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Photochemical Dimerization of 2-Acyl-1,4-benzoquinones in the Presence of Rose Bengal

Kazuhiro Maruyama* and Noritsugu Narita

Department of Chemistry, Faculty of Science, Kyoto University, Kitashirakawaoiwake-cho, Sakyo-ku, Kyoto 606, Japan

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Irradiation of 2-acyl-1,4-benzoquinone 1 in the presence of rose bengal afforded the quinone dimer 2-acyl-3-(3-acyl-4-hydroxyphenoxy)-1,4-benzoquinone 2 in good yields.[9] This type of dimer was quite different from another dimer 3, which was obtained in the photoreaction of 2-acyl-1,4-benzoquinone 1 in the absence of rose bengal.[8] In this photoreaction in the presence of rose bengal, the excited state of rose bengal played a very important role. However, singlet oxygen generated by rose bengal sensitization is not involved in the photodimerization reaction of quinones. On the other hand, 2-acyl-1,4-benzoquinone 1 can quench the rose bengal sensitized photooxygenation of α-pinene and simultaneously dimerize to give the same dimer 2 mentioned above. In addition, photolysis of the acylquinone 1 in a heterogeneous system using rose bengal coated silica gel as sensitizer also afforded the same dimer 2 obtained in the homogeneous system in comparable yields.

Photoexcitation results in the formation of the molecular entities having basically different electronic structures and drastically high chemical reactivities as compared with those of the parent molecules in their respective ground states. The change in electronic nature is impressively represented by the decrease of the ionization potential and the gain in the chemical free energy coupled with a high propensity for electronic energy transfer. Photoexcitation is associated with photoelectronic phenomena through simultaneous gain of electron affinity and of oxidizability of the same excited system which may also undergo addition reactions with ground-state systems, yielding excited complexes as intermediate steps. This may result in the deactivation of the excited molecule by electron transfer.[1] It has been shown that even molecules of the same species can act as effective quenchers in electron-transfer reactions.[2]

The present type of photodimerization of quinones seems to involve electron transfer from the excited state of rose bengal to an acylquinone in its ground state and the attack of the anion radical of the acylquinone on another molecule of the acylquinone in its ground state.

The deactivation of excited states may also proceed via transient complexation including exciplex formation which may also play an important role in the aforementioned electron-transfer processes.

Benzoquinone has been found to quench very efficiently oxygen-transfer reactions photosensitized by eosin.[3] The inhibition does not depend on the nature or the concentration of the substrate but is due to the very fast reaction between the excited dye and benzoquinone. An analogous inhibition of excitation has been observed with the sensitizing dye rose bengal and duroquinone.[4] During irradiation the ESR signal of the duroquinone component of the complexed radical pair was observed. The duroquinone and excited rose bengal decay to regenerate the respective molecules in their ground states.[4]

The present work has been done to find the true reason for the dramatic difference observed in the photochemical behavior of 2-acyl-1,4-benzoquinones in the presence and the absence of rose bengal and other sensitizing dyes.[8,9]

Table I. Yields of the Dimer 2 in the Presence of Rose Bengal

product	R_1	R_2	R_3	irradn time, h	yield,[a] %
2a	H	H	Me	8	60
2b	H	Me	Me	8	60
2c	H	Me	Et	12	55
2d	H	Me	Pr	18	50
2e	H	Me	*i*-Pr	24	45

[a] Values are isolated yields and are based on the quinone used.

Table II. Conversion of 1a and Yield of 2a in the Presence of Dye

dye	irradn time, h	conversion, %	yield, %
rose bengal	8	100	60
methylene blue	16	100	60
eosin (blue)	24	85	50

Results

Dimerization of 2-Acyl-1,4-benzoquinone in the Presence of Sensitizing Dye. When a deoxygenated solution of 2-acetyl-1,4-benzoquinone (**1a**) in acetonitrile in the presence of rose bengal was irradiated with light of wavelength longer than 490 nm, the dimer 2-acetyl-3-(3-acetyl-4-hydroxyphenoxy)-1,4-benzoquinone (**2a**) (see Figure 1) was obtained in 60% yield. The structure of the dimer was determined by spectroscopic methods (see Experimental Section).

This type of dimerization reaction occurred, in general, when 2-acyl-1,4-benzoquinones were irradiated in the presence of rose bengal. The yields of the quinone dimer 2 (Figure 2) are listed in Table I.

