PHOTOCHEMICAL REACTION OF 2-BROMO-3-METHOXY-1,4-NAPHTHOQUINONE WITH SILYLENOLETHER — ONE-POT SYNTHESIS OF POLYCYCLIC AROMATIC COMPOUNDS

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Abstract — 5-Hydroxybenz[a]anthracene, 2-aryl-2,6-dihydroxy-5-formyl-2,3-dihydronaphtho[1,2-b][1,4]dioxin, and 4-arylnaphtho[2,3-d][1,3]-dioxepin derivatives were synthesized by one-pot photochemical reaction of 2-bromo-3-methoxy-1,4-naphthoquinone with trialkylsilylenolether.

Polycyclic aromatics have been one of the most attracting classes of compounds due to their expected physico-chemical as well as biological properties. However, the wider-ranging studies on the nature of the polycyclic aromatic compounds have been hampered partly because of their synthetic difficulties. The synthetic approaches introducing appropriate substituents into the parent polycyclic aromatics are, in general, rather limited. As an alternative the photochemical reaction of 2-bromo-3-methoxy-1,4-naphthoquinone with 1,1-diarylethylene can serve to give polycyclic aromatic compounds in fairly good yields. The photochemical reaction, in spite of the apparent similarity to the thermal Diels-Alder type cyclization reaction, proceeds in regioselective manner which gives rise to the marked contrast with thermal Diels-Alder type cyclization. Here the photochemical reactivity of 2-bromo-3-methoxy-1,4-naphthoquinone with 1-aryl-1-trialkylsilyloxyethylene was investigated, resulting in the formation of three different classes of polycyclic aromatic compounds. Of these, 4-arylnaphtho[2,3-d][1,3]dioxepin-6,11-dione and 2-aryl-2,6-dihydroxy-5-formyl-2,3-dihydronaphtho[1,2-b][1,4]dioxin are the new members of polycyclic aromatic compounds. And the third one, 5-hydroxybenz[a]anthracene derivatives would be expected to show biological activity as a possible metabolite of benz[a]anthracenes. Thus, the photochemical reactions of 2-bromo-3-methoxy-1,4-naphthoquinone with 1-aryl-1-trialkylsilyloxyethylene would open a facile synthetic route to the three different classes of polycyclic aromatic compounds.
Typically a solution of 2-bromo-3-methoxy-1,4-naphthoquinone (Ja)(1 mmol) in a mixed solvent (benzene/hexane=20 ml/380 ml) was irradiated by high pressure Hg arc lamp in the presence of 1-t-butylidimethylsilyloxyethylene (2a)(2 mmol). The original pale yellow color of the reaction mixture turned to red and 2-bromo-3-methoxy-1,4-naphthoquinone (Ja) was completely consumed in several hours at room temperature. Purification of the resulting reaction mixture gave two discrete classes of final products: 5-t-butylidimethylsilyloxybenz[a]anthracene-7,12-dione (4a) and 2-t-butylidimethylsilyloxy-5-formyl-6-hydroxy-2-phenyl-2,3-dihydrophtal,[1,2-b][1,4]dioxin (5a), accompanied by an intermediate, 2-(2-t-butylidimethylsilyloxy-2-phenyl)ethenyl-3-methoxy-1,4-naphthoquinone (3a) (Scheme 1). The structure of 4a was determined by deriving 4a to the known compound: 5-methoxybenz[a]anthracene-7,12-dione (Scheme 2). The structure of 2,3-dihydrophtal,[1,2-b]-[1,4]dioxin (5a) was suggested by its spectral data and was further confirmed by the chemical reactivities shown in Scheme 3. 2-(2-t-Butylidimethylsilyloxy-2-phenyl)ethenyl-3-methoxy-1,4-naphthoquinone (3a) was found to be a common intermediate to both 4a and 5a, since further irradiation of 3a gave both 4a and 5a in reasonable yields. Formation of 4a via 3a was explained on the basis of the photochemical cyclization with eliminating methanol. Elemental analysis and the MS data of 5a indicated that one more oxygen atom should be incorporated in 5a during the processes of its derivation from 3a. Actually, a solution of 3a deoxygenated completely by freeze-thaw cycle gave none of 5a upon irradiation. Thus, the extra-oxygen atom is originated in the dissolved oxygen in the reacting mixture. The possible routes to 5a from 3a is tentatively illustrated in Scheme 4, although the detailed mechanism remains to be clarified. Consequently the yields of the products are quite dependent upon the irradiation time and the amounts of oxygen present in
the reacting mixture. The yields shown in Table 1 were based on the starting quinones at a time when they were completely consumed. Similarly 1-aryl-1-t-butyldimethylsilyloxyethylene containing hetero-atom such as 1-t-butyldimethylsilyloxy-1-(2-thienyl)ethylene(2f) afforded sulfur-containing polycyclic aromatic compounds, 5f and 5f, in its reaction with 1a.

