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The Photochemical Synthesis of 2-Chloro-3-(2-furyl)-1,4-naphthoquinones

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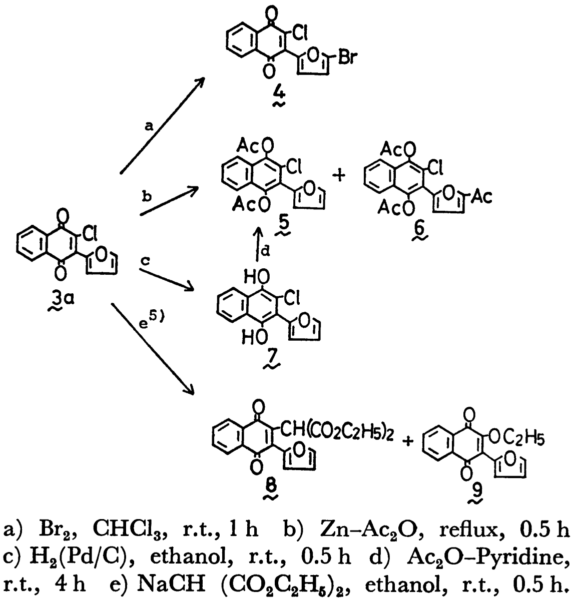
Synopsis. Upon the irradiation of a benzene solution of 2,3-dichloro-1,4-naphthoquinone, **1**, and furan derivatives, **2**, 2-chloro-3-(2-furyl)-1,4-naphthoquinones, **3**, were obtained, accompanyed by a liberation of hydrogen chloride. The formation of a CT-complex between **1** and **2** was essential for the progress of the reaction. The ^{1}H-CIDNP signals which were observed during irradiation suggest an intervention of a radical pair in the reaction.

Many workers have reported synthetic methods of a variety of quinones, applying the addition reaction of radicals to quinones,[1] the reaction of organometallic reagents with quinones,[1] and the photochemical reaction of quinones with aldehydes.[2] Here we wish to report on a new photochemical synthetic route to 2-furyl derivatives of 1,4-naphthoquinones.

Results and Discussion

As a typical example the photochemical reaction of 2,3-dichloro-1,4-naphthoquinone, **1**, with the **2a** furan will be illustrated. The irradiation of a benzene solution of **1** and **2a** by a high-pressure Hg arc lamp gave a photo-substitution product, **3a**, as red needles in a yield of 82%, accompanied by the liberation of hydrogen chloride. The hydrogen chloride liberated in the reaction was estimated by titration with a standardized aqueous sodium hydroxide solution; the amount of it reached 84% of that of **3a**. The structure of **3a** was compatible with its spectral data and was further confirmed by its chemical reactions (Scheme 1).[3-5]

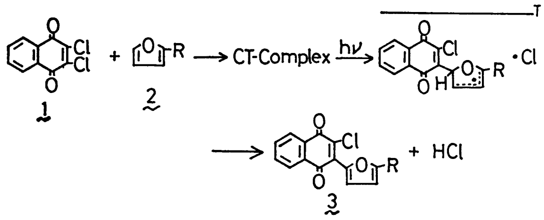


a) Br_2, $CHCl_3$, r.t., 1 h b) Zn-Ac_2O, reflux, 0.5 h c) H_2(Pd/C), ethanol, r.t., 0.5 h d) Ac_2O-Pyridine, r.t., 4 h e) NaCH $(CO_2C_2H_5)_2$, ethanol, r.t., 0.5 h.

Scheme 1.

When the photochemical reaction was examined by means of the ^{1}H-CIDNP technique, strongly polarized signals were observed during the course of the reaction (Fig. 1). The polarized signals, 1, 2, and 3, were all assignable to furyl-ring protons of **3a**. This suggests that the photo-substitution product, **3a**, is produced *via* a radical pair.

When **2a** was added to a benzene solution of **1** (λ_{max}: 439 nm), a new absorption band (λ_{max}: 465 nm) (shoulder) appeared which was ascribable to the CT-complex between **1** and **2a**.[6,7] When the CT-band was irradiated by the light of a selected wavelengthth (λ_{max}: 488 nm, $\Delta_{1/2}$=20 nm), the product, **3a**, was exclusively produced, the yield being improved to 92%. This result indicates an important contribution of the CT-complex in the initial stage of the reaction (Scheme 2).



R=**a**: H, **b**: CH_3, **c**: CH_2OCH_3, **d**: $CH_2OC_2H_5$, **e**: $CH_2OC_3H_7$, **f**: CH_2O-phytyl **g**: CH_2O-tetra-*O*-acetyl-*β*-D-glycopyranosyl, **h**: CH_2OCOCH_3, **i**: CH_2OCO-CH_2N-phthaloyl.

Scheme 2.