The irradiation time listed in Table I was the period required to completely consume the quinone. The yield of 2 is based on the quinone used. Another product isolated in this photoreaction was the 2-acylhydroquinone in a yield of 5-10%.[5] Other products of the reaction were obtained as a reddish brown viscous oil, and their structures could not be determined. 2-Acyl-1,4-benzoquinone

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(1) E. Fujimori and R. Livingston, *Nature (London)*, 180, 1036 (1957).

(2) H. K. Wong, *Photochem. Photobiol.*, 7, 377 (1968).

(3) G. O. Schenck and K. H. Ritter, *Naturwissenschaften*, 41, 374 (1954).

(4) G. O. Schenck and R. Wolgast, *Naturwissenschaften*, 48, 737 (1961).

(5) 2-Acylhydroquinones were stable on irradiation with and without rose bengal in acetonitrile. In addition, presence of 2-acylhydroquinone in the reacting mixture had no effect. When an acetonitrile solution of an equimolar mixture of 2-acetyl-1,4-benzoquinone (**1a**) and 2-acetylhydroquinone was irradiated in the presence of rose bengal, the dimer **2a** was formed in 60% yield.

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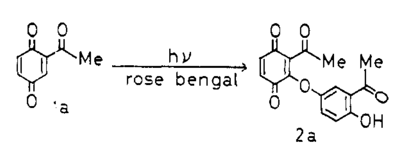
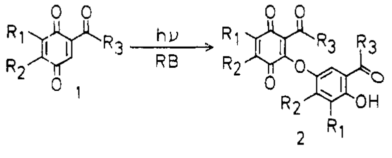


Figure 1. Photoreaction of 2-acetyl-1,4-benzoquinone (**1a**) in the presence of rose bengal afforded the dimer 2-acetyl-3-(3-acetyl-4-hydroxyphenoxy)-1,4-benzoquinone (**2a**).



	R_1	R_2	R_3	
1a	H	H	Me	2a
b	H	Me	Me	b
c	H	Me	Et	c
d	H	Me	Pr	d
e	H	Me	i-Pr	e

Figure 2. Photoreaction of 2-acyl-1,4-benzoquinones in the presence of rose bengal afforded the dimer **2** in good yields.

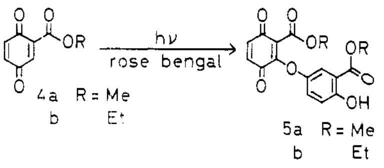


Figure 3. Photoreaction of 2-(carboalkoxy)-1,4-benzoquinone **4** in the presence of rose bengal afforded the dimer **5**.

1 was, in general, thermally unstable and even at room temperature gradually changed into a red oil whose structure was hard to determine.

Photoreactions of **1a** in the presence of other dyes were examined. Methylene blue and eosin were also effective as the sensitizing dye. Photolysis of **1a** (0.1 mol dm^{-3}) in the presence of the dye (1.0 × 10^{-3} mol dm^{-3}) in acetonitrile afforded the dimer **2a** in good yield. The results are given in Table II. Yields were calculated on the basis of the quinone used.

Unsubstituted 1,4-benzoquinone was stable under the same irradiation conditions, and after irradiation for 12 h the substrate was recovered unchanged. 2-Methyl-1,4-benzoquinone was also inactive under the same conditions. However, 2-(carbomethoxy)-1,4-benzoquinone (**4a**) gave the dimer 2-(carbomethoxy)-3-[3-(carbomethoxy)-4-hydroxyphenoxy]-1,4-benzoquinone (**5a**) in a good yield (Figure 3). In a similar fashion, 2-(carboethoxy)-1,4-benzoquinone (**4b**) dimerized to the dimer **5b** under the same irradiation conditions. On the other hand, monohalogenated 1,4-benzoquinones 2-chloro- and 2-bromo-1,4-benzoquinone were unreactive during similar irradiation at the long-wavelength absorption band of rose bengal and after 16 h were recovered almost quantitatively.

Photoirradiation in a Heterogeneous System. Rose bengal and methylene blue coated silica gel were prepared according to the method of Nilsson and Kearns.[6] Benzene and dichloromethane were used as solvents. In these heterogeneous systems, 2-acetyl-1,4-benzoquinone (**1a**) was dimerized to **2a**. The results are listed in Table III.