The regioselective cyclization was confirmed by choosing 2-bromo-3-methoxy-1,4-naphthoquinone derivatives as starting quinone such as 1b and 1c. For example, 2-bromo-3,8-dimethoxy-1,4-naph-
Table 1. Yields of Products

<table>
<thead>
<tr>
<th>Starting Materials</th>
<th>Irradiation Time(h)</th>
<th>Products(%)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>la</td>
<td>3a</td>
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</tr>
<tr>
<td>la</td>
<td>3b</td>
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<td>3g:trace</td>
</tr>
<tr>
<td>lc</td>
<td>3h</td>
<td>3h:23</td>
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</tbody>
</table>

thoquinone(\(\text{Ib}\)) gave exclusively 5-t-butyldimethylsilyloxy-8-methoxybenz[a]anthracene-7,12-dione(4g) and 2-t-butyldimethylsilyloxy-5-formyl-6-hydroxy-7-methoxy-2-phenyl-2,3-dihybronaphtho[1,2-b][1,4]dioxin(5g) in its reaction with \(\text{Za}\). None of the possible isomers, 5-t-butyldimethylsilyloy-11-methoxybenz[a]anthracene-7,12-dione(4h) nor 2-t-butyldimethylsilyloxy-5-formyl-6-hydroxy-10-methoxy-2-phenyl-2,3-dihybronaphtho[1,2-b][1,4]dioxin(5h), were detected in the reaction mixture. Those isomers, \(\text{4h}\) and \(\text{5h}\), were formed when 2-bromo-3,5-dimethoxy-1,4-naphthoquinone(\(\text{Ic}\)) was subjected to the reaction with \(\text{Za}\). The regioselective cyclization is reasonably explained by assuming the step-by-step ring-formation via \(\text{3}\) as an intermediate(as illustrated in Scheme 1)[21] Of these products, 5-t-butyldimethylsilyloybenz[a]anthracene-7,12-diones, \(4g\) and \(4h\), are easily transformed to the polyhydroxy derivatives of benz[a]anthracenes such as 5,8-dihydroxy- and 5,11-dihydroxybenz[a]anthracene, which were recently suggested to be the ultimate biologically active form.6) Thus, the present photochemical reaction could provide a regioselective synthetic method to metabolites of benz[a]anthracenes of biological importance.

