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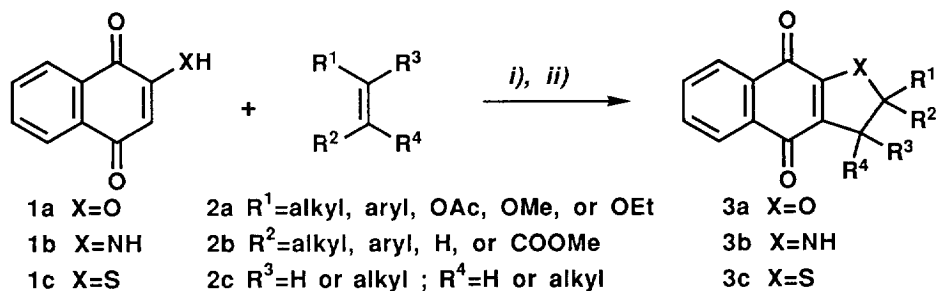
## Photoinduced Molecular Transformations. Part 156.<sup>1</sup> New Photoadditions of 2-Hydroxy-1,4-naphthoquinones with Naphthols and Their Derivatives

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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 (±)-(6α,6β,12αβ,12β)-6a,6b,12a,12b-tetrahydro-12b-hydroxydinaphtho[1,2-*α*;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 2-hydroxy-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-methoxydinaphtho[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<sup>2,3,4</sup> we reported on one-step formations of 2,3-dihydronaphtho[2,3-*b*]furan-4,9-diones **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-1,4-naphthoquinones with alkenes **2a-c** was then successfully applied to a new synthesis of natural quinone, matorinone.<sup>2</sup> We then found that 2-hydroxy-1,4-benzoquinones and various alkenes also give analogous (3+2) regioselective photoadducts.<sup>5</sup>



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

### Scheme 1

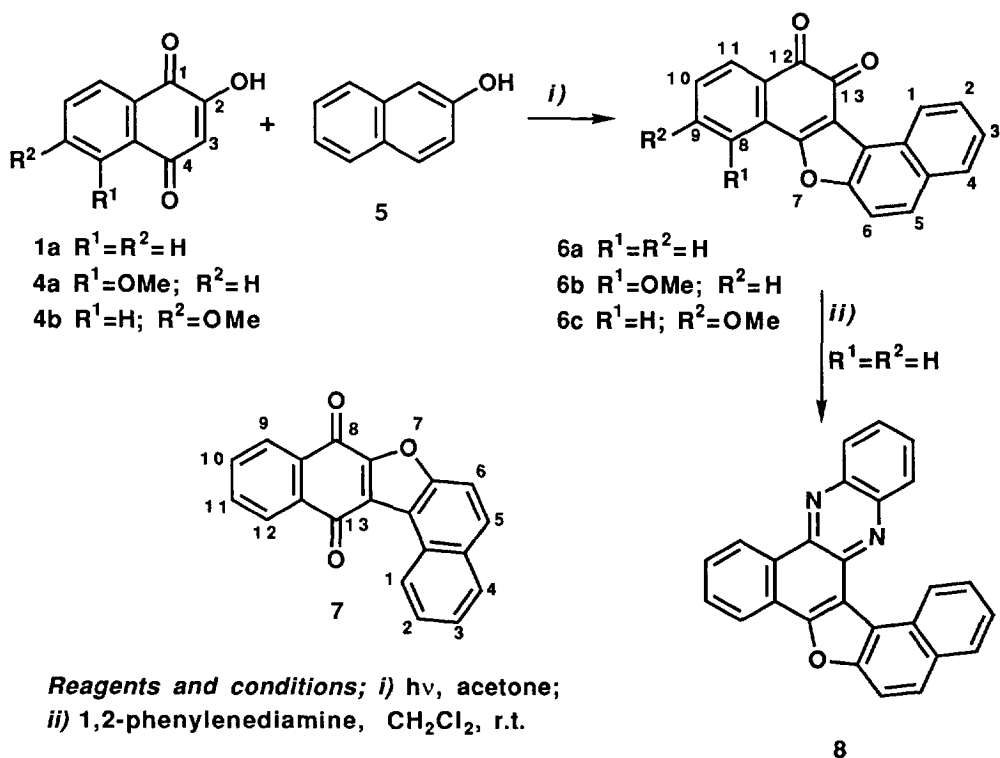
In this paper we report on new photoadditions of 1,4-naphthoquinones with arenes activated by an electron-donating group. We have found that a (3+2)-type photoaddition takes place between an excited 2-hydroxy-1,4-naphthoquinone with 2-naphthol to give an orthoquinone adduct, while (2+2) photoaddition 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,<sup>6,7</sup> 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** (Lawson), and its 5- and 6-methoxy derivatives, **4a** and **4b**,<sup>8</sup> 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  $4.0 \times 10^{-2}$  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  $C_{20}H_{10}O_3$  by high-resolution mass spectrometry. The IR spectrum indicated the absorption bands at 1655 and 1649  $cm^{-1}$  assignable to the quinone carbonyl group.



