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Photo-induced Reaction of 2-Alkoxy-3-bromo-1,4-naphthoquinones with Acetylenes: Formation of 2-Aryl-substituted Naphtho[2,3-*b*]furan-4,9-diones

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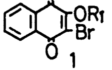
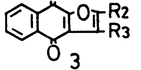
Synopsis. 2-Aryl-substituted naphtho[2,3-*b*]furan-4,9-diones **3** were obtained as a major product in the photochemical reaction of 2-alkoxy-3-bromo-1,4-naphthoquinones with acetylenes.

The photochemical reaction of 2-alkoxy-3-bromo-1,4-naphthoquinones with several acetylenes has been investigated. One of the major products in the reaction was product **3**. Interestingly, the reaction product is of a quite different type from that of the reaction of 2-alkoxy-3-bromo-1,4-naphthoquinone with olefins.[1] Pappas and Farid,[2] on the other hand, have reported the photochemical reaction of 2-alkoxy-1,4-naphthoquinones with acetylenes, but their products were cyclobutene derivatives, which are different from those of the present reaction.


1

R_2-C≡C-R_3

2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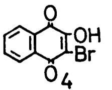
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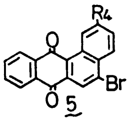
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As a typical example, the photochemical reaction of 2-bromo-3-methoxy-1,4-naphthoquinone with phenylacetylene is described. On irradiating the benzene solution of 2-bromo-3-methoxy-1,4-naphthoquinone **1a** ($R_1=CH_3$) and phenylacetylene **2a** ($R_2=C_6H_5$, $R_3=H$) by means of a high pressure Hg arc lamp, 2-phenylnaphtho[2,3-*b*]furan-4,9-dione **3a** ($R_2=C_6H_5$, $R_3=H$) was obtained as a major product (63% yield), accompanying with **4** and **5a** ($R_4=H$). Otherwise, **3a** can be synthesized from 2-hydroxy-1,4-naphthoquinone and phenylacetaldehyde by four reaction steps,[3] but the overall yield is not so good (about 13%). Therefore, this photochemical reaction could provide a new synthetic route to 2-arylnaphtho[2,3-*b*]furan-4,9-diones, though the applicability is rather limited. The reductive acetylation of **3a** gave 4,9-diacetoxy-2-phenylnaphtho[2,3-*b*]furan. Product **4** is likely to be the by-product of a side-reaction since it is formed on irradiation of **1a** in benzene. The structure of **5a** ($R_4=H$), which is produced in trace, was deduced by comparison of its spectral data with those of benz[*a*]anthracene-7,12-diones.[1]

The similar reaction was found to proceed in other combinations of quinones and acetylene derivatives (Table 1). The change of relative yields of **3** against those of **4** would be explicable in terms of the reactivity of the acetylenes used. Diphenylacetylene **2g** ($R_2=R_3=C_6H_5$), for example, may be hard to react with **1**, presumably due to its steric requirements. The alkyl group lost in the course of the photochemical reaction was detected as ethyl bromide (GLC) in the case of the reaction of **1b** ($R_1=C_2H_5$) with **2a**. As mentioned above, Pappas and Farid and their co-workers obtained cyclobutene derivatives in the photochemical reaction of 2-alkoxy-1,4-naphthoquinones with acetylenes.[2] Their products were different from those of the present investigation; the difference probably originates from the presence of the labile C–Br bond in the quinones examined by the present author. The pathway of the present reaction may be formularized as the following:

