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Photoinduced Alkylation Reaction of Benzo[*f*]indole-4,9-dione with Arylalkenes

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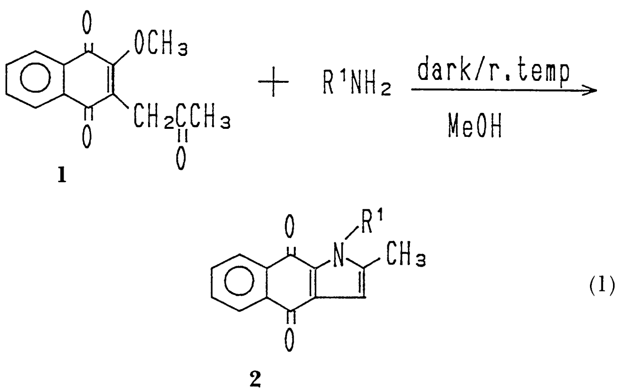
Synopsis. Photoreaction of 1-alkyl-2-methyl-1*H*-benz[*f*]indole-4,9-diones (indolequinones) with arylalkenes in benzene gave 3-alkylated products. Irradiation of 1-allyl substituted indolequinone in benzene gave 1,3-hydrogen shift product in the presence or absence of arylalkenes. The fluorescence of 1,2-dimethyl-1*H*-benz[*f*]indole-4,9-dione exhibits a large bathochromic shift in polar solvents, indicating polar charge-transfer character for its S_1-state.

Photochemistry of quinones has been a subject of many extensive investigations. As a result, a variety of photoreactions of quinones, including photoreduction, photocycloaddtion, photoisomerization, and photosubstitution have appeared in the literature.[1] However, photochemical alkylation reaction of quinones has been much less characterized so far.

Recently, we developed a convenient synthetic method of 1*H*-benz[*f*]indole-4,9-dione (**2**) by the thermal condensation reaction of 2-acetonyl-3-methoxy-1,4-naphthoquinone (**1**) with primary aliphatic amines.[2] The compound **2** has an interesting structure containing pyrrole ring fused with naphthoquinone necleus. Since the naphthoquinone structure is electron-deficient and the pyrrole ring is electron-rich, the former ring is expected to be potential electron acceptor for the latter, thus achieving an intramolecular charge-transfer state.



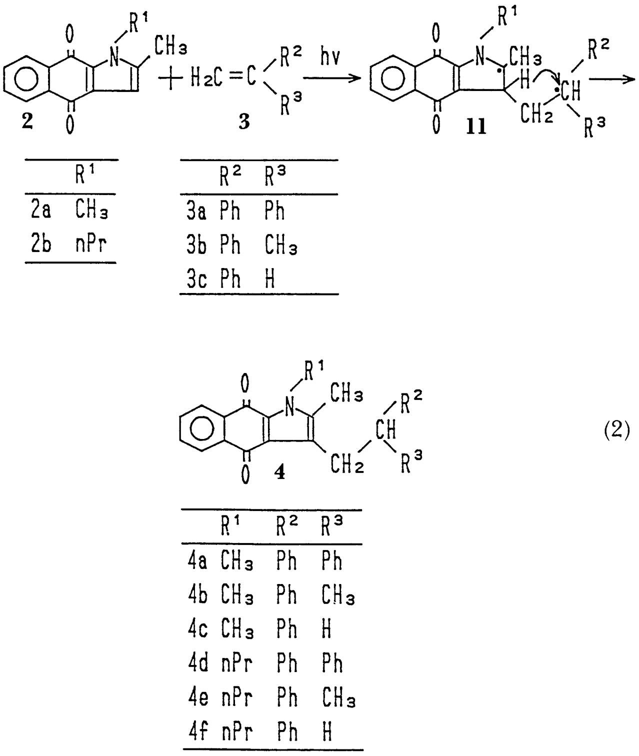
(1)

Described herein is a novel photoinduced alkylation of **2** with arylalkenes.