The concentration of the dye was 1.0 × 10^{-3} mol dm^{-3}. Under comparable irradiation conditions, with optimal quantities of the dye dissolved in acetonitrile (homogeneous system), quantitative conversion of **1a** and a 60% yield of **2a** were obtained for the same period of irradiation (see Table I).

Table III. Heterogeneous Photodimerization of 1a in Various Solvents

solvent	irradn time, h	dye[a]	conversion, %	yield,[b] %
C_6H_6	8	RB[c]	28	20
CH_2Cl_2	8	RB	20	15
C_6H_6	16	MB[d]	25	18
CH_2Cl_2	16	MB	20	15

[a] Dye was deposited on the surface of silica gel particles. [b] Yields were calculated on the basis of the amount of 1a used. [c] RB represents rose bengal. [d] MB represents methylene blue.

Table IV. Effect of 1a on the Rate of Oxygen Transfer to α-Pinene

[1a], mmol dm^{-3}	dO_2/dt,[a] mL h^{-1}	Φ_0/Φ	[1a], mmol dm^{-3}	dO_2/dt,[a] mL h^{-1}	Φ_0/Φ
0	106.5	1	3.0	34.5	4.00
1.0	87.6	1.23	5.0	22.0	5.82
2.0	55.0	2.78	10.0	5.0	21.3

[a] O_2 refers to the volume of O_2 gas.

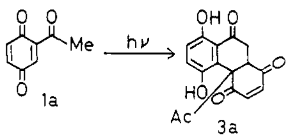


Figure 4. Photoreaction of 2-acetyl-1,4-benzoquinone in the absence of rose bengal afforded the dimer **3a** in good yield.

Rose Bengal Sensitized Photooxygenation of α-Pinene. The sole product of this reaction, after $NaBH_4$ reduction, *trans*-3-hydroxypin-2(10)-ene, is formed in high yield.[7]

The inhibition of this reaction by 2-acetyl-1,4-benzoquinone (**1a**) was investigated by measuring the oxygen consumption rate as a function of 2-acetyl-1,4-benzoquinone concentration. Standard solutions of 1.0 × 10^{-3} mol dm^{-3} of rose bengal in acetonitrile containing 0.5 mol dm^{-3} of α-pinene were irradiated in the presence of 1.0 × 10^{-2}–1.0 × 10^{-3} mol dm^{-3} of 2-acetyl-1,4-benzoquinone (**1a**). The oxygen consumption was plotted as a function of time. The plots showed straight lines at the lower concentrations of quinone; at high **1a** concentrations the rate of oxygen consumption decreased with time because of bleaching. The rates listed in Table IV were taken from the linear parts of the records. Table IV also lists the relative consumption rate of oxygen in the absence (Φ_0) and in the presence (Φ) of the quencher **1a**. In all experiments the amounts of hydroperoxide formed proved to closely correspond to the amount of oxygen consumed.

Photoreaction of 2-Acetyl-1,4-benzoquinone (1a) under Oxygen. A solution of 2-acetyl-1,4-benzoquinone (**1a**) in acetonitrile (0.1 mol dm^{-3}) was irradiated under oxygen in the presence of rose bengal (1.0 × 10^{-3} mol dm^{-3}) with a 300-W high-pressure mercury-arc lamp. No oxygen consumption was recorded during 1 h of irradiation. After irradiation for 8 h, no oxygen had been absorbed, 2-acetyl-1,4-benzoquinone was completely consumed, and the dimer **2a** was obtained in 60% yield.

Photoreaction of 2-Acetyl-1,4-benzoquinone in the Absence of Rose Bengal. It has been reported that

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[6] R. Nilsson and D. R. Kearns, *Photochem. Photobiol.*, **19**, 181 (1974).

[7] C. W. Jefford, A. F. Boschung, R. M. Moriarty, C. G. Rimbault, and M. H. Laffer, *Helv. Chim. Acta*, **56**, 2649 (1974).

