

## One-step Synthesis of 2,3-Dihydronaphtho[2,3-*b*]thiophene-4,9-diones by a New Regioselective [3 + 2] Photoaddition of Photogenerated 2-Mercapto-1,4-naphthoquinone with Alkenes<sup>1</sup>

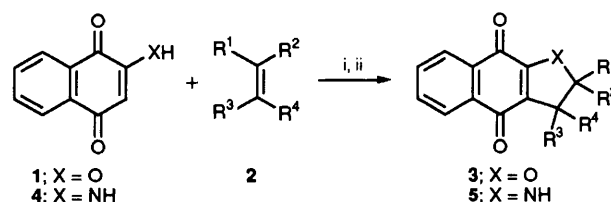
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2,3-Dihydronaphtho[2,3-*b*]thiophene-4,9-diones are formed in one-step reactions in 6–41% yields by an unprecedented regioselective [3 + 2] photoaddition of 2-mercapto-1,4-naphthoquinone, generated by the photochemical decarbonylation of 5-hydroxynaphth[2,1-*d*]-1,3-oxathiol-2-one, with alkenes.

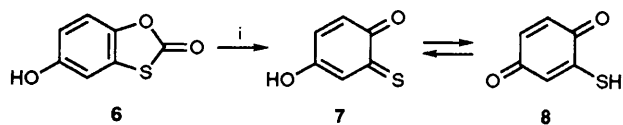
In a previous paper<sup>2</sup> we reported on the one-step exclusive formation of 2,3-dihydronaphtho[2,3-*b*]furan-4,9-diones **3** in high yields by a new [3 + 2] regioselective photoaddition of 2-hydroxy-1,4-naphthoquinones **1** with a variety of alkenes **2**. The new photoreaction was then successfully applied to a two-step synthesis of the natural quinone, matorinone.<sup>2</sup> Subsequently, we also found that 2,3-dihydro-1*H*-benz[*f*]indole-4,9-diones **5** can be obtained in one-step in high yields by similar [3 + 2] photoadditions of 2-aminonaphthoquinone **4** with various electron-rich alkenes **2**, as outlined in Scheme 1.

These [3 + 2] photoadditions of 2-hydroxy- or 2-aminonaphthoquinone with alkenes have been extended to a 2-hydroxy- or 2-amino-1,4-anthracenedione series.<sup>4</sup>

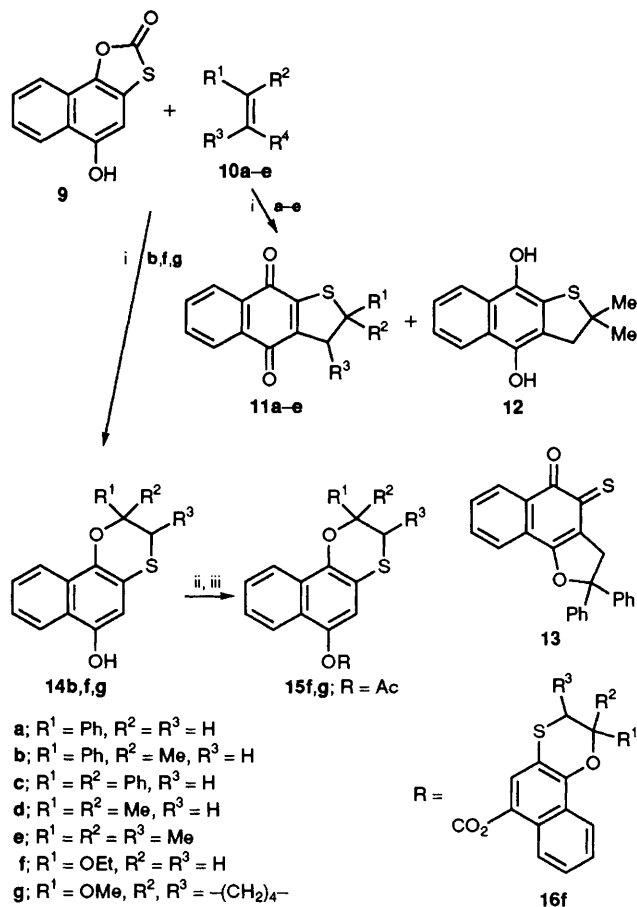


R<sup>1</sup> = alkyl, aryl, OAc, OMe, or OEt  
 R<sup>2</sup> = alkyl, aryl, H, or CO<sub>2</sub>Me  
 R<sup>3</sup> = H, alkyl  
 R<sup>4</sup> = H or alkyl