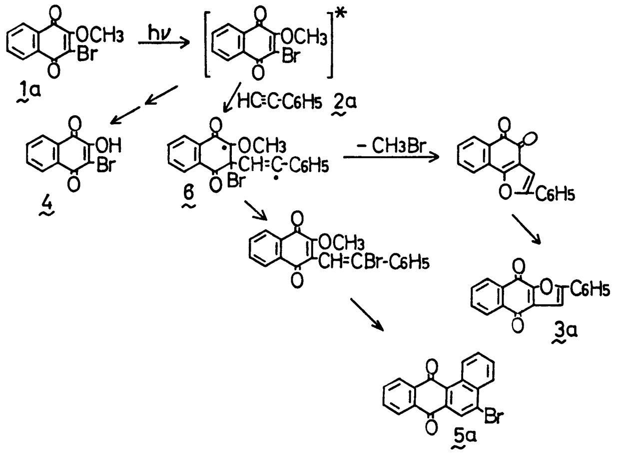

TABLE 1. THE YIELD OF THE PRODUCT IN THE PHOTOCHEMICAL REACTION

1	2	3	4	5
1a ($R_1=CH_3$)	**2a** ($R_2=C_6H_5$, $R_3=H$)	**3a**: 63% ($R_2=C_6H_5$, $R_3=H$)	8%	**5a**: trace ($R_4=H$)
1a ($R_1=CH_3$)	**2b** ($R_2=p$-CH_3-C_6H_4, $R_3=H$)	**3b**: 38% ($R_2=p$-CH_3-C_6H_4, $R_3=H$)	10%	**5b**: 9% ($R_3=CH_3$)
1a ($R_1=CH_3$)	**2c** ($R_2=p$-C_2H_5-C_6H_4, $R_3=H$)	**3c**: 48% ($R_2=p$-C_2H_5-C_6H_4, $R_3=H$)	15%	**5c**: 4% ($R_4=C_2H_5$)
1a ($R_1=CH_3$)	**2d** ($R_2=p$-C_3H_7-C_6H_4, $R_3=H$)	**3d**: 45% ($R_2=p$-C_3H_7-C_6H_4, $R_3=H$)	16%	**5d**: 5% ($R_4=C_3H_7$)
1a ($R_1=CH_3$)	**2e** ($R_2=p$-t-C_4H_9-C_6H_4, $R_3=H$)	**3e**: 31% ($R_2=p$-t-C_4H_9-C_6H_4, $R_3=H$)	14%	**5e**: 6% ($R_4=t$-C_4H_9)
1a ($R_1=CH_3$)	**2f** ($R_2=C_4H_9$, $R_3=H$)	**3f**: 5% ($R_2=C_4H_9$, $R_3=H$)	47%	—
1a ($R_1=CH_3$)	**2g** ($R_2=R_3=C_6H_5$)	0	61%	0
1b ($R_1=C_2H_5$)	**2a** ($R_2=C_6H_5$, $R_3=H$)	**3a**: 7% ($R_2=C_6H_5$, $R_3=H$)	36%	**5a**: trace ($R_4=H$)

Experimental

Starting Materials. 2-Bromo-3-methoxy-1,4-naphthoquinone and 2-bromo-3-ethoxy-1,4-naphthoquinone were prepared by the bromination of the corresponding 2-alkoxy-1,4-naphthoquinones.[4] Phenylacetylene, diphenylacetylene, and 1-hexyne were commercially available and subjected to the reaction without further purification. The other acetylenes were synthesized from substituted acetophenones.[5]

General Procedure. The benzene solution (20 ml) of a 2-alkoxy-3-bromo-1,4-naphthoquinone (0.5 mmol) and an acetylene derivative (1.0 mmol) was irradiated by means of a high pressure Hg arc lamp (300 W). After the consumption of the quinone (about 8 h), the reaction mixture was extracted with saturated sodium hydrogencarbonate solution. From the alkaline soluble fraction, 2-bromo-3-hydroxy-1,4-naphthoquinone **4** was isolated.[6] On purification of the alkaline insoluble organic layer by using TLC on silica gel, 2-substituted naphtho[2,3-*b*]furan-4,9-dione **3** and 2-substituted 5-bromobenz[*a*]anthracene-7,12-dione **5** were obtained.

Identification of the Products. *2-Phenylnaphtho[2,3-*b*]furan-4,9-dione (**3a**)*: Red needles from benzene–hexane, mp 250.0—251.0 °C. Found: C, 78.60; H, 3.57%. Calcd for $C_{18}H_{10}O_3$: C, 78.82; H, 3.68%. Mass: $m/e=274$ (M^+). IR (KBr disk): 1670 cm^{-1} (C=O). NMR ($CDCl_3$): δ; 7.18 (1H, s), 7.34—7.54 (3H, m), 7.64—7.96 (4H, m), 8.14—8.30 ppm (2H, m). UVmax ($CHCl_3$): 421 nm (ε: 4.3×10^3), 290 (2.8×10^4), 270 (2.4×10^4).

*2-p-Tolylnaphtho[2,3-b]furan-4,9-dione (**3b**)*: Yellow plates from benzene–hexane, mp 266.5—267.0 °C. Found: C, 79.32; H, 4.31%. Calcd for $C_{19}H_{12}O_3$: C, 79.15; H, 4.19%. Mass: $m/e=288$ (M^+). IR (KBr disk): 1670 cm^{-1} (C=O). NMR ($CDCl_3$): δ; 2.40 (3H, s), 7.14 (1H, s), 7.16—7.40 (2H, m), 7.70—7.90 (4H, m), 8.16—8.36 ppm (2H, m). UVmax ($CHCl_3$): 437 nm (ε: 5.3×10^3), 295 (3.2×10^4), 273 (2.5×10^4).

