENE **2** UPON IRRADIATION WITH LIGHT OF WAVELENGTH (λ>400 nm). EFFECTS OF CONCENTRATION OF DMID AND REACTION TEMPERATURE ON THE RATIO OF [**5a**]/[**3a**]

Temperature	5—7 °C		20—23 °C		30—34 °C	
[**2**]/[**1a**]	conv.	[**5a**]/[**3a**]	conv.	[**5a**]/[**3a**]	conv.	[**5a**]/[**3a**]
0.5	45(%)	1.2	47(%)	1.6	52(%)	2.3
1	48	1.2	48	1.8	43	2.4
3	56	1.4	46	1.9	42	2.1
5	68	1.0	53	2.0	58	2.0

a) Irradiation time is 2 h. b) [DMID]=9.83×10^{-3} M. c) Yields were determined by ^{1}H NMR with durene as an internal standard.

independent of the concentration of xanthene. This result suggests that neither the semidione radical nor 9-xanthenyl radical reacted with xanthene. In contrast, the ratio of **5a** to **3a** gradually increased with increasing reaction temperature. The increasing yield of the combination product **3a** with decreasing reaction temperature provides us a powerful support for the concept on the geminate combination of initially formed radical pair.

d) CIDNP Examination. Light-induced reactions of DMID and NO_2–DMID with xanthene were examined by means of CIDNP. As shown in Figure 1b, the methine proton of xanthenyl moiety of **3a** appeared at δ 4.40 as enhanced absorption signal 4, the dimethyl protons of DMID moiety of **3a** appeared at δ 0.40 and 1.18 as moderately enhanced absorption signals 1 and 2, and in addition the dimethyl protons of DMID appeared at δ 1.14 as enhanced emission signal 3. We can rationalized these polarized signals in terms of the initially formed triplet radical pair composed of the semidione radical **11a** and 9-xanthenyl radical **12**. The geminate combination of **11a** and **12** produces **3a**. On the other hand, **11a** escaping from the initial triplet radical pair reproduces DMID by donating a hydrogen atom to another DMID. The Kaptein's equation[8] (Eq. 1) allows us to predict the net effect of polarization, Γ_{ne}.

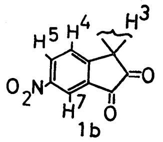
$$\Gamma_{ne} = \Delta g \varepsilon \mu A_i \qquad (1)$$

if, $\Gamma_{ne} = +$, then absorption polarized signal,
$\Gamma_{ne} = -$, then emission polarized signal.

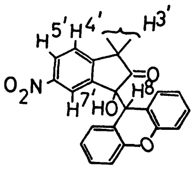
These parameters have their usual meanings. As to the enhanced absorption signal 4 in Fig. 1b, $\Delta g = -$, $\varepsilon = +$, and $A_i = -$ are to be considered, because **3a** is the geminate combination product, *g*-value of semidione radical is in general larger than that of carbon radical without exception, and the sign of hyperfine coupling constant A_i of α-hydrogen of carbon radical is assumed to be negative on the basis of the preceding reaction mechanism.[9] Thus, in Eq. 1, $+ = - \cdot + \cdot \mu \cdot -$, then μ will be positive and the triplet radical pair was indicated.

The A_i sign of the dimethyl protons of **11a** was deduced to be positive from the direction of polarization of signals 1 and 2. Then, the observed enhanced emission signal 3 due to DMID itself led us to a conclusion that DMID was reproduced as the escaping product from the initial triplet radical pair. The hydrogen transfer process as designated e in Scheme 3 was similarly proposed in the photolysis of benzaldehyde[10] and the photochemical reaction of benzophenone in 2-propanol.[11]