**Scheme 1** Reagents and conditions: i, *hν*, acetone or benzene; ii air



Scheme 2 Reagents and conditions: i, hv

Scheme 3 Reagents and conditions: i, hv, acetone; ii, Ac<sub>2</sub>O-pyridine; iii, (CCl<sub>3</sub>O)<sub>2</sub>CO, Et<sub>3</sub>N, THF

We envisaged that a photochemical annelation analogous to those of 2-hydroxy- and 2-amino-naphthoquinones should also be possible with 2-mercaptanaphthoquinone. Although 2-mercaptanaphthoquinone is an unisolated species, Chapman and McIntosh<sup>5</sup> reported that the formation of an unstable tautomeric mixture of  $\alpha$ -ketothione **7** and 2-mercaptobenzothioquinone **8**, arising from an elimination of carbon monoxide, could be observed by <sup>1</sup>H NMR spectroscopy when benzoxathiolone **6** was irradiated (Scheme 2).

We report here that 2,3-dihydronaphtho[2,3-*b*]thiophene-4,9-diones **11a-e** can be obtained by a new [3 + 2]-type regioselective photoaddition of 2-mercapto-1,4-naphthoquinone **18**, which is *in situ* photochemically generated with various alkenes.

Typically, a  $1.2 \times 10^{-1}$  mol dm<sup>-3</sup> solution of 5-hydroxy-naphth[2,1-*d*]-1,3-oxathiol-2-one<sup>6</sup> **9** (114 mg, 0.6 mmol) in acetone (5 cm<sup>3</sup>) containing styrene **10a** (624 mg, 6.0 mmol) in an atmosphere of nitrogen were irradiated using a high-pressure mercury arc for 68 h at room temperature to give a single product **11a** in 32% yield (Scheme 3). High-resolution mass spectrometry (HRMS) of the product (m.p. 124–126 °C from hexane-dichloromethane) indicated its molecular formula to be C<sub>18</sub>H<sub>12</sub>O<sub>2</sub>S. The IR spectrum exhibited two bands at 1663 and 1646 cm<sup>-1</sup> assignable to the quinone carbonyl groups. The <sup>1</sup>H NMR spectrum showed a double doublet signal (1 H) at  $\delta$  4.98 (*J* 10.56 and 3.63 Hz), a double doublet

signal (1 H) at  $\delta$  3.98 (*J* 12.21 and 10.56 Hz), and a double doublet signal (1 H) at  $\delta$  3.39 (*J* 12.21 and 3.63 Hz), while the <sup>13</sup>C NMR spectrum gave two signals at  $\delta$  39.5 and 52.6 assignable to C-3 and C-2, respectively. These spectral results indicated that the product was 2-phenyl-2,3-dihydronaphtho[2,3-*b*]thiophene-4,9-dione **11a**, arising from a [3 + 2] addition of 2-mercapto-1,4-naphthoquinone **18** (generated *in situ* by the photochemical decarbonylation of 5-hydroxy-naphthoxathiolone **9**) with styrene.

The photoaddition of **18**, generated from **9**, with styrene-derived alkenes, such as  $\alpha$ -methylstyrene **10b** and  $\alpha$ -phenylstyrene **10c**, similarly gave regioselective [3 + 2] adducts **11b**<sup>†</sup> and **c**<sup>†</sup> in 24 and 35% yields, respectively. The photoaddition with **10b** gave byproduct **14b** (19%) and that with **10c** gave byproduct **13** (41%) (Scheme 3). The structure of byproduct **14b** (19%) was confirmed as being 2,3-dihydro-2-phenyl-2-methyl-6-hydroxynaphth[1,2-*b*]-1,4-oxathiin by spectroscopic analysis.<sup>‡</sup> Byproduct **13** was an isomer of adduct **11c** (mass spectrometry) and an  $\alpha$ -oxothione structure was tentatively assigned on the basis of <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy; the C-2 and C-3 appeared at  $\delta$  70.4 and 47.2, respectively.<sup>§</sup>

Irradiation of a  $4 \times 10^{-2}$  mol dm<sup>-3</sup> solution of **9** in acetone containing 10 equiv. of isobutene **10d** and 2-methylbut-2-ene **10e** analogously gave regioselective adducts **11d** and **e** in 9 and 13% yields, respectively. The photoaddition with **10d** gave an accompanying product **12** in 6% yield. HRMS indicated the molecular formula of **12** to be C<sub>14</sub>H<sub>14</sub>O<sub>2</sub>S; from the spectroscopic analysis<sup>¶</sup> the structure proved to be a hydroquinone.