Results and Discussion

Photochemical Alkylation Reactions of 1,2-Dimethyl-1*H*-benz[*f*]indole-4,9-dione (2a) 2-Methyl-1-propyl-1*H*-benz[*f*]indole-4,9-dione (2b) with Arylakenes (3a—c). Irradiation of **2a** (1.2 mmol dm^{-3}) in the presence of 1,1-diphenylethylene (**3a**)(1.5 mmol dm^{-3}) in benzene followed by separation by column chromatography (silica gel) afforded 1,2-dimethyl-3-(2,2-diphenylethyl)-1*H*-benz[*f*]indole-4,9-dione (**4a**) as the sole photoproduct in a 40% isolated yield at 50% conversion of **2a**. The structure of **4a** was determined by its spectroscopic analysis and elemental analysis.

Similary, **2a** was photochemically alkylated at the 3-position with 2-phenyl-1-propene (**3b**) and styrene (**3c**), giving **4b** and **4c** in 38 and 28% yields, respectively. In an analogous fashion, **2b** underwent the photoalkylation at the 3-position upon irradiation



	R^1
2a	CH_3
2b	nPr

	R^2	R^3
3a	Ph	Ph
3b	Ph	CH_3
3c	Ph	H

	R^1	R^2	R^3
4a	CH_3	Ph	Ph
4b	CH_3	Ph	CH_3
4c	CH_3	Ph	H
4d	nPr	Ph	Ph
4e	nPr	Ph	CH_3
4f	nPr	Ph	H

(2)

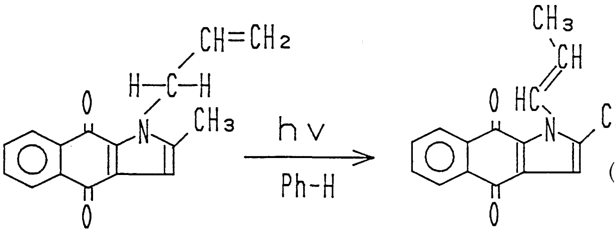
Table 1. Photochemical Alkylation Reaction of **2a** and **2b** with Arylalkene (**3a**—**c**) in Benzene

Quinone	Olefins	Irr. time/h	Conv.[a) %]	Yields[b) of 4/%]
2a	**3a**	1	50	40
2a	**3b**	1	60	38
2a	**3c**	1	48	28
2b	**3a**	0.3	45	31
2b	**3b**	0.3	57	29
2b	**3c**	0.3	39	16

a) Conversion of **2a** and **2b**. b) Isolated yields were based on the consumed amounts of **2a** and **2b**.

in the presence of **3a**—**c** in benzene. Results are summarized in Table 1. No photochemical alkylation of **2a** and **2b** did not take place with 2-methyl-1-propene, 2-methoxy-1-propene and methyl acrylate. Interestingly, the alkylation products **4** were formed only in nonpolar solvents such benzene and dichloromethane.

Photochemical Isomerization of 1-Allyl-2-methyl-1*H*-benz[*f*]indole-4,9-dione (2c). Irradiation of the *N*-allyl quinone **2c** in benzene solution led to the formation of 2-methyl-1-(1-propenyl)-1*H*-benz[*f*]indole-4,9-dione (**5**) in 52% yield at 55% conversion of **2c**. The structure of **5** was assigned on the basis of its spectroscopic properties and elemental analysis. The ^{1}H NMR spectrum of **5** showed the presence of *N*-(1-propenyl) substituent at δ=1.95 (N-CH=CH-$\underline{CH_3}$), 5.85 (N-CH=C$\underline{H}$-CH$_3$), and 7.1 (N-C$\underline{H}$=CH-CH$_3$); the mass spectrum showed a peak at 251 (M$^+$). The photoisomerization product **5** can be regarded as an intramolecular 1,3-hydrogen shift product. Irradiation of **2c** in the presence of **3a** did not give the photoalkylation product but gave **5** in 10% yield.



(3)

2c **5**

Absorption and Fluorescence Spectra of 2a. The shape and wavelength maxima(λ_{max}) of **2a** and **2c** in the absorption spectra of **2a** and **2c** do not exhibit substratial solvent polarity dependence. In contrast, the fluorescence of **2a** was found to undergo a large bathochromic shift upon the increase of solvent polarity (Table 2). The fluorescence of **2a** in benzene exhibited a broad band centered at λ_{max} 500 nm with lifetime of 3.1 ns at room temperature, while the fluorescence maximum in acetonitrile was observed at 526 nm with lifetime of 4.5 ns. These results suggest that the lowest singlet excited state (S$_1$) of **2a** has a partially charge transfer character.[3] Importantly, the floresence of **2a** was not quenched by **3a**—**c** in benzene.