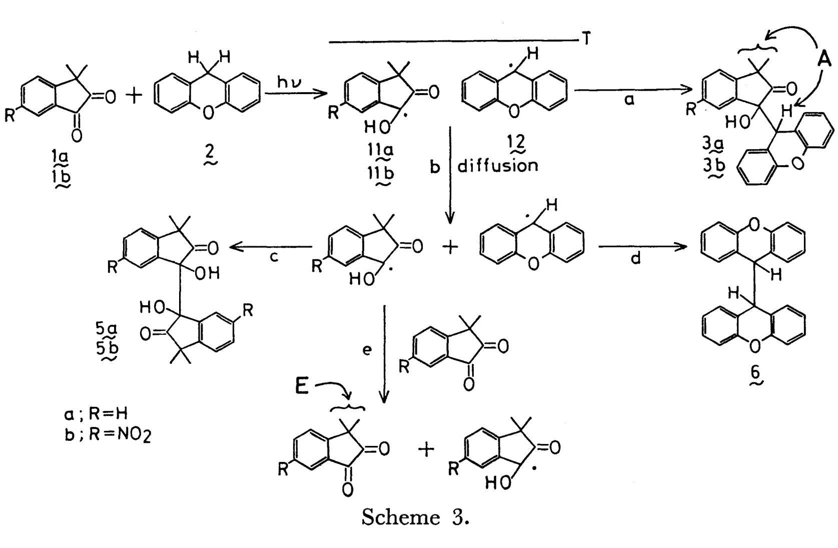
In addition to the assigned polarized signals 1, 2, 3, and 4 observed in aliphatic region, other polarized signals in aromatic region remain unassigned in the reaction of DMID with xanthene due to their complicated spin-spin coupling. Photolysis of a solution of NO_2–DMID and xanthene provides us an invaluable information on this point. Figures 2a and 2b show the spectra of a solution of NO_2–DMID and xanthene in $CDCl_3$ before and during irradiation, respectively. The patterns of ^1H NMR signals in aromatic region of both NO_2–DMID and the xanthene-adduct **3b** are rather resemble each other. Thus, from comparison of their chemical shifts and coupling patterns each proton of these compounds was assigned as follows; H^3, δ 1.55 (s, 6H); H^4, 7.80 (d, J=8 Hz, 1H); H^5, 8.60 (dd, J=2 and 8 Hz, 1H); H^7, 8.66 (J=2 Hz, 1H) in **1b**, and $H^{3'}$, 0.46 (s, 3H) and 1.21 (s, 3H); $H^{4'}$, hidden in the signals of aromatic protons of xanthenyl moiety; $H^{5'}$, 8.18 (dd, J=2 and 8 Hz, 1H); $H^{7'}$, 7.76 (d, J=2 Hz, 1H); H^8, 4.46 (s, 1H). Based on these observation, we assigned polarized signals 1, 2, 4, 5, and 7 to $H^{3'}$, $H^{3'}$, H^8, $H^{7'}$, and $H^{5'}$, respectively, and polarized signals 3, 6, 8, and 9 to H^3, H^4, H^5, and H^7, respectively. Similar to the case of DMID, it was concluded according to Eq. 1 that **3b** was the geminate combination product from the initial triplet radical pair, and that there was reproduction of NO_2–DMID *via* the escaping semidione radical. Furthermore, consulting to Eq. 1 we can



1b



3b

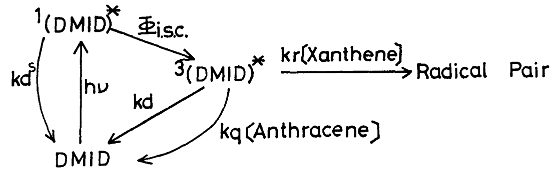


Scheme 3.

conclude from the direction of the polarized signals in aromatic region that the A_i signs of aromatic protons in the semidione radical **11b** were negative for the proton at C-7, negative for the proton at C-5, and positive for the proton at C-4, respectively.

e) Quantum Yield and Reaction Rate. The quantum yield for the disappearance of DMID in the presence of xanthene upon irradiation with light of 450 nm in a carefully degassed benzene solution was determined to be 0.71. The value of the quantum yield is significantly higher than the value of 0.07±0.01 reported for the hydrogen abstraction reaction of camphorquinone with *p*-xylene,[2)] but is nearly equal to the value of 0.7 reported for the reaction of benzil with toluene.[12)] Although the carbonyl groups of DMID are rigidly fixed in a five membered ring, the C-1 carbonyl group is not suffering from such a high steric hindrance as the C-2 carbonyl group. Since in addition the C-1 carbonyl group is conjugated with the phenyl group, the π^* orbital of the C-1 carbonyl group in alkyl phenyl diketone may be stabilized by mixing with the benzene π^* orbitals and therefore contributes more to the lowest diketone π^* orbital.[13)] Thus, the hydrogen abstraction of DMID could occur predominantly at the C-1 carbonyl group.

The lowest triplet $(n\pi)^*$ energy of DMID has been measured to be about 52 kcal/mol.[14)] The photoreaction of DMID with xanthene was not quenched by phenanthrene (E_T=62 kcal/mol), but quenched by anthracene (E_T=42 kcal/mol) upon irradiation with 450 nm monochromatic light. There are some spectroscopic evidences[15)] that the abstracting state is the lowest $^3(n\pi)^*$.