Such furan derivatives as **2a**—**i**, which formed CT-complexes with **1**, behaved similarly in the photochemical reaction and gave photo-products, **3a**—**i**, in fairly good yields (*cf.* Experimental). Thus, the present reaction provides a good method of synthesizing 2-chloro-3-(2-furyl)-1,4-naphthoquinones. During the course of all the reactions, the ring- and α-protons of furyl ring due to the corresponding photo-substitution products, **3a**—**i**, showed polarized ^{1}H-CIDNP signals (Figs. 1—3). In contrast, such furan derivatives as **2j**—**n**, which gave no indication of CT-complex formation with **1**, did not undergo a similar photo-substitution reaction. The importance of the formation of the CT-complex was further supported by the results of the photochemical reactions of other 1,4-naphthoquinones with **2a**. That is, 2,3-dibromo-1,4-naphthoquinone gave a photo-substitution product, **10**, in the reaction with **2a**, but 2-chloro- and 2-bromo-1,4-naphthoquinone gave another types of products.[8]

2j—**n**

R = **j** : CHO
k : $CH(SCH_2)_2$
l : CO_2H
m : CO_2CH_3
n : Benzofuran

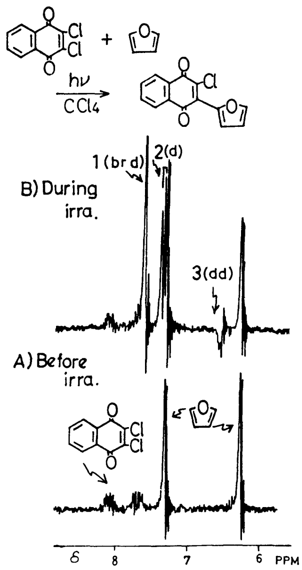


Fig. 1. ¹H-NMR spectra observed in the photochemical reaction of **1** with **2a** (Solvent: CCl$_4$). A) Before irradiation, B) during irradiation. Signal 1, 2, and 3 are polarized signals.

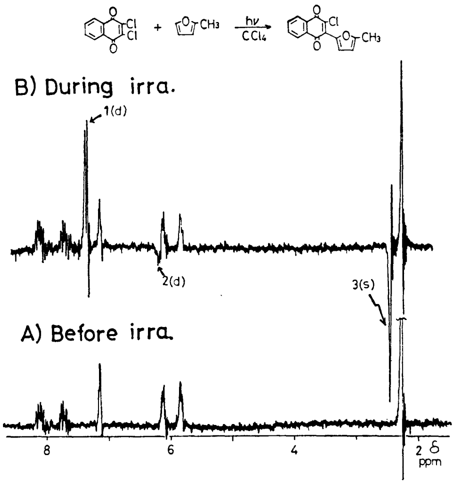


Fig. 2. ¹H-NMR spectra observed in the photochemical reaction of **1** with **2b** (Solvent: CCl$_4$). A) before irradiation, B) during irradiation. Signals 1, 2, and 3 are polarized signals.

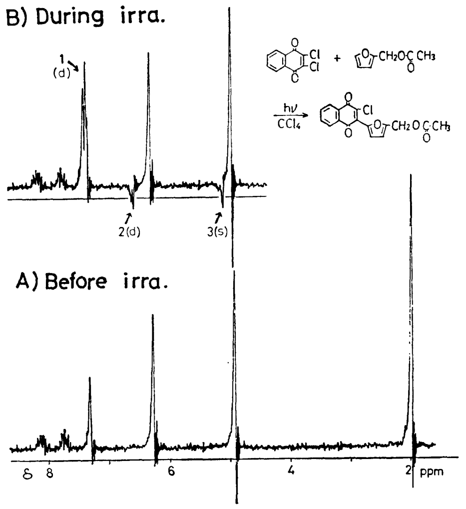


Fig. 3. ¹H-NMR spectra observed in the photochemical reaction of **1** with **2h** (Solvent: CCl$_4$). A) Before irradiation, B) during irradiation. Signals 1, 2, and 3 are polarized signals.

Experimental

General Procedure. A benzene solution of 2,3-dichloro-1,4-naphthoquinone, **1** (1.5×10^{-3} M), and an excess amount of a furan derivative, **2** (*ca.* 4.5×10^{-2} M), was irradiated by means of a high-pressure Hg arc lamp (300 W) at room temperature. After the complete consumption of **1**, the photosubstitution product, **3**, was isolated using chromatography on silica gel.