Contrary to 1-aryl-1-t-butyldimethylsilyloxyethylene \(\text{2}\), 1-aryl-1-trimethylsilyloxyethylene \(\text{6}\) behaves in completely different manner when it is subjected to the photochemical reaction with \(\text{1a}\), presumably because of the lability of its ether linkage against hydrolysis. When 2-bromo-3-methoxy-1,4-naphthoquinone \(\text{1a}\) was irradiated in the presence of \(\text{6}\), the possible intermediate analogous to \(\text{3}\) was not identified in the reaction mixture. Instead, 2-{2-(2-aryl-2-oxo)ethyl-1,4-naphthoqui-
quinone 8 was isolated as well as 4-arylnaphtho[2,3-d][1,3]dioxepin-6,11-dione 9 (Scheme 5). The former 8 may be formed via hydrolysis of the expected intermediate 7 and the subsequent ketonization. Dioxepin 9 was concluded to be the secondary product derived upon irradiation of 8. The authentic sample of 8a was synthesized independently from 2-hydroxy-1,4-naphthoquinone and phenylacetaldehyde. The structure of [1,3]dioxepin was confirmed by its chemical reactivities (Scheme 6) as well as its spectral data. Although some possible routes are shown for derivation of 2 from 8 (Scheme 7), the route (a) would be the most probable on the basis of the result that no D-atom was incorporated at position of 5 of 2 in its derivation from 2-bromo-3-trideuterio-methoxy-1,4-naphthoquinone (1a-d3). 1-(2-Thienyl)-1-trimethylsilyloxyethylene 6c also serves as a hetero-atom containing silylenolether, resulting in the formation of 8c and 9c in its reaction with 1a. The yields of [1,3]dioxepins 9 and their precursors 8 are shown in Table 2.

![Scheme 5]

Table 2. Yields of Products\textsuperscript{a})

<table>
<thead>
<tr>
<th>Starting Materials</th>
<th>Products(%)</th>
</tr>
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<tbody>
<tr>
<td>8a</td>
<td>8a:28</td>
</tr>
<tr>
<td>8b</td>
<td>8b:22</td>
</tr>
<tr>
<td>8c</td>
<td>8c:20</td>
</tr>
</tbody>
</table>
| a) The yields shown were calculated after irradiation for 10h.

![Scheme 6]

(a(i))H\textsubscript{2}-Pd/EOH, rt, 6h  
(b)Zn/\textit{Ac}_2O, \Delta, 30min  
(c)HBr/EOH, 2,4-Dinitrophenylhydrazine, \Delta, 6h  

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Summarizing the results, the photochemical reaction of 2-bromo-3-methoxy-1,4-naphthoquinones with 1-aryl-1-trialkylsilyloxyethylene proceeds in a quite different manner, depending upon the lability of the ether linkage against hydrolysis, providing a regioselective one-pot synthetic route to three different classes of polycyclic aromatic compounds.

Experimental

Photochemical reaction (general procedure)\(^9\)

2-Bromo-3-methoxy-1,4-naphthoquinone (1)(1 mmol) was dissolved in an appropriate solvent, e.g., benzene/hexane = 20 ml/380 ml, and irradiated by high pressure Hg arc lamp (300W) in the presence of silylenolether (2)(2 mmol) at room temperature.\(^{10,11}\) After the complete consumption of \(1\) (4-9 h), the reaction mixture was concentrated in vacuo and was chromatographed over silica gel.

Physical properties of the products

Although the intermediate \(2\) could not be isolated in a pure state due to their high sensitivity against light, the formation of \(2\) was unambiguously confirmed by their spectral properties.\(^{2f}\)

The yields of \(3\) were calculated on the basis of the integration of their NMR signals by using the methyl-\(H\) of acetophenone as an internal standard.
5-<SUP>-b</SUP>utyldimethylsilyloxybenz[a]anthracene-7,12-dione (4a): pale yellow needles (from hexane-benzene), mp 180.0-180.5°C. m/e: 288 (M<sup>+</sup>). IR (KBr): 1660, 1580, 1280, 1120, 816-8.44 (3H, m), 7.97 (1H, d, J=9Hz). UV max (CHCl<sub>3</sub>): 428 (3.47), 363 (3.14), 328 (3.50), 303 (4.50), 292 (4.50), 247 (4.20). Calcd for C<sub>24</sub>H<sub>24</sub>O<sub>3</sub>Si: C, 74.19; H, 6.23. Found: C, 74.44; H, 6.16.