Mechanistic Consideration of the Photoinduced Alkylation Reaction of 2 with 3a—c. The fact that the fluorescence of **2a** was not quenched by **3a**—**c** strongly indicated the triplet origin for the formation of **4**. In accord with this consideration, the photoinduced alkylation reaction was sensitized by benzil (E_T=53 kcal mol^{-1}),[4] but was efficiently quenched by anthracene (E_T=42 kcal mol^{-1}).[4] In ether–isopentane–ethanol (EPA) matrix at 77 K, a broad phosphorescence band of **2a** was observed at λ_{max} 564 nm. Thus, the energy of the lowest triplet excited state(T_1) of **2a** estimated from 0–0 phosphorescence band was ca 51.2 kcal mol^{-1}. In the presence of **3a**, this phosphorescence band was very weakened as compared with that in the absence of **3a**, indicating a decaying path for T_1-state of **2a** through the intereraction of **3a**. Electron transfer from **3a**—**c** to ^{3}(**2a**)* may be excluded, since the Rehn–Weller estimation[5] of free energy charges (ΔG) associated with the triplet electron transfer gives rather high positive values(+8—+10 kcal mol^{-1}).[6] A plausible mechanism for the formation of **42** is shown in Eq. 2. The reaction of T_1 of **2a** with **3** leads to the formation of 1,4-biradical **11**, which will give the 3-alkylated product **4** by disproportionation. When the photoreaction of **2a** with **3a**—**c** was conducted in benzene-d_6, no incorporation of deuterium atom in **4** was observed. Therefore, intramolecular 1,3-hydrogen shift may be predominant for the pathway from the intermediate **11** to **4**. In the *N*-allyl compound **2c**, the intramolecular hydrogen adstraction[7] by the quinone carbonyl group from the γ-position and subsequent disproportionation may account for the formation of **5**. Probably, this intramolecular process is much faster as compared to the intermolecular quenching by **3a**—**c**.

Table 2. Fluorescence Maxima of **2a** in Various Solvents[a),b)]

Solvent	Maxima wavelength (λ_{max}/nm)	τ/ns
Benzene	500	3.1
Chloroform	510	5.9
Acetone	519	4.9
Acetonitrile	526	4.5

a) Excited wavelength, 326 nm. b) In air-saturated solvents at room temperature; [**2a**]=4.4×10^{-5} mol dm^{-3}.

Experimental

Apparatus. Melting points were measured on Yanagimoto micro-melting points apparatus and uncorrected. Infrared spectra were taken on a JASCO-IR-1A spectrometer. Fluorescence spectra and lifetimes were measured by a JASCO FP-550 spectrometer and a Horiba NAES-1100 timeresolved spectrofluorimeter, respectively. Phosphorescence spectra were measured by a Shimazu RF-502A spectrometer. NMR spectra were recorded on a JEOL GX-400 (400 MHz), a JEOL GX-270 (270 MHz), and a JEOL FX-900 (90 MHz) spectrometer with use of tetramethylsilane as an internal standard and the chemical shifts are expressed in δ values. UV spectra were taken by using a JASCO UVIDEC-1 spectrometer. Elemental analyses were performed at the Microanalytical Laboratory of Kyoto University and Advanced Instrumentation Center for Chemical Analysis, Ehime University. Mass spectra were recorded on a Hitachi M-2000 spectrometer.

Materials. 1-Alkyl-3-methyl-1*H*-benz[*f*]indole-4,9-dione **2a**—**c** were prepared according to a procedure in the literature.[2] Alkenes **3a**—**c** were commercially available and purified by distillation.