Scheme 4.

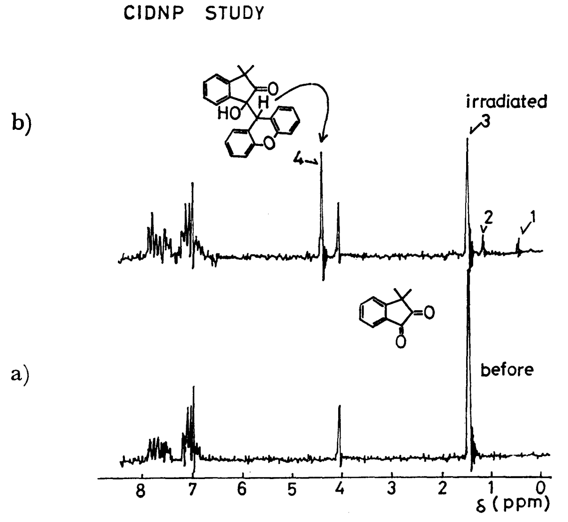


Fig. 1. ¹H NMR spectra observed in the photochemical reaction of DMID with xanthene in $CDCl_3$; a) before irradiation, b) during irradiation.

The possible reaction mechanism is described in Scheme 4, DMID in its ground state is excited to its $^3(n\pi)^*$ in the rate of $I\cdot\Phi_{isc}$: I; light intensity, Φ_{isc}; intersystem crossing yield. The ^{3}(DMID)* is consumed through two paths. The one is *via* self-decaying path (rate constant; k_d) involving both thermal and light emission, and the other is *via* hydrogen abstraction reaction from xanthene (rate constant; k_r). The hydrogen transfer process from the semidione radical to DMID can be neglected in Scheme 4, because there is no net change in the concentration of DMID. From the linear Stern-Volmer plots of Φ_d^{-1} *vs.* [xanthene]$^{-1}$ and Φ_d^{-1} *vs.* [anthracene], the quantum yield of

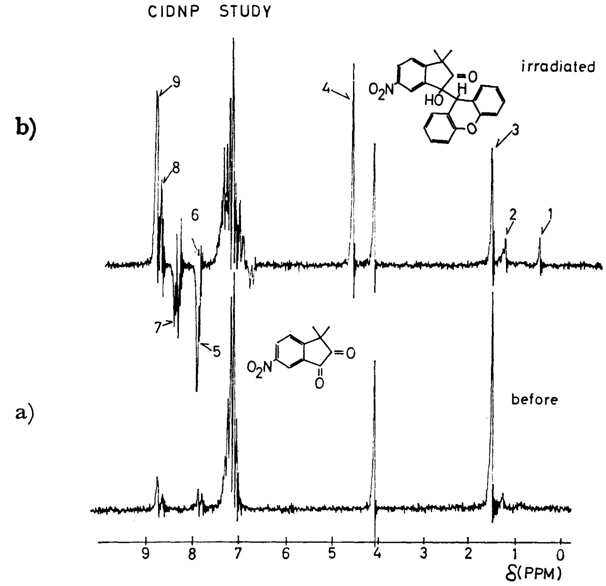


Fig. 2. ¹H NMR spectra observed in the photochemical reaction of NO_2-DMID with xanthene in $CDCl_3$; a) before irradiation, b) during irradiation.

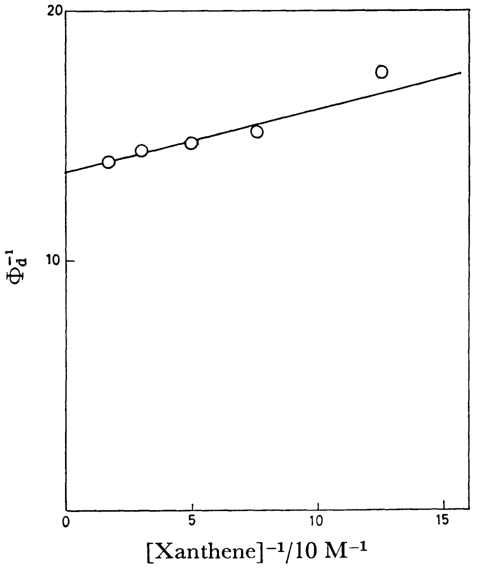


Fig. 3. Stern-Volmer plot of Φ_d^{-1} *vs.* [xanthene]$^{-1}$ in the photochemical reaction of DMID with xanthene.