5-<SUP>-b</SUP>utyldimethylsilyloxy-2-methylbenz[a]anthracene-7,12-dione (4b): orange needles (from hexane-benzene), mp 195.5-196.5°C. m/e: 402 (M<sup>+</sup>). IR (KBr): 1660, 1580, 1295, 1120, 830, 5.42 (6H, s), 1.12 (9H, s), 2.59 (3H, s), 7.1-8.3 (7H, m), 9.95 (1H, s). UV max (CHCl<sub>3</sub>): 442 (3.64), 379 (3.55), 309 (4.41), 301 (4.43), 261 (4.53). Calcd for C<sub>25</sub>H<sub>26</sub>O<sub>3</sub>Si: C, 74.59; H, 6.51. Found: C, 74.67; H, 6.57.

5-<SUP>-b</SUP>utyldimethylsilyloxy-2-methoxybenz[a]anthracene-7,12-dione (4c): yellow needles (from ethanol-chloroform), mp 191.0-192.0°C. m/e: 418 (M<sup>+</sup>). IR (KBr): 1660, 1580, 1230, 1120, 816-8.3 (3H, m), 9.28 (1H, d, J=3Hz). UV max (CHCl<sub>3</sub>): 461 (3.64), 379 (3.55), 309 (4.41), 301 (4.43), 261 (4.53). Calcd for C<sub>25</sub>H<sub>26</sub>O<sub>4</sub>Si: C, 71.74; H, 6.26. Found: C, 71.98; H, 6.31.

5-<SUP>-b</SUP>utyldimethylsilyloxy-3-methoxybenz[a]anthracene-7,12-dione (4d): yellow needles (from ethanol-chloroform), mp 180.5-181.5°C. m/e: 418 (M<sup>+</sup>). IR (KBr): 1660, 1580, 1295, 1225, 830. NMR (CDCl<sub>3</sub>): <br>δ 0.42 (6H, s), 1.12 (9H, s), 3.90 (3H, s), 6.94 (1H, d, J=7Hz), 7.4-7.8 (5H, m), 8.0-8.1 (2H, m), 9.27 (1H, d, J=9Hz). UV max (CHCl<sub>3</sub>): 477 (3.58), 354 (3.74), 316 (4.50), 295 (4.36), 250 (4.36). Calcd for C<sub>25</sub>H<sub>26</sub>O<sub>4</sub>Si: C, 71.74; H, 6.26. Found: C, 71.92; H, 6.23.

5-<SUP>-b</SUP>utyldimethylsilyloxy-4-methoxybenz[a]anthracene-7,12-dione (4e): red needles (from ethanol-chloroform), mp 163.5-164.0°C. m/e: 418 (M<sup>+</sup>). IR (KBr): 1665, 1580, 1280, 1140, 840. NMR (CDCl<sub>3</sub>): <br>δ 0.36 (6H, s), 1.08 (9H, s), 3.88 (3H, s), 6.94 (1H, d, J=7Hz), 7.4-7.8 (4H, m), 8.0-8.1 (2H, m), 9.27 (1H, d, J=9Hz). UV max (CHCl<sub>3</sub>): 477 (3.58), 354 (3.74), 316 (4.50), 295 (4.36), 250 (4.36). Calcd for C<sub>25</sub>H<sub>26</sub>O<sub>4</sub>Si: C, 71.74; H, 6.26. Found: C, 71.92; H, 6.23.

4-<SUP>-b</SUP>utyldimethylsilyloxyanthra[2,1-b]thiophene-6,11-dione (4f): yellow crystals (from hexane-benzene), mp 178.0-179.0°C. m/e: 418 (M<sup>+</sup>). IR (KBr): 1660, 1545, 1295, 825. NMR (CDCl<sub>3</sub>): δ 0.39 (6H, s), 1.08 (9H, s), 7.4-7.8 (4H, m), 8.1-8.3 (2H, m), 8.61 (1H, d, J=6Hz). UV max (CHCl<sub>3</sub>): 418 (3.50), 373 (3.37), 306 (4.46), 292 (4.48), 246 (4.23). Calcd for C<sub>22</sub>H<sub>22</sub>O<sub>3</sub>SiS: C, 66.97; H, 5.62. Found: C, 67.02; H, 5.67.

