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Photoinduced Molecular Transformations. Part 156.¹ New Photoadditions of 2-Hydroxy-1,4-naphthoquinones with Naphthols and Their Derivatives

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Abstracts: Dinaphtho[2,1-b;1',2'-d]furan-12,13-diones are produced in one-step in up to 45% yield by a (3+2) photoaddition of 2-hydroxy-1,4-naphthoquinones with 2-naphthol, while (\pm)-(6a α ,6b β ,12a β ,12b α)-6a,6b,12a,12b-tetrahydro-12b-hydroxydinaphtho-[1,2-a;1',2'-c]cyclobutenes (14-16%), arising from the stereoselective addition of a (2+2) photoaddition, are products in the photoaddition of 2-hydroxy-1,4-naphthoquinone with 2-methoxynaphthalene and with 2-naphthyl acetate. The photoaddition of 2hydroxy-1,4-naphthoquinone with 2-methoxynaphthalene also gave 2-hydroxy-3-(2-methoxynaphth-1-yl)-1,4-naphthoquinone (23%) as an accompanying product. Similar irradiation of a solution of 2-hydroxy-1,4-naphthoquinone with 1-methoxynaphthalene in acetone gave *cis*-6a,13a-dihydro-13a-methoxyd:inaphtho[1,2-b; 2',3'-d]furan-7,12-dione arising from a (3+2) photoaddition in 24% yield. The probable mechanisms for the formation of the photoadducts are discussed.

In previous papers^{2,3,4} we reported on one-step formations of 2,3-dihydronaphtho[2,3-b]furan-4,9diones **3a**, 2,3-dihydronaphtho[2,3-b]indole-4,9-diones **3b**, and 2,3-dihydrobenz[2,3-b]thiophene-4,9-diones **3c** by the regioselective photoaddition of 2-hydroxy- **1a**, 2-amino- **1b**, and 2-mercapto-1,4-naphthoquinone **1c** with various alkenes in acetone, as outlined in Scheme 1. The new (3+2) photoaddition of 2-hydroxy-1,4naphthoquinones with alkenes **2a-c** was then successfully applied to a new synthesis of natural quinone, maturinone.² We then found that 2-hydroxy-1,4-benzoquinones and various alkenes also give analogous (3+2) regioselective photoadducts.⁵



Reagents and conditions; i) hv, acetone or benzene; ii) air

Scheme 1

In this paper we report on new photoadditions of 1,4-naphthoquinones with arenes activated by an electron-donating group. We have found that a (3+2)-type photoaddition takes place between an excited 2-hydroxy-1,4-naphthoquinone with 2-naphthol to give an orthoquinone adduct, while (2+2) photoaddition takes place between an excited orthoquinone form of 2-hydroxy-1,4-naphthoquinone and 2-methoxynaphthalene or

2-acetoxynaphthalene in acetone with Pyrex-filtered light. Although the formation of (2+2) photoadducts between naphthol and olefins has been reported,^{6,7} the (2+2) and (3+2) additions, between quinones and naphthol, to our knowledge, have never been recorded.

RESULTS AND DISCUSSION

Commercially available 2-hydroxy-1,4-naphthoquinone 1a (Lawsone), and its 5- and 6-methoxy derivatives, 4a and 4b,⁸ were used as the quinone counterparts, while 2-naphthol 5, 2-methoxynaphthalene 9a, 2-naphthyl acetate 9b, and 1-methoxynaphthalene 12 were used as the arene counterparts in this work.

The irradiation of a 4.0×10^{-2} M solution of 2-hydroxy-1,4-naphthoquinone 1a in acetone containing excess 2-naphthol with a 500-W high-pressure Hg arc through a Pyrex-filter for 34 h under nitrogen gave a crystalline adduct 6a in 15% yield (Scheme 2). The molecular formula of the product 6a was established to be C₂₀H₁₀O₃ by high-resolution mass spectrometry. The IR spectrum indicated the absorption bands at 1655 and 1649 cm⁻¹ assignable to the quinone carbonyl group.