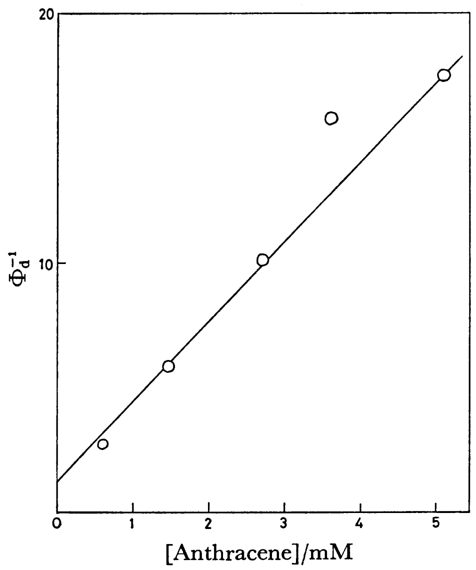


Fig. 4. Stern-Volmer quenching of the photochemical reaction of DMID and xanthene by anthracene.

intersystem crossing (Φ_{isc}) and the reaction rate constant (k_r) were estimated to $\Phi_{isc}=0.75$ and $k_r=5.7\times10^7\ M^{-1}\ s^{-1}$, respectively.16)

In conclusion, the hydrogen abstraction reaction of DMID with xanthene is a cosiderably fast process. The ^{3}(DMID)* shows high reactivity in the hydrogen abstraction reaction and behaves as one of aromatic α-diketones such as benzil rather than one of sterically hindered α-diketones.

Experimental

Apparatus. The melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. Micro analyses were performed by the Micro analytical Laboratory of Kyoto University. IR spectra were recorded with a JASCO DS-402G spectrometer, and ^{1}H NMR spectra were taken with a JEOL PS-100 spectrometer with use of tetramethylsilane as an internal standard and the chemical shifts are expressed in δ value. UV irradiations were carried in a Pyrex glass tube at room temperature, using an Eikosha 300-W high-pressure mercury lamp.

Materials. 3,3-Dimethyl-1,2-indanedione (mp 104—105 °C) and 3,3-dimethyl-6-nitro-1,2-indanedione (mp 172—174 °C) were prepared by the method of Koelsh.17) 1,1′-Dihydroxy-3,3,3′,3′-tetramethyl-2,2′-dioxo-1,1′-biindanyl (mp 123—125 °C) was prepared by the photoreduction of DMID in 2-propanol.

Photochemical Reaction of DMID with Xanthene. A degassed solution of DMID (1 mmol) and xanthene (1.2 mmol) in 30 ml of benzene was irradiated for an hour in a Pyrex glass tube, using a 300-W high-pressure mercury lamp from outside. After removal of the solvent, the residual oil was chromatographed on silica gel (Wakogel C-100). Elution with light petroleum ether (1%) gave colorless crystals of 9,9′-bixanthenyl **6** (46%). The isolated **6** was identified by comparison of IR and ^{1}H NMR spectra with those of the authentic sample. Elution with light petroleum ether (5%) gave colorless prisms of 1-hydroxy-3,3-dimethyl-1-(9-xanthenyl)-2-indanone **3a** (49%); mp 133—134 °C. Found: C, 80.72; H, 5.53%. Calcd for $C_{24}H_{20}O_3$: C, 80.86; H, 5.67%. Elution with light petroleum ether (10%) gave colorless oil of 2-hydroxy- 3,3-dimethyl-1-indanone **4** (12%). Found: C, 74.72; H, 6.99% Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86%. The hydroxy ketone **4** was also prepared by the reduction of DMID with $NaBH_4$ in ethanol in a yield of 68%.