5-<SUP>-b</SUP>utyldimethylsilyloxy-8-methoxybenz[a]anthracene-7,12-dione (4g): yellow needles (from ethanol), mp 171.0-172.0°C. m/e: 418 (M<sup>+</sup>). IR (KBr): 1660, 1580, 1280, 1115, 865. NMR (CDCl<sub>3</sub>): δ 0.43 (6H, s), 1.11 (9H, s), 4.02 (3H, s), 7.1-8.0 (6H, m), 8.27 (1H, d, J=8Hz), 9.64 (1H, d, J=8Hz). UV max (CHCl<sub>3</sub>): 433 (3.92), 378 (3.56), 302 (4.52), 291 (4.54). Calcd for C<sub>25</sub>H<sub>26</sub>O<sub>4</sub>Si: C, 71.74; H, 6.26. Found: C, 71.93; H, 6.20.
5-β-Butyldimethylsilyloxy-11-methoxybenz[a]anthracene-7,12-dione(5h): yellow needles(from ethanol), mp 149.5-150.0°. m/e: 418(M^+). IR(KBr): 1660, 1580, 1260, 1100. NMR(CDC13): δ 0.40(6H,s), 1.11(9H,s), 4.03(3H,s), 6.9-8.1(6H,m), 8.25(1H,d,J=8Hz), 9.40(1H,d,J=8Hz). UV max(CHCl3)(log e): 414(3.75), 393(3.76), 337(3.61), 301(4.60), 291(4.58). Calcd for C_{25}H_{26}O_{4}Si: C, 71.74; H, 6.26. Found: C, 71.76; H, 6.41.

2-β-Butyldimethylsilyloxy-5-formyl-6-hydroxy-2-phenyl-2,3-dihydronaphtho[1,2-b][1,4]dioxin(5a): yellow crystals(from petroleum ether), mp 125.0-126.0°. m/e: 436(M^+). IR(KBr): 1630, 1605, 1310, 960. NMR(CDC13): δ -0.32(3H,s), -0.17(3H,s), 0.76(9H,s), 3.86(1H,d,J=11Hz), 4.36(1H,d,J=11Hz), 7.4-7.6(4H,m), 7.6-7.8(3H,m), 8.14(1H,d,J=8Hz), 8.40(1H,d,J=8Hz), 10.20(1H,s), 12.93(1H,s). UV max(CHCl3)(log e): 427(3.41), 309(3.69), 300(3.80), 285(4.22), 276(4.17). Calcd for C_{25}H_{28}O_{5}Si: C, 68.78; H, 6.46. Found: C, 68.78; H, 6.49.

2-β-Butyldimethylsilyloxy-5-formyl-6-hydroxy-2-β-tolyl-2,3-dihydronaphtho[1,2-b][1,4]dioxin(5b): yellow crystals(from petroleum ether), mp 132.5-133.0°. m/e: 450(M^+). IR(KBr): 1635, 1310, 1170, 1090, 955. NMR(CDC13): δ -0.32(3H,s), -0.16(3H,s), 0.76(9H,s), 4.13(1H,d,J=11Hz), 4.32(1H,d,J=11Hz), 7.2-7.8(2H,m), 7.57(2H,d,J=8Hz), 7.95(2H,d,J=8Hz), 8.14(1H,d,J=9Hz), 8.37(1H,d,J=9Hz), 10.38(1H,s), 13.12(1H,s). UV max(CHCl3)(log e): 428(3.39), 308(3.66), 286(4.23), 276(4.18). Calcd for C_{26}H_{30}O_{5}Si: C, 69.30; H, 6.71. Found: C, 69.18; H, 6.99.

