Photochemical Reaction of 1,4-Naphthoquinone Derivatives with Pyrrole Derivatives. Synthesis of 2-(2-Pyrrolyl)-1,4-naphthoquinone Derivatives

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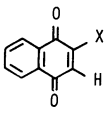
(Received April 24, 1985)

Synopsis. Photochemical reaction of 2-bromo-1,4-naphthoquinone derivatives with pyrrole derivatives in benzene gave regioselectively 2-(2-pyrrolyl)-1,4-naphthoquinone derivatives. Photoinduced electron transfer process may be involved in the reaction.

Thermal reaction of *p*-benzoquinone with pyrrole derivatives has attracted much attention from the viewpoint of dye development,[1] but that of less reactive 1,4-naphthoquinone derivatives has never been investigated. In our previous papers[2] it was reported that photochemical reactions of 2,3-dichloro-1,4-naphthoquinone (**1j**) with furan and thiophene derivatives gave 2-chloro-3-(2-furyl)- and (2-thienyl)-1,4-naphthoquinone derivatives. In this paper, we shall describe photochemical reactions of 1,4-naphthoquinone derivatives **1** with pyrrole derivatives **2**. Some of the reactions afforded 2-(2-pyrrolyl)-1,4-naphthoquinone derivatives **3**, but others failed to give the similar products **3**. The success of the photoreaction to yield **3** depends upon the formation of the charge transfer (CT) complex of **1** with **2** in the ground state.

Results and Discussion

When a benzene solution of 2-bromo-3-methoxy-1,4-naphthoquinone (**1a**) and 1-methylpyrrole (**2a**) was irradiated by a high pressure mercury arc lamp, the yellow solution immediately turned to pale red. Upon only five minutes irradiation at room temperature, 57% of **1a** was consumed and 2-methoxy-3-(1-methyl-2-pyrrolyl)-1,4-naphthoquinone **3a** was isolated as a sole product after the purification of the reaction mixture by column chromatography.



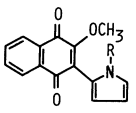
1f—i

1f; X = OCH_3
g; X = CH_3
h; X = H
i; X = Cl

2b—e

2b; R = H
c; R = C_2H_5
d; R = $CH_2C_6H_5$
e; R = $COCH_3$

The photochemical reactions of a variety of 1,4-naphthoquinone derivatives **1b—j** with **2a** were examined. The reactions of **1b—d** with **2a** gave **3b—d**, but those of **1e—j** with **2a** gave no similar compounds **3**. The pyrrole **2a** formed CT complexes with **1a—d**, **h—j** depending upon their reduction potentials $E_{1/2}$.[3] The formation of the CT complexes whose formation constants K reflect $E_{1/2}$ of **1** is an important requisition for the photochemical reaction. Moreover, the rather weak C–Br bond is necessary for the successful formation of **3**. The important contribution of the CT complex formation was further suggested by perturbing the pyrrole moiety. Pyrrole derivatives **2b—d** formed CT complexes with **1a**. Photoreactions of **1a** with **2b—d** gave 2-methoxy-3-(2-pyrrolyl)-1,4-naphthoquinone derivatives **3e—g**. Pyrrole derivative **2e** containing electron-withdrawing substituent formed no CT complex and induced no similar reaction. On the other hand, 1,2,5-trimethylpyrrole



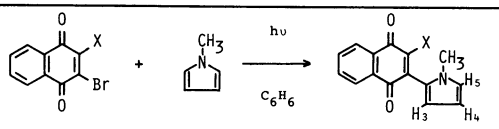
3e—g

3e; R = H
f; R = C_2H_5
g; R = $CH_2C_6H_5$

(**2f**) formed CT complex with **1a**. The photoreaction of **1a** with **2f**, however, gave no similar product because both the reactive α-positions of the pyrrole were blocked by methyl groups. The reaction of **1a** with 1-methylindole (**2g**) also gave similar products. In this case, the products were consisted of two isomers; *i.e.*, α-substituted **3h** (50%) and isomeric β-substituted **3i** (10%) (see Scheme 1). Any products photosubstituted on positions of fused benzene ring of **2g** were not obtained.