Photochemical Reaction of 3,3-Dimethyl-6-nitro-1,2-indanedione. A degassed solution of **1b** (1 mmol) and xanthene (2 mmol) in 30 ml of benzene was irradiated for 6 houres in a Pyrex tube. White crystals were deposited and then filtered off (15%). The substance showed characteristic absorptions at 3500 (OH) and 1749 cm^{-1} (C=O), and changed to the starting **1b** on heating. The mass spectrum of it showed *m/e* at 219 and 221 corresponding to the molecular ions of NO_2–DMID and the hydroxy ketone, respectively, probably produced by disproportionation of the semidione cation radical. Therefore, the crystals were determined to be 1,1′-dihydroxy-3,3,3′,3′-tetramethyl-6,6′-dinitro-1,1′-biindan-2,2′-dione **5b** (pinacol). After removal of the solvent, the residual oil was chromatographed on silica gel column (Wakogel C-100). In addition to 9,9′-bixanthenyl **6** (75%), 1-hydroxy-3,3-dimethyl-6-nitro-1-(9-xanthenyl)-2-indanone **3b** (70%) was obtained. Colorless prisms; mp 170—171 °C; IR (KBr) 3520 (OH), 1725 (C=O), 1515 and 1250 cm^{-1}. Found: C, 71.80; H, 4.70; N, 3.52%. Calcd for $C_{24}H_{19}O_5$: C, 71.81; H, 4.77; N, 3.49%.

2-Anisoyloxyl-3,3-dimethyl-1-indanone; Ester A. A solution of **4** (1 mmol) in benzene (30 mL) was added *p*-anisoylchloride (1.1 mmol) at room temperature. The mixture was stirred for an hour, poured into water, and neutralized with $NaHCO_3$. Extraction with ether followed by drying (Na_2SO_4) and evaporation of the solvent afforded yellow oil. Separation on silica gel chromatography gave ester **A** (56%). Colorless needles; mp 98 °C; IR (KBr) 1757 (C=O), 1721 (ester), 1255 and 1032 cm^{-1}: ^{1}H NMR 1.24 (s, 3H), 1.64 (s, 3H), 3.38 (s, 3H), 5.56 (s, 1H), and 6.90—8.12 (m, 8H). Found: C, 73.45; H, 5.79%. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85%.

Photochemical Reaction of DMID with p-*Anisaldehyde.* A degassed solution of DMID (1 mmol) and *p*-anisaldehyde (1 mmol) in 30 ml of benzene was irradiated for 8 hours in a Pyrex tube. After removal of the solvent, the residual oil was chromatographed on silica gel (Wakogel C-200). 1-Anisoyloxy-3,3-dimethyl-2-indanone; ester **B** was obtained in 4% yield. Colorless oil; IR (CCl_4) 1774 (C=O), 1723 (ester), 1252 and 1034 cm^{-1}: ^{1}H NMR (CCl_4) 1.40 (s, 3H), 1.48 (s, 3H), 3.82 (s, 3H), 6.23 (s, 1H), and 6.78—8.01 (m, 8H). Found: C, 73.61; H, 5.89%. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85%.

*Hydrolysis of Ester **A** and **B**.* A solution of **A** or **B** (30 mg) in aqueous 50% ethanol was added to a solution of 0.1 N KOH (5 ml), neutralized with $NaHCO_3$, extracted with ether, dried, and chromatographed on preparative TLC. In addition to *p*-anisic acid (80%), the hydroxy ketone **4** was obtained in 60% and 56% yields in the reaction of the ester **A** and **B**, respectively.

*3,3-Dimethylspiro(indan-1,2′-[1,3]dithiolan)-2-one **13** and 3,3-Dimethylspiro(indan-2,2′-[1,3]dithiolan)-1-one **14**.* A solution of DMID (1.0 mmol) and 1,2-ethanedithiol (1.1 mmol) in 20 ml of acetic acid was cooled at 0 °C and boron trifluoride etherate (1.1 mmol) was added with stirring. The mixture was allowed to stand 30 minutes at room temperature and was poured into water, and neutralized with $NaHCO_3$. Extraction with ether followed by drying with Na_2SO_4 and evaporation of the solvent afforded yellow semisolid oil. Separation on silica gel column chromatography gave **13** (67%); mp 77—78 °C: pale yellow needles. IR (KBr) 2970, 1774

(C=O), 1473, 1270, and 1047 cm^{-1}; ^{1}H NMR (CCl$_4$) 1.42 (s, 6H), 3.40—3.84 (m, 4H), and 7.04—7,32 and 7.48—7.64 (m, 4H). Found: C, 62.31; H, 5.60; S, 25.61%. Calcd for $C_{13}H_{14}OS_2$: C, 62.36; H, 5.64; S, 25.61%. And **14** (24%); pale yellow oil. IR (CCl$_4$) 2970, 1727 (C=O), 1608, 1543, 1255, and 1212 cm^{-1}; ^{1}H NMR (CCl$_4$) 1.54 (s, 6H), 3.12—3.60 (m, 4H), and 7.20—7.76 (m, 4H); Found: C, 62.45; H, 5.58; S, 25.75.%. Calcd for $C_{13}H_{14}OS_2$: C, 62.36 H, 5.64; S, 25.61%. The structures of these two regioisomers were determined by comparison of the characteristic bands due to the carbonyl group of **13** with that of **14**; namely, phenyl conjugated ketone **14** shows an absorption at smaller wave number compared with nonconjugated ketone **13.**