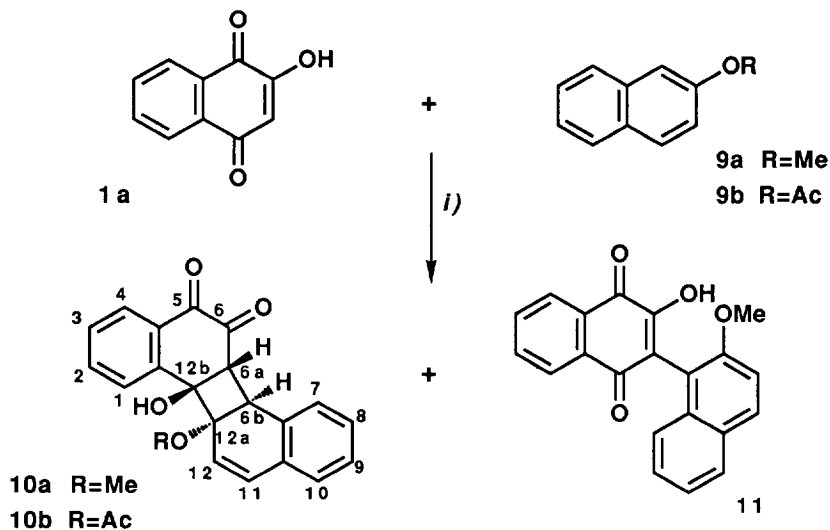
Scheme 2

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 procedure<sup>9</sup> 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 recorded<sup>10</sup>. 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 <sup>13</sup>C-NMR of quinones are available, a comparison of proton-decoupled <sup>13</sup>C NMR spectrum of product **6a** with those of 2-hydroxynaphthalene-1,4-dione **1a**<sup>12</sup> and paraquinone **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 <sup>13</sup>C-NMR spectrum of product **6a** (CDCl<sub>3</sub> - a few percent of CD<sub>3</sub>OD) exhibited the signals at  $\delta$  152.1, 155.0, 181.4, and 183.9 while that of paraquinone **7** (in the same solvent) exhibited the signals at  $\delta$  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 paraquinone **7** on the basis of comparison with the <sup>13</sup>C-NMR spectra of 2-hydroxynaphthalene-1,4-dione **1a**,<sup>12</sup> naphthalene-1,4-dione,<sup>13</sup> and naphthalene-1,2-dione.<sup>13</sup>

The photoaddition of 5-methoxy- and 6-methoxy-2-hydroxy-1,4-naphthoquinones, **4b** and **4c**, with 2-naphthol **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<sub>21</sub>H<sub>16</sub>O<sub>4</sub>. The IR spectrum exhibited bands at 1774 and 1686 cm<sup>-1</sup> assignable to the  $\alpha$ -diketo group of 1,2,2a,8b-tetrahydrocyclobuta[a]naphthalene-3,4-dione structure,<sup>14</sup> as well as a band at 3280 cm<sup>-1</sup> due to the OH group. The <sup>1</sup>H NMR spectrum showed signals at  $\delta$  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.<sup>14</sup>

Combustion analysis and mass spectrometry of product **11** indicated that it had the molecular formula C<sub>21</sub>H<sub>14</sub>O<sub>4</sub>. The IR spectrum exhibited bands due to the hydroxyl and *para*-quinone carbonyl. The <sup>1</sup>H 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*)  $h\nu$ , acetone

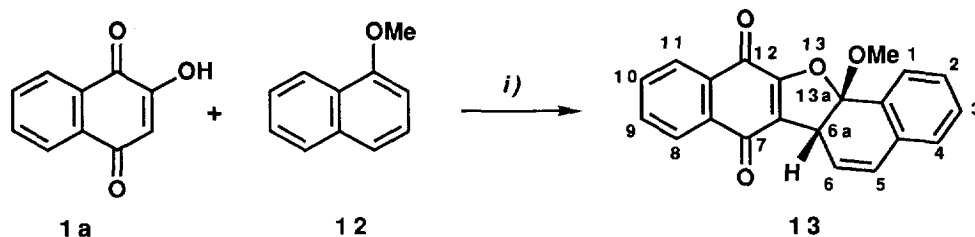
### Scheme 3

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<sub>22</sub>H<sub>16</sub>O<sub>5</sub> 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<sub>21</sub>H<sub>14</sub>O<sub>4</sub> 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<sup>-1</sup> (shoulder at 1635 cm<sup>-1</sup>) and a weaker band at 1619 cm<sup>-1</sup>, 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-<sup>2</sup> and orthoquinones.<sup>14</sup> 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,<sup>15</sup> and a natural product having this skeleton has been described.<sup>16</sup>