General Procedure for the Photochemical Reaction of 1-Alkyl-3-methyl-1*H*-benz[*f*]indole-4,9-dione 2 with Alkenes 3 and Product Isolation: A degassed solution of **2** (1.50 mmol) and **3** (1.80 mmol) in 300 cm^3 of benzene in a Pyrex vessel, using a 300-W high-pressure mercury lamp. The progress of the reaction was followed by TLC (Merck, Kieselgel 60F$_{254}$), or NMR. After evaporation of the solvent, the residual oil was separated by column chromatography on silica gel (Wakogel C-200, 74-149 μm) with benzene/dichloromethane as an eluent.

Physical Properties of Photoproducts. 1,2-Dimethyl-3-(2,2-diphenylethyl)-1*H*-benz[*f*]indole-4,9-dione (4a): Mp

217—219 °C; ^1H NMR (270 MHz, $CDCl_3$) δ=1.90 (3H, s), 3.50 (2H, d, J=7.6 Hz), 3.90 (3H, s, NMe), 4.40 (1H, t, J=7.6 Hz), 7.20 (10H, s), 7.6—7.7 (2H, m), 8.1—8.2 (2H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ=19.0 (q), 31.9 (q), 32.7 (t), 51.2 (d), 121.8 (s), 125.2 (s), 126.1 (d), 128.2 (d), 128.4 (d), 129.9 (s), 130.6 (s), 134.3 (s), 138.6 (s), 144.6 (s), 175.4 (s, C=O), 181.8 (s, C=O); IR (KBr) 1646, 1588, 1470, 1258, 722, 706 cm^{-1}. MS (20 eV), m/z 405(M$^+$); UV (λ_{max}, nm (log ε), CH_3CN) 270 (4.53), 334 (3.66), 431 (3.74). Found: C, 82.84; H, 5.70; N, 3.41%. Calcd for $C_{28}H_{23}N_1O_2$: C, 82.94; H, 5.72; N, 3.45%.

1,2-Dimethyl-3-(2-phenylpropyl)-1*H*-benz[*f*]indole-4,9-dione (4b): Mp 148—149 °C; ^1H NMR (270 MHz, $CDCl_3$) δ=1.36 (2H, d, J=6.7 Hz), 1.79 (3H, s), 2.83 (1H, m), 3.10 (1H, dd, J=5.5 and 13 Hz), 3.18 (1H, dd, J=7 and 12 Hz), 3.93 (3H, s), 7.2 (5H, s), 7.6—7.7 (2H, m), 8.1—8.2 (2H, m); IR (KBr) 2960, 2924, 1646, 1590, 1498, 1252, 1178, 980, 722, 700 cm^{-1}. MS (20 eV) m/z 343 (M$^+$); UV(λ_{max} nm (log ε), CH_3CN) 270 (4.69), 366 (3.82), 428 (3.87). Found: C, 80.60; H, 6.01; N, 4.19%. Calcd for $C_{23}H_{21}N_1O_2$; C, 80.44; H, 6.16; N, 4.08%.

1,2-Dimethyl-3-(2-phenylethyl)-1*H*-benz[*f*]indole-4,9-dione (4c):Mp 146—147 °C; ^1H NMR (270 MHz, $CDCl_3$) δ=1.85 (3H, s), 2.90 (2H, t, J=7.5 Hz), 3.1 (2H, t, J=7.5 Hz), 3.95 (3H, s), 7.2 (5H, s), 7.6—7.7 (2H, m), 8.1—8.2 (2H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ=9.2 (q), 27.5 (t), 32.8 (q), 36.5 (t), 123.2 (s), 125.8 (d), 126.2 (d), 128.3 (d), 128.9 (d), 132.7 (d), 132.8 (d), 134.4 (s), 137.9 (s), 142.2 (s), 175.5 (s, C=O), 181.9 (s, C=O); IR (KBr) 1645, 1587, 1498, 1410, 1249, 1196, 956, 790, 725, 705 cm^{-1}. MS (20 eV) m/z 329 (M$^+$); UV (λ_{max}, nm (log ε), CH_3CN) 269 (4.49), 335 (3.50), 426 (3.53). Found: C, 80.08; H, 5.70; N, 4.19%. Calcd for $C_{22}H_{19}N_1O_2$: C, 80.22; H, 5.81; N, 4.25%.