Table V. Photodimerization of Substituted 1,4-Benzoquinone

substituent	$-E_{1/2}$,[a] V	photodimerization
none	0.51, 1.17	no
Me	0.58, 1.12	no
$COCH_3$ (1a)	0.306, 0.98	yes
CO_2CH_3 (4a)	0.315, 0.91	yes
Cl	0.34, 0.97	no
Br	0.325, 0.95	no

[a] $E_{1/2}$ is the half-wave potential of quinone in acetonitrile (0.1 mol dm^{-3} TEAP) vs. SCE at 25 °C. K. M. C. Davis et al., *Trans. Faraday Soc.*, **61**, 1516 (1965).

photolysis of 2-acyl-1,4-benzoquinones, for example **1a**, in benzene or carbon tetrachloride afforded another quinone dimer (**3a**) in high yields[8] (Figure 4). An acetonitrile solution of **1a** (0.1 mol dm^{-3}) was irradiated with a 300-W high-pressure mercury-arc lamp, and the reported dimer **3a** was obtained in a high yield. 2-Acetyl-1,4-benzoquinone (**1a**) has no absorption beyond 500 nm in acetonitrile. So, after irradiation with light of wavelength longer than 490 nm in the absence of rose bengal, **1a** was recovered almost quantitatively.

Discussion

The results of photolysis using light of wavelength longer than 490 nm, in which region 2-acetyl-1,4-benzoquinone (**1a**) has no absorption, indicated that the photoexcited state of rose bengal played an important part of photodimerization of **1a** to **2a**. This type of photodimerization occurred in the presence or absence of oxygen. Thus the singlet oxygen produced by rose bengal was not responsible for the formation of the dimer **2a**, though the presence of oxygen in the reaction system somewhat supressed the conversion of **1a**. 2-Acetyl-1,4-benzoquinone (**1a**) quenched the rose bengal sensitized photooxygenation of α-pinene. These results indicate that the photoexcited state of rose bengal was deactivated competitively by both oxygen and **1a**.

The mechanism of quenching of photoexcited rose bengal by **1a** is not completely clear, but it seems to involve electron-transfer processes as in the case of rose bengal and duroquinone.[4] Thus, it may be reasonable to consider that the formation of the dimer **2** occurs as follows. Electron transfer from the photoexcited rose bengal (probably triplet) to the ground state of the quinone is followed by attack of the anion radical of the quinone on another molecule of the quinone in the ground state. Back-donation of an electron to the rose bengal radical cation would result in the formation of quinone dimer **2** and rose bengal.

The relationship between the photodimerizing reactivity and the reduction potential of the quinone is tabulated in Table V.

1,4-Benzoquinone derivatives which dimerize in the presence of rose bengal (e.g., **1a** and **4a**) have lower reduction potentials than those of 1,4-benzoquinones which do not give the dimer (e.g., 1,4-benzoquinone and 2-methyl-1,4-benzoquinone). This seems to support the proposed mechanism. Quinones **1a** and **4a** could accept an electron from the excited rose bengal more easily than 1,4-benzoquinone or 2-methyl-1,4-benzoquinone. In addition, the 3-position of **1a** or **4a** could be easily attacked by anionic species.[10] Competitive quenching of the excited rose bengal by acylquinones and oxygen in addition to the solid-state photoactivation of acylquinones by the silica gel coated by rose bengal is highly suggestive for the proposed mechanism.

Table VI. Yields and Melting Points of 1,4-Benzoquinones

	yield, %	mp,[a] °C		yield, %	mp,[a] °C
1a	90	63.0-64.0	1e	60	oil
1b	90	78.0-79.0	4a	80	54.0-55.0
1c	88	40.0-41.0	4b	75	48.0-49.0
1d	65	36.0-38.0			

[a] Melting points were uncorrected.

Experimental Section

Rose bengal and other dyes were obtained in pure crystalline form by recrystallization from ethanol.

2-Acyl-1,4-benzoquinones were prepared by oxidation of 2-acylhydroquinones with silver oxide in benzene in the presence of potassium carbonate or magnesium sulfate.[11] Yields and melting points of reactant 1,4-benzoquinones were listed in Table VI.

2-(Carboalkoxy)-1,4-benzoquinones and 2-halogenated 1,4-benzoquinones were also prepared according to the above-mentioned method.

Rose bengal and methylene blue coated silica gel particles were prepared according to the method of Nilsson and Kearns.[6]

Acetonitrile was purified by distillation (twice from P_2O_5 and once from K_2CO_3).

Other chemicals were either prepared or obtained commercially and had the highest purity.

The ^1H NMR spectra were determined on a JOER PS-100 spectrometer using deuteriochloroform as solvent. Chemical shifts are expressed as parts per million with reference to tetramethylsilane.