This reaction did not proceed by heat,[6] but only by light. The CT formation between two reactants seems to be prerequisite for the successful product formation as described above. In addition, it was reported that cyanide ion dominantly attacked α-position of cation radical of **2a** and attacked both α-position (85%) and β-position (15%) of cation radical of **2g**.[7] The photochemical reaction had the same regioselectivity. Judging from the above facts, the photo-

TABLE 1. REACTION OF 2-BROMO-1,4-NAPHTHOQUINONE DERIVATIVE **1a—e** WITH 1-METHYLPYRROLE **2a**



1a—e **2a** **3a—d**

X		$E_{1/2}$[a]/V	K[b]/dm³ mol⁻¹	Yield[c]/%
$N(CH_3)_2$	(**1e**)	−1.18	0	*[d]
CH_3	(**1b**)	−0.97	0.04	38 (**3b**)
OCH_3	(**1a**)	−0.92	0.09	64 (**3a**)
H	(**1c**)	−0.86	0.15	4 (**3c**)
Br	(**1d**)	−0.77	0.20	75 (**3d**)

a) Determined by cyclic voltammetry using Ag/0.01 mol dm^{-3} $AgClO_4$ (in CH_3CN) as a reference electrode. See Ref 4). b) Determined by UV technique at 22°C. See Ref 2). c) All yields were based on consumed **1**. d) The only product isolated was 2-bromo-3-methylamino-1,4-naphthoquinone which did not react with **2a**. See Ref. 5).

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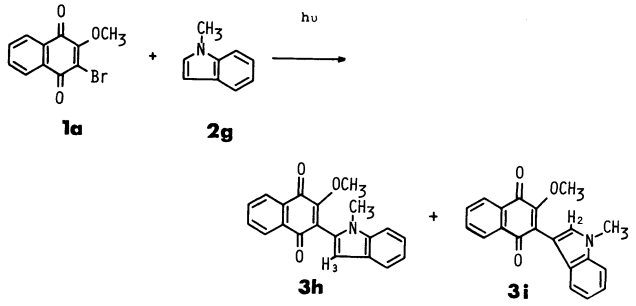

Scheme 1.

chemical reaction may include initial electron-transfer process from **2** to **1**.[8]

Experimental

General Procedure. A benzene solution (30 ml) of **1** (0.1 mmol) and 10 equivalents of **2** (1 mmol) was irradiated by a high pressure mercury arc lamp (300 W) through $CuSO_4$ aq solution filter under nitrogen atmosphere at room temperature. After irradiation for a suitable time[9] the starting quinone **1** and the photosubstituted product **3** were isolated by using column chromatography on silica gel with benzene as an eluent. All yields were based on consumed **1**.

Identification of the Products. *2-Methoxy-3-(1-methyl-2-pyrrolyl)-1,4-naphthoquinone* ***3a***: 64% yield; purple needles; mp 119—120 °C (from ethanol); UV (ethanol) 494.5 nm (ε 1800); IR (KBr) 1660 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=3.5 (3H, s), 3.75 (3H, s), 6.2—6.4 (2H, m, H_3 and H_4), 6.8—6.9 (1H, m, H_5), 7.7—7.9 (2H, m), and 8.1—8.3 (2H, m); ^{13}C NMR ($CDCl_3$) δ=35.00 (q), 60.59 (q), 108.51 (d, C-H_3), 113.78 (d, C-H_4), 121.66 (s), 121.99 (s), 124.50 (d, C-H_5), 126.29 (d), 126.61 (d), 131.33 (s), 131.98 (s), 133.44 (d), 134.09 (d), 157.89 (s), 181.28 (s), and 184.60 (s); MS *m/z* (rel intensity) 267 (M^+; 100), 252 (M^+—CH_3; 20), 238 (M^+—NCH_3; 10), 224 (30), 184 (8), 170 (17), 157 (14), 156 (45), and 142 (60); Found: C, 72.08; H, 4.92; N, 5.27%; *m/z* 267.0875. Calcd for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24%; M, 267.0895.

2-Methyl-3-(1-methyl-2-pyrrolyl)-1,4-naphthoquinone ***3b***: 38% yield; red needles; mp 99.5—100.5 °C; Found: C, 76.24; H, 5.42; N, 5.52%; M^+, 251. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57%; M, 251.