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 1-methoxynaphthalene. On the other hand, (±)-(6α,6β,12αβ,12βα)-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)  $h\nu$ , acetone**

### Scheme 4

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

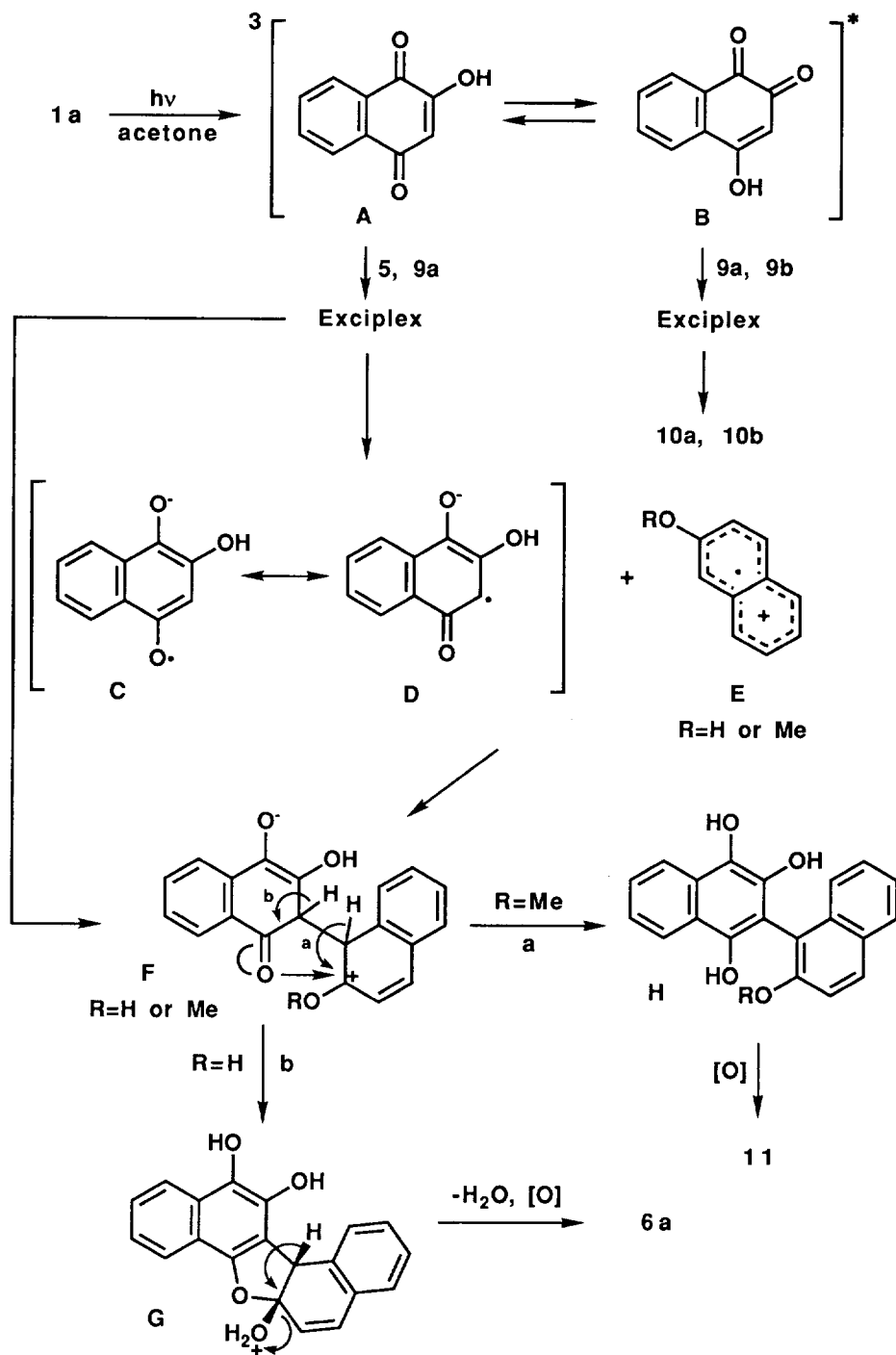
The probable gross reaction pathways leading to these (3+2) and (2+2) photoadducts are outlined in Scheme 5. It has been known that the  $S_1 \rightarrow T_1$  intersystem crossing of excited quinones (58 kcal for 1,4-naphthoquinone<sup>17</sup>) generally occur with high efficiency ( $\Phi = 0.8-1.0$ ).<sup>18</sup> 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.<sup>19</sup> 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.<sup>20</sup> 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**.<sup>21,22</sup> 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.<sup>22</sup> The alkoxy 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.<sup>2-5</sup> The proton-decoupled <sup>13</sup>C NMR spectrum (68 MHz) was measured in CDCl<sub>3</sub> containing a small amount of CD<sub>3</sub>OD (SiMe<sub>4</sub> 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 cm<sup>3</sup>) 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<sub>F</sub> 0.60 (1:1 THF-hexane); m.p 278-281°C (from chloroform).  $\nu_{\max}/\text{cm}^{-1}$  1655, 1649 (orthoquinone carbonyl), 1590;  $\delta_{\text{H}}$  (270