Identification of the Products. *2-Chloro-3-(2-furyl)-1,4-naphthoquinone (3a)*; red needles, mp 137—138 °C; yield, 82 %. Found: C, 64.95; H, 2.88; Cl, 13.69%. Calcd for $C_{14}H_7O_3Cl$: C, 65.00; H, 2.73; Cl, 13.71%. Mass m/e=260, 258 (M$^+$). IR(KBr) 1680, 1665 cm^{-1}. NMR(CDCl$_3$) δ 6.60 (1H, d of d, J=4 and 2Hz), 7.40 (1H, d, J=4 Hz), 7.72 (1H, d, J=2 Hz), 7.6—7.8 (2H, m), 8.0—8.2 (2H, m). UV λ_{max} (CHCl$_3$): 443 nm (ε: 5.5×10^3), 321 (sh) (5.6×10^3), 272 (2.2×10^4). *2-Chloro-3-(5-methyl-2-furyl)-1,4-naphthoquinone (3b)*; red crystals, mp 123 °C; yield, 65%. Mass m/e=272 (M$^+$). *2-Chloro-3-(5-methoxymethyl-2-furyl)-1,4-naphthoquinone (3c)*; red crystals; mp 107—108 °C; yield, 49%. Mass m/e=304, 302 (M$^+$). *2-Chloro-3-(5-ethoxymethyl-2-furyl)-1,4-naphthoquinone (3d)*; red crystals; mp 68 °C; yield, 38%. Mass m/e=318, 316 (M$^+$). *2-Chloro-3-(5-propoxymethyl-2-furyl)-1,4-naphthoquinone (3e)*; red crystals; mp 51.5—53.0 °C; yield, 51%. Mass m/e=322,330 (M$^+$). *2-Chloro-3-(5-phytyloxymethyl-2-furyl)-1,4-naphthoquinone (3f)*; yellow oil; yield 7%. IR (KBr) 1680 cm^{-1}. NMR(CDCl$_3$) δ 0.8—2.2 (36 H, m), 4.10 (2H, d, J=8 Hz), 4.54 (2H, s), 5.36 (1H, t, J=8 Hz), 6.56 (1H, d, J=4 Hz), 7.42 (1H, d, J=4 Hz), 7.7—7.9 (2H, m), 8.0—8.2 (2H, m). *2-Chloro-3-[5-(tetra-O-acetyl-β-*D*-glucopyranosyloxymethyl)-2-furyl]-1,4-naph-thoquinone (3g)*; red crystals; mp 160 °C (dec); yield, 22%. IR(KBr) 1755, 1735, 1720, 1675 cm^{-1}. NMR(CDCl$_3$) δ 2.00 (3H, s), 2.04 (6H, s), 2.12 (3H, s), 4.1—5.3 (9H, m), 6.64 (1H, d, J=4 Hz), 7.48 (1H, d, J=4 Hz), 7.7—7.9 (2H, m), 8.1—8.3 (2H, m). *2-Chloro-3-(5-acetoxymethyl-2-furyl)-1,4-naphthoquinone (3h)*; red crystals; mp 96—97 °C; yield, 47%. Mass m/e=322,330 (M$^+$). *2-Chloro-3-[5-(*N*-phthaloylglycyloxymethyl)-2-furyl]-1,4-naphthoqiunone (3i)*; red crystals; mp 140—142 °C; yield, 25%. IR(KBr) 1770, 1750, 1720, 1670 cm^{-1}. NMR(CDCl$_3$) δ 4.48 (2H, s), 5.26 (2H, s), 6.66 (1H, d, J=4 Hz), 7.38 (1H, d, J=4 Hz), 7.6—8.0 (6H, m), 8.0—8.2 (2H, m). *2-Bromo-3-(2-furyl)-1,4-naphthoquinone (10)*; red crystals; mp 146—147 °C; yield, 40%. Mass m/e=304,302(M$^+$).

References

1) K. T. Finkley, in "The Chemistry of the Quinonoid Compounds," ed by S. Patai, John Wiley & Sons, London (1974), p. 877.

2) J. M. Bruce, in "The Chemistry of Quinonoid Compounds," ed by S. Patai, John Wiley & Sons, London (1974), p. 465; K. Maruyama and Y. Miyagi, *Bull. Chem. Soc. Jpn.*, **47**, 1303 (1974).

3) 2-Acetyl-3-(2-furyl)-1,4-naphthoquinone has been prepared by the thermal reaction of 2-acetyl-1,4-naphthoquinone with furan; *cf.* C. H. Eugster and P. Bosshard, *Helv. Chim. Acta*, **46**, 815 (1963); N. B. Bauman, S. Fumagalli, G. Weisgerber, and C. H. Eugster, *ibid.*, **49**, 1794 (1966).

4) In the present reaction neither cyclobutanes nor oxetanes were isolated, in contrast to the usual photochemical reaction of furan derivatives with 1,4-naphthoquinone; *cf.* C. H. Krauch and S. Farid., *Tetrahedron Lett.*, **1960**, 4783.

5) The substitution of the chlorine atom of 2,3-dichloro-1,4-naphthoquinone has been reported; *cf.* Fr. Michel, *Chem. Ber.*, **33**, 2402 (1900).

6) *K*, the equilibrium constant for complex formation, was estimated to be 2.8 l/mol by the aid of the Benesi-Hidebrand relation.

7) The new absorption band was comparable to that of the CT-complex between **1** and hexamethylbenzene; *cf.* S. Chatterjee, *J. Chem. Soc., B*, **1971**, 2194. Furan has been reported to form CT-complexes with some electron acceptors, such as chloranil; *cf.* Z. Yoshida and T. Kobayashi, *Tetrahedron*, **26**, 267 (1970).

8) Upon irradiation with 2-chloro- or 2-bromo-1,4-naphthoquinones, the **2a** furan yielded the usual [2+2] photoaddition products.