*2-p-Ethylphenylnaphtho[2,3-b]furan-4,9-dione (**3c**)*: Yellow crystals, mp 186.0—189.0 °C. Mass: $m/e=302$ (M^+). IR (KBr disk): 1685 cm^{-1} (C=O). NMR ($CDCl_3$): δ; 1.24 (3H, t, $J=8$ Hz), 2.70 (2H, q, $J=8$ Hz), 7.16 (1H, s), 7.34 (2H, d, $J=10$ Hz), 7.70—7.90 (2H, m), 7.84 (2H, d, $J=10$ Hz), 8.12—8.32 ppm (2H, m).

*2-p-Propylphenylnaphtho[2,3-b]furan-4,9-dione (**3d**)*: Yellow crystals, mp 167.0—169.0 °C. Mass: $m/e=316$ (M^+). IR (KBr disk): 1665 cm^{-1} (C=O). NMR ($CDCl_3$): δ; 0.96 (3H, t, $J=6$ Hz), 1.70 (2H, m), 2.68 (2H, t, $J=8$ Hz), 7.16 (1H, s), 7.34 (2H, d, $J=6$ Hz), 7.72—7.90 (2H, m), 7.84 (2H, d, $J=6$ Hz), 8.08—8.16 ppm (2H, m).

*2-p-t-Butylphenylnaphtho[2,3-b]furan-4,9-dione (**3e**)*: Yellow crystals, mp 169.0—172.0 °C. Mass: $m/e=330$ (M^+). IR (KBr disk): 1660 cm^{-1} (C=O). NMR ($CDCl_3$): δ; 1.36 (9H, s), 7.16 (1H, s), 7.52 (2H, d, $J=8$ Hz), 7.68—7.84 (2H, m), 7.86 (2H, d, $J=8$ Hz), 8.10—8.30 ppm (2H, m).

*2-Butylnaphtho[2,3-b]furan-4,9-dione (**3f**)*: Yellow crystals, mp 160 °C. IR (KBr disk): 1680 cm^{-1} (C=O). NMR ($CDCl_3$): δ; 0.80—2.30 (9H, m), 6.42 (1H, s), 7.68—7.86 (2H, m), 8.04—8.22 ppm (2H, m).

*5-Bromo-2-methylbenz[a]anthracene-7,12-dione (**5b**)*: Yellow crystals from petroleum ether, mp 180.0—182.0 °C. Mass: $m/e=352$, 350 (M^+). IR (KBr disk): 1665 cm^{-1} (C=O). NMR ($CDCl_3$): δ; 2.62 (3H, s), 7.30—8.42 (7H, m), 9.84 ppm (1H, br s). UV max ($CHCl_3$): 414 nm (ε: 2.4×10^3), 364 (sh) (2.5×10^3), 333 (3.4×10^3), 290 (3.1×10^4), 251 (2.6×10^4).

*5-Bromo-2-ethylbenz[a]anthracene-7,12-dione (**5c**)*: Yellow crystals, mp 146.0—151.0 °C (dec). Mass: $m/e=366$, 364 (M^+). IR (KBr disk): 1665 cm^{-1} (C=O). NMR ($CDCl_3$): δ; 1.40 (3H, t, $J=8$ Hz), 2.98 (2H, q, $J=8$ Hz), 7.50—8.40 (7H, m), 9.62 ppm (1H, br s).

*5-Bromo-2-propylbenz[a]anthracene-7,12-dione (**5d**)*: Yellow crystals, mp 149.0—151.0 °C. Mass: $m/e=380$, 378 (M^+). IR (KBr disk): 1667 cm^{-1} (C=O). NMR ($CDCl_3$): δ; 1.02 (3H, t, $J=6$ Hz), 1.80 (2H, m), 2.90 (2H, t, $J=8$ Hz), 7.50—8.40 (7H, m), 9.80 ppm (1H, br s).

*5-Bromo-2-t-butylbenz[a]anthracene-7,12-dione (**5e**)*: Yellow crystals, mp 161.0—164.0 °C. Mass: $m/e=394$, 392 (M^+). IR (KBr disk): 1667 cm^{-1} (C=O). NMR ($CDCl_3$): δ; 1.52 (9H, s), 7.40—8.40 (7H, m), 9.98 ppm (1H, br s).

*The Reductive Acetylation of **3a**.* **3a** (10 mg) was refluxed with 3 ml of acetic anhydride and 100 mg of zinc dust for 30 min and filtered. The filtrate was poured into 10 ml of water and extracted with 20 ml of ether. Purification by using TLC on silica gel afforded 4,9-diacetoxy-2-phenylnaphtho[2,3-*b*]furan: white needles, mp 211—214 °C (yield: 54%). Mass: $m/e=360$ (M^+). IR (KBr disk): 1765 cm^{-1} (C=O). NMR ($CDCl_3$): δ; 2.56 (3H, s), 2.60 (3H, s), 6.96 (1H, s), 7.32—7.56 (5H, m), 7.76—8.00 ppm (4H, m).

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