Scheme 5

MHz, DMSO). 7.17-8.35 (10H, m, aromatic protons):  $\delta_C$  (68 MHz,  $CDCl_3$  containing a few percent of  $CD_3OD$ ) 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).  $\lambda_{max}/nm$  (MeOH) 226 ( $\epsilon$  32500), 271 ( $\epsilon$  12500), 330 ( $\epsilon$  3700), and 477 ( $\epsilon$  890). (Found:  $M^+$ , 298.0679.  $C_{20}H_{10}O_3$  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-1,4-naphthoquinone and 2-naphthol in pyridine under reflux by the published procedure. m.p. 283-285 °C (from diethyl ether-chloroform). (lit.<sup>9a</sup> 270-271 °C; lit.<sup>9b</sup> 272-273°C; lit.<sup>9c</sup> 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);  $\delta$  (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  $cm^3$ ) and 1,2-phenylenediamine (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)  $\nu_{max}/cm^{-1}$  1634 and 1597;  $m/z$  370 ( $M^+$ , 1.02) and 246 (100 %); (Found  $M^+$ , 370.1126.  $C_{26}H_{14}ON_2$  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  $cm^3$ ) was irradiated for 30 h in the same manner as described for the preparation of dinaphthofurandione **6a** to give, after purification by PLC on  $SiO_2$ , adduct **6b** (17 mg, 24%);  $R_F$  0.29 (1:1 THF-hexane); m.p.>300°C (from dichloromethane-hexane);  $\nu_{max}/cm^{-1}$  1654, 1640, 1620, and 1586 ;  $\delta$  (90 MHz) 3.96 (3H, s), 7.1-7.9 (9H, m);  $m/z$  328 ( $M^+$ , 100). (Found :  $M^+$ , 328.0729.  $C_{21}H_{12}O_4$  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  $cm^3$ ) for 100 h gave adduct **6c** (39 mg, 35%);  $R_F$  0.42 (1:1 THF-hexane); m.p.>300°C (from EtOAc- $CH_2Cl_2$ -hexane);  $\nu_{max}/cm^{-1}$  1654, 1645, and 1589 ;  $\delta$  (90 MHz, DMSO- $d_6$ ) 3.92 (3H, s), 7.0-7.9 (9H, m);  $m/z$  328 ( $M^+$ , 100). (Found :  $M^+$ , 328.0725.  $C_{21}H_{12}O_4$  requires  $M$ , 328.0735).

*(±)-(6 $\alpha$ ,6 $\beta$ ,12 $\alpha$ ,12 $\beta$ )-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  $cm^3$ ) 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-Et $_2$ O);  $\nu_{max}/cm^{-1}$  3280, 1774, 1686, and 1631 ;  $\delta$  (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.  $C_{21}H_{16}O_4$  requires C, 75.89; H, 4.85). **11** :  $R_F$  0.32 (1:3 THF-hexane); m.p. 257-258°C (from chloroform)  $\nu_{max}/cm^{-1}$  3282, 1667, and 1649 ;  $\delta$  (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.  $C_{21}H_{14}O_4$  requires C, 76.35; H, 4.27).

*(±)-(6 $\alpha$ ,6 $\beta$ ,12 $\alpha$  $\beta$ ,12 $\beta$  $\alpha$ )-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-Et<sub>2</sub>O);  $\nu_{max}/cm^{-1}$  3466, 1775, 1736, and 1697 ;  $\delta$  (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 0.98 Hz, 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), 8.20 (1H, dd, *J* 7.81, and 0.98 Hz); *m/z* 360 ( $M^+$ , 6.1), 144 (100). (Found :  $M^+$ , 360.0994.  $C_{22}H_{16}O_5$  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 cm<sup>3</sup>) for 80 h gave **13** (79 mg, 24%);  $R_F$  0.48 (1:2 THF-hexane); m.p. 136-140°C (from hexane-Et<sub>2</sub>O-CH<sub>2</sub>Cl<sub>2</sub>);  $\nu_{max}/cm^{-1}$  1655 and 1619 ;  $\delta$  (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.  $C_{21}H_{14}O_4$  requires C, 76.35; H, 4.27).



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