2-Hydroxy-3,3-dimethylspiro(indan-1,2'-[1,3]dithiolane) **10** *and 1-Hydroxy-3,3-dimethylspiro(indan-1,2'-[1,3]dithiolane)* **9.** Both **13** and **14** were reduced with sodium borohydride in ethanol to give **10** (90%) and **9** (89%), respectively. Alcohol **10**; colorless needles; mp 72 °C; IR (KBr) 3490 (OH), 2990, 1545, 1133, and 1087 cm^{-1}: ^{1}H NMR (CCl$_4$) 1.08 (s, 3H), 1.33 (s, 3H), 2.86 (mobile, 1H), 3.30—3.41 (m, 4H), 4.12 (s, 1H), and 6.98—7.30 and 7.44—7.60 (m, total 4H). Found: C, 61.89; H, 6.65; S, 25.46%. Calcd for $C_{13}H_{16}OS_2$: C, 61.86; H, 6.39; S, 25.41%. Alcohol **9**; colorless oil: IR (CCl$_4$) 3490 (OH), 2990, 1547, and 1135 cm^{-1}: ^{1}H NMR (CCl$_4$) 1.31 (s, 3H), 1.51 (s, 3H), 3.02 (mobile, 1H), 2.09—3.40 (m, 4H), 5.18 (s, 1H), and 6.39—7.40 (m, 4H). Found: C, 62.53; H, 6.20; S, 25.09%. Calcd for $C_{13}H_{16}OS_2$: C, 61.86; H, 6.39; S, 25.41%.

Oxidative Hydrolysis of **9** *and* **10.** Both **9** and **10** were hydrolyzed with mercury(II) chloride by the method of Corey.$^{18)}$ The hydroxy ketone **4** was obtained in 55% and 68% yields in the oxidative hydrolysis of **9** and **10**, respectively.

CIDNP Examination. PS-100 type NMR instruments equipped with ^{1}H NMR probe for irradiation (manufactured by JEOL) were used in CIDNP examinations. For irradiation, 1 kW super-high-pressure Xe lamp was applied.

Measurement of Quantum Yield. The absolute value of quantum yield for the disappearance of DMID in the reaction with xanthene was measured using 450 nm monochromatic light with application of both VY 42 and 45 KL filters (Toshiba). Disappearance of DMID in a carefully degassed benzene solution was measured at 505.7 nm. Light intensity was measured by means of tris(oxalato)ferrate(III) actinometry. In Stern-Volmer examination, we plotted the value calculated from relative quantum yields to the standard solution, using a merry-go-round.

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15) Both of S_1-S_n absorption and T_1-T_n absorption were observed at 470—500 nm and 400—500 nm, respectively. Life time of T_1-T_n absorption was dramatically shortened in the presence of oxygen or xanthene, but xanthene had no effect on life time of S_1-S_n absorption. (Private communication from Dr. H. Hayashi; the Institute of Physical and Chemical Reseach, Saitama, Japan.)

16) The realtion between Φ_d and [xanthene] and the relation between Φ_d and [anthracene] were derived by application of the stationary state approximation to [^{3}(DMID)*].

$$\frac{1}{\Phi_d} = \frac{1}{\Phi_{isc}} + \frac{k_d}{\Phi_{isc}\cdot k_r\cdot[\text{xanthene}]} \tag{2}$$

$$\frac{1}{\Phi_d} = \frac{1}{\Phi_{isc}} + \frac{k_d}{\Phi_{isc}\cdot k_r\cdot[\text{xanthene}]} + \frac{k_q[\text{anthracene}]}{\Phi_{isc}\cdot k_r\cdot[\text{xanthene}]} \tag{3}$$

As the value of the quenching rate constant k_q in this experiment, we used the value of the quenching rate constant (5.6×10^9 M^{-1} s^{-1}) reported for benzophenone–naphthalene system in benzene at room temperature. (P. J. Wagner and I. Kochevar, *J. Am. Chem. Soc.*, **90**, 2232 (1968).)

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