The photoaddition of photogenerated 2-mercapto-1,4-naphthoquinone **18** with vinyl ethers, such as ethyl vinyl ether **10f** and 1-methoxycyclohexene **10g**, under the same conditions as the photoaddition with styrene, however, followed a different course to give products **14f** and **g** in 40 and 48% yields, respectively. HRMS of an oily product **14f** indicated its molecular formula to be C<sub>14</sub>H<sub>14</sub>O<sub>3</sub>S. Acetylation of **14f** with acetic anhydride in pyridine at room temperature gave the monoacetate **15f**. Spectroscopic analysis of **14f**<sup>‡</sup> and its acetate **15f** indicated that **14f** was 2,3-dihydro-2-ethoxy-6-hydroxynaphth[1,2-*b*]-1,4-oxathiin. Further support for this structure was found by treating **14f** in tetrahydrofuran (THF) with

<sup>†</sup> Selected data for **11b**: m.p. 146–149 °C from hexane–benzene.

For **11c** m.p. 229–230 °C from hexane–benzene: <sup>1</sup>H NMR  $\delta$  3.91 (2 H, s, 3-H), 7.28–7.47 (10 H, m), 7.60–7.71 (2 H, m) and 7.96–8.05 (2 H, m); <sup>13</sup>C NMR  $\delta$  46.9 (C-3), 67.5 (C-2), 178.7 and 181.3 (4- and 9-C=O).

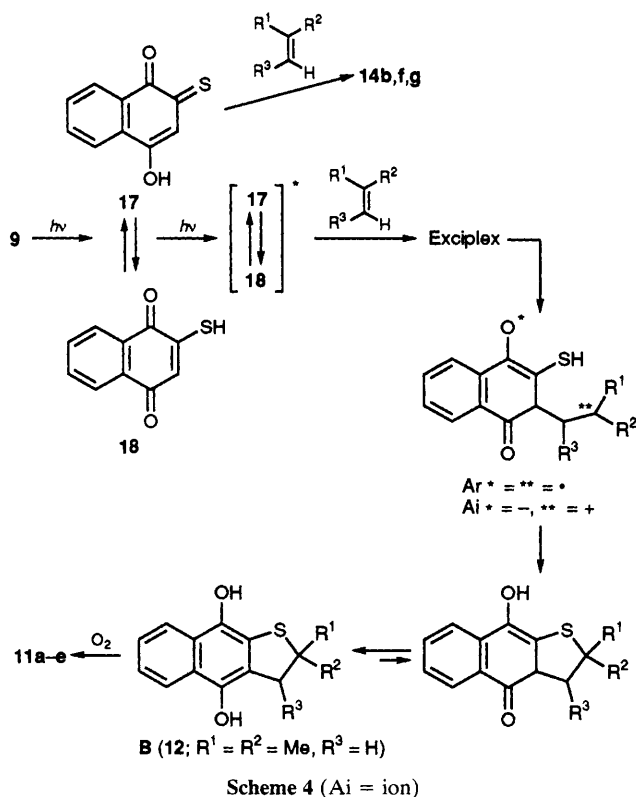
<sup>‡</sup> Selected data for **14b** oil;  $\nu_{\max}/\text{cm}^{-1}$  3372 (OH); *m/z* 308 (M<sup>+</sup>, 100); <sup>1</sup>H NMR  $\delta$  (270 MHz, CDCl<sub>3</sub>) 1.80 (3 H, s, 2-Me), 3.22 (each 1 H, d, *J* 13.20 Hz, 3-H), 6.42 (1 H, s, 5-H), 7.26–7.51 (5 H, m, aromatic H), 8.05–8.08 (1 H, m, aromatic H), and 8.28 (1 H, d, *J* 8.57 Hz).