Photooxygenation of α-pinene was carried out according to the method of Jefford et al.,[7] but rose bengal was used as a sensitizer. After reduction by $NaBH_4$, *trans*-3-hydroxypin-2(10)-ene was obtained in 90% yield.

A vigorously stirred solution of α-pinene (5 mmol), rose bengal (10 mg), and **1a** (1 mmol) in 10 mL of acetonitrile was irradiated under an oxygen atmosphere at 0 °C. The oxygen consumed was measured with a gas buret. After 8 h, no oxygen consumption was observed, and α-pinene was recovered.

The general procedure for photoreaction of 1,4-benzoquinones in the presence of rose bengal was as follows. The quinone (1 mmol) and rose bengal (10 mg) were dissolved in 10 mL of acetonitrile and irradiated with light of wavelength longer than 490 nm (Toshiba color glass filters VY-49 × 1 and VY-48 × 1 were used). After the quinone was completely consumed, the solvent was evaporated. The residue was short-column chromatographed over Florisil to remove rose bengal with ether as the eluent. The solvent was removed under reduced pressure, and a small amount of chloroform was added. Insoluble substituted hydroquinone was filtered off, and the chloroform was evaporated. The residue was recrystallized from ether.

Photolysis of 2-acetyl-1,4-benzoquinone (**1a**) in the presence of rose bengal afforded the dimer 2-acetyl-3-(3-acetyl-4-hydroxyphenoxy)-1,4-benzoquinone (**2a**) in 60% yield: red needles; mp 120.0-121.0 °C; UV_{max} (CH_3CN) 440 nm (sh, ϵ 860), 346 (4200), 250 (21 600), 223 (21 600); IR (KBr disk) 3340 (OH), 1700, 1670, 1650 (C=O), 1190 cm^{-1} (O); NMR ($CDCl_3$) δ 2.40 (s, 3), 2.62 (s, 3), 6.78 (s, 2), 6.92 (d, 1, J = 9 Hz), 7.18 (dd, 1, J = 9 and 3 Hz), 7.40 (d, 1, J = 3 Hz), 12.10 (s, 1, OH); MS m/e 300 (M^+), 151, 149. Anal. Calcd for $C_{16}H_{12}O_6$: C, 64.00; H, 4.03. Found: C, 63.71; H, 3.80.

In the ^1H NMR spectrum of **2a**, the protons attached to carbon C-5 and C-6 of the quinone moiety appeared as a singet at δ 6.78. Similarly, the aromatic hydrogens on C-5 and C-6 of 2-acetyl-3-

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(8) Y. Miyagi, K. Kitamura, K. Maruyama, and Y. L. Chow, *Chem. Lett.*, 33 (1978).

(9) K. Maruyama, N. Narita, and Y. Miyagi, *Chem. Lett.*, 1033 (1978).

(10) F. Farina, *Synthesis*, 315 (1971).

(11) (a) M. C. Kloetzel, R. P. Dayton, and B. Y. Abadir, *J. Org. Chem.*, **20**, 38 (1955). (b) P. R. Hammond, *J. Chem. Soc.*, 471 (1964).

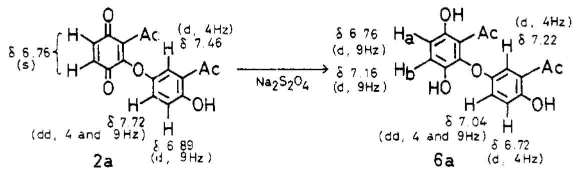

Figure 5. Reduction of **2a** with sodium hydrosulfite afforded 2-acetyl-3-(3-acetyl-4-hydroxyphenoxy)-1,4-dihydroxybenzene (**6a**).

alkoxy-1,4-benzoquinones appeared as a singlet at δ 6.73–6.68.[10]

For confirmation of the structure of **2a**, reduction with sodium hydrosulfite was carried out. A solution of sodium hydrosulfite (60 mg, 0.35 mmol) in water (20 mL) was added to a stirred solution of **2a** (50 mg, 0.17 mmol) in ether (50 mL). After the mixture was stirred at room temperature for 30 min, the color of the organic phase was changed from red to yellow. The ethereal phase was washed with water, dried over magnesium sulfate, and concentrated to yield 2-acetyl-3-(3-acetyl-4-hydroxyphenoxy)-1,4-dihydroxybenzene (**6a**) in 80% yield (Figure 5). The ^{1}H NMR spectrum of **6a** showed two doublets at δ 6.76 and 7.16 (J = 9 Hz), due to the aromatic protons H_a and H_b (solvent CD_3CN). This result clearly indicates the presence of two groups of vicinal hydrogens.