While the mass spectrum of product 6a exhibited an almost identical fragmentation pattern with that of paraquinone, dinaphtho [2,1-b;2',3'-d] furan-8,13-dione 7 (prepared according to the published procedure⁹ by us), a direct comparison indicated that the product 6a differed from paraquinone 7. This suggested that the product 6a was an orthoquinone, dinaphtho[2,1-b;1',2'-d]furan-12,13-dione, an isomer of the paraquinone 7. Electronic spectrum of product 6a in methanol exhibited a strong absorption maximum at 226 nm due to $\pi \rightarrow \pi^*$ transition and a maximum at 477 nm and a long tail absorption extending into ca 600 nm while that of paraquinone 7 (insoluble to methanol) in hexane (absorption maxima at 240, 295, 330 and 430 nm) has already been recorded¹⁰. In agreement with the assumed orthoquinone structure, product **6a** gave the quinoxaline derivative 8 by a treatment with 1,2-phenylenediamine in dichloromethane. Although only a limited range of data concerning ¹³C-NMR of quinones are available, a comparison of proton-decoupled ¹³C NMR spectrum of product 6a with those of 2-hydroxynaphthalene-1,4-dione $1a^{12}$ and paraguinone 7 supported the orthoquinone structure of product 6a. A part from the signals due to the 10 aromatic carbons bearing a hydrogen and 6 aromatic and trigonal carbons having no hydrogen (see Experimental) the proton-decoupled ¹³C-NMR spectrum of product 6a (CDCl₃ - a few percent of CD₃OD) exhibited the signals at δ 152.1, 155.0, 181.4, and 183.9 while that of paraquinone 7 (in the same solvent) exhibited the signals at δ 153.1, 155.5, 175.1, and 181.0 in their downfield regions. These signals were safely assignable to C(6a), C(7a), C(12), and C(13) for 6a, and to C(6a), C(7a), C(13), and C(8) for paraguinone 7 on the basis of comparison with the 13 C-NMR spectra of 2-hydroxynaphthalene-1,4-dione 1a,¹² naphthalene-1,4-dione,¹³ and naphthalene-1,2-dione.¹³

The photoaddition of 5-methoxy- and 6-methoxy-2-hydroxy-1,4-naphthoquinones, **4b** and **4c**, with 2naphthol 5 under the above-mentioned conditions similarly gave 8-methoxydinaphtho[2,1-b;1',2'-d]furan-12,13-dione **6b** and its 9-methoxy isomer **6c** in 24 and 35% yield. Their structures were confirmed by the spectroscopic analysis.

The photoaddition of 2-hydroxy-1,4-naphthoquinone 1a and 2-methoxynaphthalene 9a in acetone under the conditions mentioned above, on the other hand, gave products 10a and 11 (Scheme 3). Combustion analysis and mass spectrometry of product 10a indicated that it had the molecular formula, $C_{21}H_{16}O_4$. The IR spectrum exhibited bands at 1774 and 1686 cm⁻¹ assignable to the α -diketo group of 1,2,2a,8b-tetrahydrocyclobuta[a]naphthalene-3,4-dione structure,¹⁴ as well as a band at 3280 cm⁻¹ due to the OH group. The ¹H NMR spectrum showed signals at δ 3.02 (3H, s), 3.39 (1H, d, J 2.44 Hz), 3.46 (1H, d, J 2.44 Hz), 6.19 (1H, dd, J 10.25 and 1.47 Hz), and 6.93 (1H, d, J 10.25 Hz). These spectral results indicate that the product was cyclobutanol 10a derived from a (2+2) photoaddition of a tautomeric 4-hydroxy-1,2-naphthoquinone with 2-methoxynaphthalene. The signals mentioned above were assigned to the OMe, 6b-H, 6a-H, 12-H, and 11-H, respectively. The stereochemistry of the adduct should be *cis-transoid-cis* based on the coupling constant between 6a-H and 6b-H (2.44 Hz). The formation of similar cyclobutanols by stereo- and regioselective (2+2) photoaddition of an excited enol form of 2-amino-1,4-naphthoquinone with vinylarenes has previously been reported by us.¹⁴

Combustion analysis and mass spectrometry of product 11 indicated that it had the molecular formula $C_{21}H_{14}O_4$. The IR spectrum exhibited bands due to the hydroxyl and *para*-quinone carbonyl. The ¹H NMR spectrum showed signals due to the methoxyl group and a series of aromatic protons, but no signal due to the aliphatic proton. These results indicated that it was a 2-hydroxy-3-(2-methoxynaphth-1-yl)-1,4-naphthoquinone 11.



Reagents and conditions; i) hv, acetone

Scheme 3

A similar photoaddition of hydroxyquinone 1a with 2-naphthyl acetate 9b gave a (2+2) adduct 10b as a single product in 14% yield. A spectroscopic analysis (see Experimental) of adduct 10b, $(C_{22}H_{16}O_5$ according to high-resolution mass spectrometry) indicated that it was cyclobutanol 10b analogous to the (2+2)photoadduct 10a arising from a (2+2) photoaddition of a tautomeric 4-hydroxy-1,2-naphthoquinone with the substituted naphthalene.