2-(1-Methyl-2-pyrrolyl)-1,4-naphthoquinone ***3c***: 4% yield; red plates; mp 95—6 °C; Found: C, 76.11; H, 4.56; N, 5.87%; M^+, 237. Calcd for $C_{15}H_{11}NO_2$: C, 75.93; H, 4.67; N, 5.90%; M, 237.

2-Bromo-3-(1-methyl-2-pyrrolyl)-1,4-naphthoquinone ***3d***: 75% yield; purple needles; mp 156—8 °C; Found: C, 57.23; H, 3.25; N, 4.26; Br, 24.99%; M^+, 315 and 317. Calcd for $C_{15}H_{10}NO_2Br$: C, 56.99; H, 3.19; N, 4.43; Br, 25.27%; M, 315 and 317.

2-Methoxy-3-(2-pyrrolyl)-1,4-naphthoquinone ***3e***: 10% yield; purple needles; mp 115—9 °C; UV (ethanol) 521 nm (ε 4800); IR (KBr) 3400 cm^{-1} (NH); Found: C, 70.95; H, 4.37; N, 5.29%; M^+, 253. Calcd for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N, 5.53%; M, 253.

2-(1-Ethyl-2-pyrrolyl)-3-methoxy-1,4-naphthoquinone ***3f***: 60% yield; purple needles; mp 114—9 °C; Found: C, 72.35; H, 5.33; N, 4.81%; M^+, 281. Calcd for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.37; N, 4.98%; M, 281.

2-(1-Benzyl-2-pyrrolyl)-3-methoxy-1,4-naphthoquinone ***3g***: 50% yield; purple needles; mp 119—121 °C; Found: C,76.78; H, 4.88; N, 4.03; M^+, 343. Calcd for $C_{22}H_{17}NO_3$: C, 76.95; H, 4.99; N, 4.08%; M, 343.

2-Methoxy-3-(1-methyl-2-indolyl)-1,4-naphthoquinone ***3h***: 50% yield; red needles: mp 192—5 °C; UV (ethanol) 487 nm (ε 1200); ^1H NMR ($CDCl_3$) δ=6.6 (1H, m, H_3); Found: C, 75.45; H, 4.60; N, 4.32%; M^+, 317. Calcd for $C_{20}H_{15}NO_3$: C, 75.69; H, 4.76; N, 4.41%; M, 317.

2-Methoxy-3-(1-methyl-3-indolyl)-1,4-naphthoquinone ***3i***: 10% yield; purple needles; mp 131—5 °C; UV (ethanol) 513 nm (ε 2900); ^1H NMR ($CDCl_3$) δ=7.56 (1H, m, H_2); Found: C, 75.54; H, 4.79; N, 4.54%; M^+, 317. Calcd for $C_{20}H_{15}NO_3$: C, 75.69; H, 4.76; N, 4.41%; M, 317.

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2) K. Maruyama and T. Otsuki, *Bull. Chem. Soc. Jpn.*, **50**, 3429 (1977); *Chem. Lett.*, **1977**, 851.

3) When **2a** was added to a benzene solution of **1a**, a new absorption band (λ_{max}=449 nm) appeared. The CT formation of **1e—g** with **2a** was not recognized.

4) K. Maruyama, T. Otsuki, and S. Tai, *J. Org. Chem.*, **50**, 52 (1985).

5) D. W. Cameron and R. G. F. Giles, *J. Chem. Soc. (C)*, **1968**, 1461.

6) Reaction of **1** with **2** gave no similar product even by refluxing in benzene under nitrogen atmosphere.

7) K. Yoshida, *J. Am. Chem. Soc.*, **101**, 2116 (1979).

8) The electron transfer may occur *via* the excitation of the CT complex of **1** with **2** or the formation of the encounter complex of photo-excited **1** with **2**. Then the formed ion radical pair or exciplex seemed to give **3** (see Ref. 4). Therefore, the reaction showed solvent effect; in polar solvents (acetonitrile, methanol) it gave no **3** but in nonpolar solvents (hexane, carbon tetrachloride, benzene) it gave **3**.

9) Irradiation time was 5 min for **3a**, **f**, **g**, 10 min for **3e**, **h**, **i**, 30 min for **3b**,**c**, and 10 h for **3d**.