Photolysis of 2-acetyl-5-methyl-1,4-benzoquinone (**1b**) in the presence of rose bengal afforded the dimer 2-acetyl-5-methyl-3-(3-acetyl-6-methyl-4-hydroxyphenoxy)-1,4-benzoquinone (**2b**): 60% yield; red needles; mp 134.0–135.0 °C; $\mathrm{UV_{max}}$ (CH_3CN) 480 nm (sh, ϵ 306), 340 (4240), 260 (26 600), 226 (22 000); IR (KBr disk) 3320 (OH), 1700, 1670, 1650 (C=O), 1182 cm^{-1} (O); NMR ($CDCl_3$) δ 2.08 (d, 3, J = 2 Hz), 2.32 (s, 3), 2.36 (s, 3), 2.56 (s, 3), 6.64 (q, 1, J = 2 Hz), 6.88 (s, 1), 7.22 (s, 1), 11.64 (s, 1, OH). Anal. Calcd for $C_{18}H_{16}O_6$: C, 65.85; H, 4.91. Found: C, 65.70; H, 4.92.

When 2-propanoyl-5-methyl-1,4-benzoquinone (**1c**) was used, 2-propanoyl-5-methyl-3-(3-propanoyl-6-methyl-4-hydroxyphenoxy)-1,4-benzoquinone (**2c**) was obtained: 55% yield; red crystals; mp 124.0–125.0 °C; NMR ($CDCl_3$) δ 1.02 (t, 3, J = 8 Hz), 1.20 (t, 3, J = 8 Hz), 2.08 (d, 3, J = 2 Hz), 2.34 (s, 3), 2.61 (q, 2, J = 8 Hz), 2.92 (q, 2, J = 8 Hz), 6.66 (q, 1, J = 2 Hz), 6.90 (s, 1), 7.28 (s, 1), 11.72 (s, 1, OH). Anal. Calcd for $C_{20}H_{20}O_6$: C, 67.40; H, 5.66. Found: C, 67.14; H, 5.79.

When 2-butanoyl-5-methyl-1,4-benzoquinone (**1d**) was irradiated in the presence of rose bengal, the quinone dimer 2-butanoyl-5-methyl-3-(3-butanoyl-6-methyl-4-hydroxyphenoxy)-1,4-benzoquinone (**2d**) was obtained: 50% yield; yellow needles; mp 109.0–110.0 °C; IR (KBr disk) 3320 (OH), 1700, 1650 (C=O), 1180 cm^{-1} (O); NMR ($CDCl_3$) δ 0.88 (t, 3, J = 8 Hz), 0.98 (t, 3, J = 8 Hz), 1.58 (sext, 2, J = 8 Hz), 1.72 (sext, 2, J = Hz), 2.04 (d, 3, J = 1.5 Hz), 2.32 (s, 3), 2.54 (t, 2, J = 8 Hz), 2.82 (t, 2, J = 8 Hz), 6.60 (q, 1, J = 1.5 Hz), 6.82 (s, 1), 7.18 (s, 1), 11.78 (s, 1, OH). Anal. Calcd for $C_{22}H_{24}O_6$: C, 68.73; H, 6.29. Found: C, 68.67; H, 6.50.

Photolysis of 2-(2-methylpropanoyl)-5-methyl-1,4-benzoquinone (**1e**) afforded 2-(2-methylpropanoyl)-5-methyl-3-[3-(2-methylpropanoyl)-6-methyl-4-hydroxyphenoxy]-1,4-benzoquinone (**2e**): 40% yield; red needles; mp 115.0–116.0 °C; IR (KBr disk) 3320 (OH), 1700, 1650 (C=O), 1185 cm^{-1} (O); NMR ($CDCl_3$) δ 1.16 (d, 6, J = 8 Hz), 1.18 (d, 6, J = 8 Hz), 2.02 (d, 3, J = 1.5 Hz), 2.32 (s, 3), 2.84 (q, 1, J = 8 Hz), 3.36 (q, 1, J = 8 Hz), 6.60 (q, 1, J = 1.5 Hz), 6.84 (s, 1), 7.14 (s, 1), 12.28 (s, 1, OH). Anal. Calcd for $C_{22}H_{24}O_6$: C, 68.73; H, 6.29. Found: C, 68.58; H, 6.44.