The photoaddition of 2-hydroxy-1,4-naphthoquinone 1a with 1-methoxynaphthalene 12 in acetone under similar conditions as those mentioned above gave a photoadduct 13 in 24% yield (Scheme 4). The molecular formula of the product 13 was established to be $C_{21}H_{14}O_4$ by combustion analysis and mass spectrometry. The spectroscopic analysis indicated that it was either 6a,13a-dihydro-13a-methoxydinaphtho[1,2-*b*;2',3'-*d*]furan-7,12-dione 13 or its paraquinone isomer arising from a regioselective (3+2) photoaddition. The IR spectrum exhibited an intense band at 1655 cm⁻¹ (shoulder at 1635 cm⁻¹) and a weaker band at 1619 cm⁻¹, which were assignable to the quinone group of paraquinone 13 rather than its orthoquinone isomer by comparing with the band position of their analogous para-² and orthoquinones.¹⁴ The *cis* ring fusion rather than *trans* is assigned to quinone 13 on the basis of the consideration of their relative stability.

The preparation of the dinaphtho[1,2-b;2',3'-d]furan-7,12-dione skeleton has been reported,¹⁵ and a natural product having this skeleton has been described.¹⁶

The foregoing experiments indicated that the (3+2) photoadducts, 6 and 13, were produced in one step in 15-35% yields by the irradiation of 2-hydroxy-1,4-naphthoquinones with 2-naphthol and 1methoxynaphthalene. On the other hand, (\pm)-($6a\alpha$, $6b\beta$, $12a\beta$, $12b\alpha$)-6a,6b,12a,12b-tetrahydro-12b-hydroxydinaphtho[1,2-*b*;1',2'-*c*]cyclobutenes (14-16%), arising from stereoselective (2+2) photoadditions, were products in the photoaddition of 2-hydroxy-1,4-naphthoquinone with 2-methoxynaphthalene as well as with 2-



Reagents and conditions; i) hv, acetone

Scheme 4

naphthyl acetate. The photoaddition of 2-hydroxy-1,4-naphtho-quinone with 2-methoxynaphthalene also gave 2-hydroxy-3-(2-methoxynaphth-1-yl)-1,4-naphthoquinone as a minor accompanying product.

The probable gross reaction pathways leading to these (3+2) and (2+2) photoadducts are outlined in Scheme 5. It has been known that the $S_1 \rightarrow T_1$ intersystem crossing of excited quinones (58 kcal for 1,4-naphthoquinone¹⁷) generally occur with high efficiency ($\Phi = 0.8 \cdot 1.0$).¹⁸ A comparison of the electronic absorption spectrum of 2-hydroxy-1,4-naphthoquinone **1a** with that of 2-methoxy-1,4-naphthoquinone indicates that no orthoquinone form of the quinone **1a** exists in the solution.¹⁹ Irradiation of quinone **1a** in acetone may thus generate tautomeric triplet excited species A and B. The exciplex formed between the orthoquinone B and the substituted naphthalene, **9a** or **9b**, gives products **10a** or **10b** arising from the [2+2] photoaddition.²⁰ The exciplex formed between the paraquinone A and naphthol **5** or 2-methoxynaphthalene **9a** collapses to give a pair of radical ions [C \Leftrightarrow D] and E.^{21,22} This pair combines to give a zwitterion F which successively forms either orthoquinone **6a** or paraquinone **11** by air oxidation of intermediate G or H generated by the removal of protons. The zwitterion F may alternatively be formed *via* an electron transfer from a polarized exciplex.²² The alkoxyl or hydroxyl group thus stabilizes the regioisomer F of the zwitterionic intermediates and directs the regiochemistry of this (3+2) photoaddition.

EXPERIMENTAL

For descriptions of the instruments and the general procedure of photolysis, see our previous papers.²⁻⁵ The proton-decoupled ¹³C NMR spectrum (68 MHz) was measured in CDCl₃ containing a small amount of CD₃OD (SiMe₄ as internal reference) with a JEOL-EX-270 spectrometer. The solutions in a Pyrex tube were irradiated externally with a 500-W high-pressure Hg arc lamp.