1-Propyl-2-methyl-3-(2,2-diophenylethyl)-1*H*-benz[*f*]indole-4,9-dione (4d): Mp 181—182 °C; ^1H NMR (90 MHz, $CDCl_3$) δ=0.8 (3H, t, J=7.3 Hz), 1.5—1.8 (2H, m), 1.6 (3H, s), 3.45 (2H, d, J=7.7 Hz), 4.1—4.4 (3H, m), 7.2 (10H, s), 7.5—7.7 (2H, m), 8.0—8.2 (2H, m); IR (KBr) 2960, 2920, 1645, 1588, 1495, 1288, 720, 700 cm^{-1}. MS (20 eV) m/z 433 (M$^+$); UV (λ_{max}, nm (log ε), CH_3CN) 271 (4.87), 336 (4.04), 432 (4.10). Found: C, 83.20; H, 6.23; N, 3.33%. Calcd for $C_{30}H_{27}N_1O_2$: C, 83.11; H, 6.28; N, 3.23%.

1-Propyl-2-methyl-3-(2-phenylpropyl)-1*H*-benz[*f*]indole-4,9-dione (4d): Mp 79—81 °C; ^1H NMR (270 MHz, $CDCl_3$) δ=0.91 (3H, t, J=7.3 Hz), 1.40 (3H, dd, J=7.0 Hz), 1.66 (2H, m), 1.72 (3H, s), 2.76 (1H, m), 3.11 (1H, dd, J=6.7 and 13.7 Hz), 3.21 (1H, dd, J=6.3 nad 12.7 Hz), 4.20 (1H, m), 4.38 (1H, m), 7.2 (5H, s), 7.5—7.7 (2H, m), 8.0—8.2 (2H, m); IR (KBr) 2966, 2934, 1651, 1591, 1497, 1460, 1251, 1172, 988, 762, 719, 702 cm^{-1}. MS (20 eV) m/z 371 (M$^+$); UV (λ_{max}, nm (log ε), CH_3CN) 271 (4.49), 337 (3.66), 429 (3.70). Found: C, 81.11; H, 6.84; N, 3.72%. Calcd for $C_{25}H_{25}N_1O_2$: C, 80.83; H, 6.78; N, 3.77%.

1-Propyl-2-methyl-3-(2-phenylethyl)-1*H*-benz[*f*]indole-4,9-dione (4f): Mp 116—117 °C; ^1H NMR (90 MHz, $CDCl_3$) δ=0.9 (3H, t, J=7.0 Hz), 1.62 (2H, m), 1.80 (3H, s), 3.0—3.2 (4H, m), 4.3 (2H, t, J=7.0 Hz), 7.2 (10H, s), 7.5—7.7 (2H, m), 8.0—8.2 (2H, m); IR (KBr) 2920, 1640, 1590, 1492, 1459, 1430, 1228, 720, 695 cm^{-1}. MS (20 eV) m/z 357 (M$^+$); UV (λ_{max}, nm (log ε), CH_3CN) 271 (4.70), 335 (3.87), 429 (3.90). Found: C, 80.90; H, 6.67; N, 3.93%. Calcd for $C_{24}H_{23}N_1O_2$: C, 80.64; H, 6.48; N, 3.92%.

1-(1-Propenyl)-2-methyl-1*H*-benz[*f*]-indole-4.9-dione (5): Mp 154—156 °C; ^1H NMR (400 MHz, $CDCl_3$) δ=1.95 (3H, d, J=0.92 Hz), 2.35 (3H, s), 5.86 (1H, sext, J=7 Hz), 6.55 (1H, s), 7.16 (1H, dd, J=7 and 1 Hz), 7.6—7.7 (2H, m), 8.1—8.2 (2H, m); IR (KBr) 3120, 2920, 1657, 1621, 1585, 1500, 1415, 1235, 980, 710 cm^{-1}. MS (20 eV) m/z 251 (M$^+$); UV (λ_{max}, nm (log ε), CH_3CN) 260 (4.60), 326 (3.88), 408 (3.62). Found: C, 76.56; H, 5.23; N, 5.61%. Calcd for $C_{16}H_{13}N_1O_2$: C, 76.48; H, 5.21; N, 5.57%.

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