2-β-Butyldimethylsilyloxy-5-formyl-6-hydroxy-2-β-methoxyphenyl-2,3-dihydronaphtho[1,2-b][1,4]dioxin(5c): yellow crystals(from hexane), mp 128.0-129.0°. m/e: 466(M^+). IR(KBr): 1630, 1605, 1300, 1185. NMR(CDC13): δ -0.32(3H,s), -0.19(3H,s), 0.76(9H,s), 3.84(3H,s), 3.81(1H,d,J=11Hz), 4.32(1H,d,J=11Hz), 6.95(2H,d,J=10Hz), 7.57(2H,d,J=10Hz), 7.3-7.8(2H,m), 8.09(1H,d,J=8Hz), 8.33(1H,d,J=8Hz), 10.32(1H,s), 13.03(1H,s). UV max(CHCl3)(log e): 429(3.52), 309(3.66), 285(4.38), 276(4.35), 241(3.94). Calcd for C_{26}H_{30}O_{6}Si: C, 66.93; H, 6.48. Found: C, 66.93; H, 6.48.

2-β-Butyldimethylsilyloxy-5-formyl-6-hydroxy-2-β-methoxyphenyl-2,3-dihydronaphtho[1,2-b][1,4]dioxin(5d): yellow needles(from petroleum ether), mp 103.5-104.5°. m/e: 466(M^+). IR(KBr): 1635, 1315, 1175, 960. NMR(CDC13): δ -0.32(3H,s), -0.13(3H,s), 0.77(9H,s), 3.83(3H,s), 3.81(1H,d,J=11Hz), 4.30(1H,d,J=11Hz), 6.7-7.7(6H,m), 8.06(1H,d,J=8Hz), 8.31(1H,d,J=8Hz), 10.29(1H,s), 13.01(1H,s). UV max(CHCl3)(log e): 429(3.46), 310(3.74), 285(4.31), 276(4.28), 242(3.75). Calcd for C_{26}H_{30}O_{6}Si: C, 66.93; H, 6.48. Found: C, 67.02; H, 6.50.

2-β-Butyldimethylsilyloxy-5-formyl-6-hydroxy-2-β-methoxyphenyl-2,3-dihydronaphtho[1,2-b][1,4]dioxin(5e): yellow crystals(from hexane), mp 162.0-162.5°. m/e: 466(M^+). IR(KBr): 1635, 1310, 1245, 1080, 950. NMR(CDC13): δ -0.28(3H,s), -0.21(3H,s), 0.73(9H,s), 3.87(3H,s), 4.23(1H,d,J=11Hz), 4.77(1H,d,J=11Hz), 6.9-7.5(6H,m), 8.15(1H,d,J=8Hz), 8.36(1H,d,J=8Hz), 10.34(1H,s), 13.04(1H,s). UV max(CHCl3)(log e): 435(3.48), 309(3.76), 285(4.35), 277(4.32), 241(3.78). Calcd for C_{26}H_{30}O_{6}Si: C, 66.93; H, 6.48. Found: C, 67.18; H, 6.69.
2-t-Butyldimethylsilyloxy-5-formyl-6-hydroxy-2-(2-thienyl)-2,3-dihydronaphtho[1,2-b][1,4]dioxin (5f): yellow crystals (from petroleum ether), mp 144.5-145.5°. IR(KBr): 1635, 1180, 1100, 990. m/e: 442 (M⁺). IR(KBr): 1635, 1310, 1180, 1100, 990. NMR(CDC1₃): δ -0.24 (3H, s), 0.79 (9H, s), 3.99 (1H, d, J=11Hz), 4.35 (1H, d, J=11Hz), 6.9-7.8 (5H, m), 10.10 (1H, s), 13.18 (1H, s). UV max (CHCl₃) (log ε): 427 (3.45), 310 (3.72), 285 (4.29), 276 (4.25), 243 (3.98).