When an acetonitrile solution of 2-(carbomethoxy)-1,4-benzoquinone (**4a**) in the presence of rose bengal was irradiated, the quinone dimer 2-(carbomethoxy)-3-[3-(carbomethoxy)-4-hydroxyphenoxy]-1,4-benzoquinone (**5a**) was obtained: 42% yield; red-yellow needles; mp 150.0–151.0 °C; $\mathrm{UV_{max}}$ (CH_3CN) 480 nm (sh, ϵ 250), 370 (sh, 1200), 320 (4460), 250 (sh, 16 700), 240 (18 100), 214 (28 900); NMR ($CDCl_3$) δ 3.68 (s, 3), 4.00 (s, 3), 6.88 (s, 2), 7.02 (d, 1, J = 10 Hz), 7.30 (dd, 1, J = 10 and 4 Hz), 7.58 (d, 1, J = 4 Hz), 10.56 (s, 1, OH).

When 2-(carboethoxy)-1,4-benzoquinone (**4b**) was irradiated, the dimer 2-(carboethoxy)-3-[3-(carboethoxy)-4-hydroxyphenoxy]-1,4-benzoquinone (**5b**) was obtained: 40% yield; yellow needles; mp 92.0–93.0 °C; $\mathrm{UV_{max}}$ (CH_3CN) 480 nm (sh, ϵ 252), 370 (sh, 1130), 298 (4580), 250 (sh, 16 300), 242 (18 000), 214 (28 200); NMR ($CDCl_3$) δ 1.20 (t, 3, J = 8 Hz), 1.40 (t, 3, J = 8 Hz), 4.06 (q, 2, J = 8 Hz), 4.40 (q, 2, J = 8 Hz), 6.78 (s, 2), 6.92 (d, 1, J = 9 Hz), 7.20 (dd, 1, J = 9 and 4 Hz), 7.70 (d, 1, J = 4 Hz), 10.70 (s, 1, OH).

1,4-Benzoquinone, 2-methyl-1,4-benzoquinone, 2-chloro-1,4-benzoquinone, and 2-bromo-1,4-benzoquinone were stable under the irradiated conditions in the presence of rose bengal and were recovered almost quantitatively.

Registry No. 1a, 1125-55-9; **1b**, 63076-94-8; **1c**, 65781-68-2; **1d**, 72926-14-8; **1e**, 72926-15-9; **2a**, 68157-88-0; **2b**, 72926-16-0; **2c**, 72926-17-1; **2d**, 72926-18-2; **2e**, 72926-19-3; **4a**, 3958-79-0; **4b**, 62830-98-2; **5a**, 72857-89-7; **5b**, 72926-20-6; **6a**, 72926-21-7; α-pinene, 80-56-8; *trans*-3-hydroxypin-2(10)-ene, 1674-08-4.

Facile Photochemical Synthesis of Polycyclic Aromatic Compounds[1]

Kazuhiro Maruyama,* Tetsuo Otsuki, and Kiichiro Mitsui

Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan

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A variety of polycyclic aromatic quinones, which are easily reduced to the corresponding aromatic hydrocarbons, were synthesized via a one-pot photocycloaddition reaction of simple 2-halogenated 1,4-naphthoquinone derivatives with 1,1-disubstituted ethylenes. The yields of the photocycloadditions are generally fairly good.

7,12-Dimethylbenz[*a*]anthracene is one of the most potent carcinogenic compounds known, and many efforts to synthesize polycyclic aromatic hydrocarbons and their heteroatom analogues have concentrated on attempts to elucidate the correlation between structure and carcinogenic activity. One basic synthetic approach to polycyclic aromatic hydrocarbons such as benz[*a*]anthracene depends on step-by-step construction of the carbon skeleton involving, for example, Friedel–Crafts acylation followed by Clemmensen reduction or Elbs condensation.[2] However, these procedures are laborious, and the overall yields are generally poor.

A one-pot synthesis of the carbon skeleton of benz[*a*]anthracenes was disclosed recently by Manning et al.[3]

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