Dinaphtho[2,1-b;1',2'-d]furan-12,13-dione 6a

A solution of 2-hydroxynaphtho-1,4-dione 1a (174 mg, 1.0 mmol) and 2-naphthol (2.88 g, 20 mmol) in acetone (25 cm³) was irradiated under nitrogen for 34h with a Pyrex-filtered light. After evaporation of the solvent, the residue was subjected to PLC on silica gel to afford **6a** (45 mg, 15%) : $R_F 0.60$ (1:1 THF-hexane); m.p 278-281°C (from chloroform). $vmax/cm^{-1}$ 1655, 1649 (orthoquinone carbonyl), 1590; δ_H (270



Scheme 5

MHz, DMSO). 7.17-8.35 (10H, m, aromatic protons): $\delta_{\rm C}$ (68 MHz, CDCl₃ containing a few percent of CD₃OD) 110.6, 118.0(d), 118.9, 123.1(d), 124.1(d), 126.2(d), 126.5(d), 127.1(d), 128.2(d), 128.2, 130.0, 130.5(d), 132.7, 133.0(d), 133.1, 134.9(d), 152.1, 155.0, 181.4, 183.9; *m/z* 298 (M⁺, 100), 270 [(M-CO)⁺, 81.4], 242 [(M-2CO)⁺, 10.0], 213 (44.5), 187 (7.7), 135 (11.74), 121 (17.5), 106 (29.8), 93 (10.6), and 44 (24.2). λ max/nm (MeOH) 226 (ε 32500), 271 (ε 12500), 330 (ε 3700), and 477 (ε 890). (Found: M⁺, 298.0679. C₂₀H₁₀O₃ requires *M*, 298.0657)

Dinaphtho[2,1-b; 2', 3'-d]furan-8,13-dione 7.

This dinaphthofurandione 7 was prepared in 90% yield by the reaction of 2,3-dichloro-1,4naphthoquinone and 2-naphthol in pyridine under reflux by the published procedure. m.p. 283-285 °C (from diethyl ether-chloroform). (lit.^{9a} 270-271 °C); lit.^{9b} 272-273 °C; lit.^{9c} 279-281 °C). m/z 298 (M⁺, 100), 270 [(M-CO)⁺, 10.7), 242 [(M-2CO)⁺, 3.8], 213 (24.5), 187 (4.0)], 135 (9.6), 121 (5.9), 106 (15.6), 93 (4.0), and 44 (3.0); δ (270 MHz) 7.65 (br. t, J 7), 7.77-7.84 (4H, m), 8.02 (2H, t, J 8), 8.27-8.38 (2H, m), and 9.75 (1H, br. d, J 8, 1-H).

A Quinoxaline Derivative 8 of Dinaphtho[2,1-b; 1', 2'-d]furan-12,13-dione 6a.

A suspended solution of 12, 13-dione 6a (60 mg, 0.2 mmol) in dichloromethane (10 cm³) and 1,2phenylenediamine (43 mg, 0.4 mmol) was stirred for 3h at room temperature. Yellow coloured crystals of quinoxaline 8 (44 mg, 60 %) crystallized out from the solution were collected by filtration. m.p. > 300°C (from chloroform-THF) vmax/cm⁻¹ 1634 and 1597; m/z 370 (M⁺, 1.02) and 246 (100 %); (Found M⁺, 370.1126. C₂₆H₁₄ON₂ requires *M*, 370.1107).

8-Methoxydinaphtho[2,1-b; 1',2'-d]furan-12,13-dione 6b

A solution of 2-hydroxy-5-methoxy-1,4-naphthoquinone **4b** (45 mg, 0.22 mmol) and 2-naphthol (635 mg, 4.4 mmol) in acetone (5.5 cm³) was irradiated for 30 h in the same manner as described for the preparation of dinaphthofurandione **6a** to give, after purification by PLC on SiO₂, adduct **6b** (17 mg, 24%); R_F 0.29 (1:1 THF-hexane); m.p.>300°C (from dichloromethane-hexane); umax/cm⁻¹ 1654, 1640, 1620, and 1586 ; δ (90 MHz) 3.96 (3H, s), 7.1-7.9 (9H, m); *m/z* 328 (M⁺, 100). (Found : M⁺, 328.0729. C₂₁H₁₂O₄ requires *M*, 328.0735).

9-Methoxydinaphtho[2.1-b; 1',2'-d]furan-12,13-dione 6c

Irradiation of 2-hydroxy-6-methoxy-1,4-naphthoquinone 4c (69 mg, 0.34 mmol) and 2-naphthol 5 (974 mg, 6.8 mmol) in acetone (18 cm³) for 100 h gave adduct 6c (39 mg, 35%); $R_F 0.42$ (1:1 THF-hexane); m.p.>300°C (from EtOAc-CH₂Cl₂-hexane); umax/cm⁻¹ 1654, 1645, and 1589; δ (90 MHz, DMSO-d₆) 3.92 (3H, s), 7.0-7.9 (9H, m); *m/z* 328 (M⁺, 100). (Found : M⁺, 328.0725. C₂₁H₁₂O₄ requires *M*, 328.0735).