2-t-Butyldimethylsilyloxy-5-formyl-6-hydroxy-7-methoxy-2-phenyl-2,3-dihydronaphtho[1,2-b][1,4]dioxin (5g): yellow crystals (from hexane), mp 182.0-182.5°. m/e: 466 (M⁺). IR(KBr): 1625, 1385, 1040. NMR(CDC1₃): δ -0.34 (3H, s), -0.20 (3H, s), 0.76 (9H, s), 3.81 (1H, d, J=11Hz), 4.01 (3H, s), 4.31 (1H, d, J=11Hz), 6.7-7.8 (8H, m), 14.78 (1H, s). UV max (CHCl₃) (log ε): 439 (3.90), 313 (3.92), 279 (4.63).


Chemical reactivity of 5a (Scheme 2).

Step (a): Hydrolysis of the ether linkage of 5a was performed by refluxing the acetic acid solution of 5a for 3 h. Purification of the reaction mixture by column chromatography on silica gel gave 5-hydroxybenz[a]anthracene-7,12-dione as reddish orange plates (from 1,2-dimethoxyethane) (yield: 91%), mp 253°. IR(KBr): 3300, 1660, 1555, 1355. UV max (CHCl₃) (log ε): 441 (3.53), 364 (3.16), 333 (3.63), 304 (4.56), 296 (4.55), 252 (4.12), 247 (4.17). Calcd for C₁₈H₁₀O₃: C, 78.82; H, 3.68. Found: C, 79.06; H, 3.62.

Step (b): 5-Methoxybenz[a]anthracene-7,12-dione was derived by treating of 5-hydroxybenz[a]anthracene-7,12-dione with diazomethane in 1,2-dimethoxyethane at room temperature for 1 h, and isolated as yellow needles (from hexane-benzene) (yield: 93%), mp 195.5-196.0°.5

Chemical reactivity of 5 (Scheme 3).

Step (a): The ethanol solution (25 ml) of 5d (100 mg) was mixed with aqueous solution (50 ml) of FeCl₃·6H₂O (125 mg) and conc. HCl (10 ml). The reaction mixture was then refluxed for 3.5 h. Purification of the reaction mixture gave 2-hydroxy-1,4-naphthoquinone (yield: 63%) and m-methoxyacetophenone (yield: 36%).

Step (b): Lithium aluminum hydride (excess amount) was added to the ether solution (8 ml) of 5e (30 mg) and stirred for 10 min at room temperature. After the usual work-up 2-t-butyldimethylsilyloxy-6-hydroxy-5-hydroxymethyl-2-phenyl-2,3-dihydronaphtho[1,2-b][1,4]dioxin was isolated as pale yellow oil in quantitative yield. IR(KBr): 3360. NMR(CDC1₃): δ -0.34 (3H, s), -0.17 (3H, s), 0.75 (9H, 1H, d, J=11Hz).
Step (c): 2-tert-Butyldimethylsilyloxyl-6-hydroxy-5-hydroxymethyl-2-phenyl-2,3-dihydronaphtho[1,2-b][1,4]dioxin (25 mg) was acetylated with acetic anhydride (10 ml) in the presence of catalytic amount of pyridine. The reaction mixture was chromatographed over silica gel. 6-Acetoxy-5-acetoxymethyl-2-tert-butyldimethylsilyloxy-2-phenyl-2,3-dihydronaphtho[1,2-b][1,4]dioxin was isolated as colorless oil in quantitative yield: m/e:522(M\(^+\)). IR(KBr):1770, 1740.

NMR(CDC\(_1\)\(_3\)): \(\delta\) -0.33(3H, s), -0.17(3H, s), 0.75(9H, s), 2.03(3H, s), 2.47(3H, s), 3.85(1H, d, J=11Hz), 4.37(1H, d, J=11Hz), 5.33(2H, s), 7.3-7.8(8H, m).