For **14f** oil;  $\nu_{\max}/\text{cm}^{-1}$  3382 (OH); *m/z* 262 (M<sup>+</sup>, 100) and 190 (63);  $\delta$  (270 MHz, CDCl<sub>3</sub>) 1.25 (3 H, t, *J* 7.10 Hz, CH<sub>2</sub>CH<sub>3</sub>), 3.12 (1 H, dd, *J* 12.86 and 4.62 Hz, 3-H), 3.26 (1 H, dd, *J* 12.86, 1.98 Hz, 3-H), 3.80 and 4.00 (each 1 H, each dq, *J* 9.90 and 7.10 Hz, CH<sub>2</sub>CH<sub>3</sub>), 5.53 (1 H, dd, *J* 4.62 and 1.98 Hz, 2-H), 6.49 (1 H, s, aromatic H), 7.39–7.52 (2 H, m, aromatic H), and 8.04–8.08 (2 H, m, aromatic H).

For **14g** oil;  $\nu_{\max}/\text{cm}^{-1}$  3394 (OH); *m/z* 302 (M<sup>+</sup>, 46); 270 [(M–MeOH)<sup>+</sup>, 38], 192 (54), and 111 (100);  $\delta$  (270 MHz, CDCl<sub>3</sub>) 1.38–2.03 (7 H, m), 2.72 (1 H, m), 3.08 (1 H, dd, *J* 12.21 and 4.29 Hz, S–CH), 3.29 (3 H, s, OMe), 6.48 (1 H, s, aromatic H), 7.38–7.52 (2 H, m, aromatic H), 8.05–8.08 (2 H, m, aromatic H) and 8.16 (1 H, dd, *J* 6.27 and 1.32 Hz, aromatic H).

<sup>§</sup> Selected data for **13** m.p. 146–147 °C from hexane–benzene; <sup>1</sup>H NMR  $\delta$  4.07 (2 H, s, 3-H), 7.23–7.44 (5 H, m), 7.63–7.74 (2 H, m), 8.01–8.14 (2 H, m); <sup>13</sup>C NMR  $\delta$  47.2 (C-3), 70.4 (C-2), 179.6 (C=O or C=S), and 180.4 (C=O or C=S).

<sup>¶</sup> Selected data for **12**: oil;  $\nu_{\max}/\text{cm}^{-1}$  3390 (OH), 1625, and 1597; *m/z* 246 (M<sup>+</sup>, 100); <sup>1</sup>H NMR  $\delta$  (270 MHz, CDCl<sub>3</sub>) 1.52 (6 H, s, 2-Me<sub>2</sub>), 2.95 (2 H, s, 3-H), and 7.35–7.5 (2 H, m, 6, 7-H).



bis(trichloromethyl)carbonate,<sup>7</sup> in the presence of triethylamine in an argon atmosphere for 3 h at room temperature, which gave a carbonate **16f** in 48% yield. Similarly, spectroscopic analysis of **14g**† indicated that it was 1,4-oxathiin (Scheme 3). The monoacetate **15g** and carbonate **16g** were obtained analogously to **14f**.

The probable reaction paths for the formation of products **11**, **12** and **14** are outlined in Scheme 4. Irradiation of 1,3-oxathiol-2-one **9** gives a tautomeric mixture of  $\alpha$ -oxothione **17** and 2-mercapto-1,4-naphthoquinone **18**. The proposed path from the excited tautomer **18** to the [3 + 2]

photoadducts **11a-e** is parallel to that from 2-hydroxy- or 2-amino-1,4-naphthoquinone to the corresponding [3 + 2] photoadducts.<sup>2,3</sup> The initial products in the present [3 + 2] additions are thus believed to be hydroquinones **B**. However, only hydroquinone **12** was isolated through all of the present photoadditions.

The dihydronaphthoxathiins **14b**, **f** and **g**, on the other hand, are considered to be products arising from thermal [2 $\pi$  + 4 $\pi$ ] cycloadditions of  $\alpha$ -oxothione **17**; there is a precedent for this reaction.<sup>8</sup>

Caldariellaquinone having a benz[*b*]thiophene-4,7-quinone skeleton has been found in nature.<sup>9</sup> Some methods for the synthesis of benz[*b*]thiophenequinones<sup>10</sup> and a naphtho[2,3-*b*]thiophene-4,9-dione<sup>11</sup> have been reported.

The present one-step formation of 2,3-dihydronaphtho[2,3-*b*]thiophene-4,9-diones, using the new photochemical method may find some value in synthesis.

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