(\pm) - $(6a\alpha,6b\beta,12a\beta,12b\alpha)$ -6a,6b,12a,12b-Tetrahydro-12b-hydroxy-12a-methoxydinaphtho[1,2-a;1',2'-c]-cyclobutene **10a** and 2-Hydroxy-3-(2-methoxynaphth-1-yl)-1,4-naphthalene-1,4-dione **11**.

Irradiation of hydroxyquinone 1a (174 mg, 1 mmol) and 2-methoxynaphthalene 9a (3.16g, 20 mmol) in acetone (25 cm³) for 46 h gave 10a (53 mg, 16%) and 11 (76 mg, 23%). 10a: R_F 0.48 (1:3 THF-hexane); m.p.128-130°C (from hexane-Et₂O); umax/cm,⁻¹ 3280, 1774, 1686, and 1631; δ (400 MHz) 3.02 (3H, s,

OMe), 3.39 (2H, br.s, 6b-H and OH), 3.46 (1H, d, J 2.44 Hz, 6a-H), 6.19 (1H, dd, J 10.25 and 1.47 Hz, 12-H), 6.93 (1H, d, J 10.25 Hz, 11-H), 7.2-7.3 (4H, m), 7.57 (1H, ddd, J 7.81, 7.33, and 1.47 Hz), 7.78 (1H, ddd, J 7.81, 7.33, and 1.47 Hz), 7.98 (1H, d, J 7.33 Hz), 8.17 (1H, dd, J 7.81 and 1.47 Hz); m/z 332 (M⁺, 4.9), 174 (26), 158 (100). (Found : C, 75.71; H, 4.52. C₂₁H₁₆O₄ requires C, 75.89; H, 4.85). **11** : R_F 0.32 (1:3 THF-hexane); m.p. 257-258°C (from chloroform) $vmax/cm^{-1}$ 3282, 1667, and 1649 ; δ (90 MHz) 3.87 (3H, s, OMe), 7.2-7.45 (4H, m), 7.65-7.95 (4H, m), 8.1-8.25 (2H, m); m/z 330 (M⁺, 100). (Found : C, 76.21; H, 4.31. C₂₁H₁₄O₄ requires C, 76.35; H, 4.27).

(\pm) - $(6a\alpha,6b\beta,12a\beta,12b\alpha)$ -6a,6b,12a,12b-Tetrahydro-12a-acetoxy-12b-hydroxydinaphtho[1,2-a;1',2'-c]-cyclobutene **10b**

Irradiation of hydroxyquinone **1a** (174 mg, 1 mmol) and 2-naphthyl acetate **9b** (3.72 g, 20 mmol) in acetone for 52 h gave **10b** (50 mg, 14%) : $R_F 0.43$ (1:2 THF-hexane); m.p. 167-169°C (from hexane-Et₂O); ν max/cm⁻¹ 3466, 1775, 1736, and 1697 ; δ (400 MHz) 1.79 (3H, s, OAc), 3.52 (1H, br.s, 6b-H), 3.56 (1H, d, J 1.95 Hz, 6a-H), 6.47 (1H. dd. J 10.26, and 0.98Hz, 12-H), 6.85 (1H, d, J 10.26 Hz, 11-H), 7.2-7.4 (4H, m), 7.61 (1H, ddd, J 8.31, 7.81, and 1.47 Hz), 7.78 (1H, ddd, J 7.81, 7.33, and 1.47 Hz), 7.83 (1H, dd, J 7.81, and 0.98 Hz); m/z 360 (M⁺, 6.1), 144 (100). (Found : M⁺, 360.0994. C₂₂H₁₆O₅ requires 360.0998.

cis-6a,13a-Dihydro-13a-methoxydinaphtho[1,2-b;2',3'-d]furan-7,12-dione 13

Irradiation of hydroxyquinone 1a (174 mg, 1 mmol) and 1-methoxynaphthalene 12 (3.16 g, 20 mmol) in acetone (25 cm³) for 80 h gave 13 (79 mg, 24%); R_F 0.48 (1:2 THF-hexane); m.p. 136-140°C (from hexane-Et₂O-CH₂Cl₂); ν max/cm⁻¹ 1655 and 1619; δ (90 MHz) 2.90 (1H, d, *J* 6.16 Hz, 6a-H), 4.04 (3H, s, OMe), 6.91 (1H, d, *J* 7.92 Hz, 6-H), 7.2-7.5 (4H, m), 7.7-7.9 (2H, m), 8.1-8.4 (3H, m); *m/z* 330 (M⁺, 100). (Found : C, 76.38; H, 4.10. C₂₁H₁₄O₄ requires C, 76.35; H, 4.27).

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