Step (d): Refluxing of the acetic acid solution (20 ml) of \(\text{S}_\text{a}\) (50 mg) for 2 h afforded the hydrolyzed product: 2,6-dihydroxy-5-formyl-2-phenyl-2,3-dihydronaphtho[1,2-b][1,4]dioxin as orange solid (yield:90%), mp 195.0-197.5°. m/e:322(M\(^+\)). IR(KBr):3380, 1630. NMR(CDC\(_1\)\(_3\)): \(\delta\) 3.16(3H, s), 3.94(1H, d, J=11Hz), 4.47(1H, d, J=11Hz), 7.4-7.8(7H, m), 8.15(1H, d, J=8Hz), 8.38(1H, d, J=8Hz), 10.38(1H, s), 13.03(1H, s).

We purified the reaction mixture as yellow crystals (yield:95%), mp 163.0-164.0°. IR(KBr):1640. NMR(CDC\(_1\)\(_3\)): \(\delta\) 3.42(2H, q, J=7Hz), 3.42(2H, q, J=7Hz), 3.88(1H, d, J=11Hz), 4.42(1H, d, J=11Hz), 7.3-7.8(7H, m), 8.06(1H, d, J=8Hz), 8.30(1H, d, J=8Hz), 10.30(1H, s), 13.00(1H, s).

Step (e): The methanol solution (20 ml) of 2,6-dihydroxy-5-formyl-2-phenyl-2,3-dihydronaphtho[1,2-b][1,4]dioxin (30 mg) was refluxed in the presence of catalytic amount of conc. HI for 2 h. Purification of the reaction mixture gave 5-formyl-6-hydroxy-2-methoxy-2-phenyl-2,3-dihydronaphtho[1,2-b][1,4]dioxin as yellow crystals (yield:95%), mp 163.0-164.0°. m/e:350(M\(^+\)). IR(KBr):1640. NMR(CDC\(_1\)\(_3\)): \(\delta\) 1.02(3H, t, J=7Hz), 3.42(2H, s), 3.88(1H, d, J=11Hz), 4.42(1H, d, J=11Hz), 7.3-7.8(7H, m), 8.06(1H, d, J=8Hz), 8.30(1H, d, J=8Hz), 10.30(1H, s), 13.00(1H, s).

Step (f): Ether exchange reaction was performed by treating the ethanol solution (20 ml) of \(\text{S}_\text{a}\) (16 mg) in the presence of catalytic amount of conc. HI under reflux for 2 h. 2-Ethoxy-5-formyl-6-hydroxy-2-phenyl-2,3-dihydronaphtho[1,2-b][1,4]dioxin was isolated as yellow crystals (yield:80%), mp 162.0-163.5°. m/e:306(M\(^+\)). IR(KBr):1660. NMR(CDC\(_1\)\(_3\)): \(\delta\) 1.02(3H, t, J=7Hz), 3.42(2H, q, J=7Hz), 3.88(1H, d, J=11Hz), 4.42(1H, d, J=11Hz), 7.3-7.8(7H, m), 8.06(1H, d, J=8Hz), 8.30(1H, d, J=8Hz), 10.30(1H, s), 13.00(1H, s).

2-Methoxy-3-(2-phenyl-2-oxo)ethyl-1,4-naphthoquinone(\(\text{g}_\text{a}\)): yellow plates(from ethanol), mp 146.0-148.0°. m/e:306(M\(^+\)). IR(KBr):1660, 1640. NMR(CDC\(_1\)\(_3\)): \(\delta\) 4.14(3H, s), 4.33(2H, s), 7.4-8.3(9H, m). UV max(EtOH)(logc):430(2.44), 405(2.77), 332(3.48), 278(4.14), 250(4.45). Calcd for C\(_{19}\)H\(_{14}\)O\(_4\): C,74.50;H,4.61. Found: C,74.28;H,4.60.

2-Methoxy-3-(2-p-tolyl-2-oxo)ethyl-1,4-naphthoquinone(\(\text{g}_\text{b}\)): yellow plates(from ethanol), mp 133.0-134.0°. m/e:320(M\(^+\)). IR(KBr):1665, 1640, 1323. NMR(CDC\(_1\)\(_3\)): \(\delta\) 2.47(3H, s), 4.15(3H, s), 4.34(2H, s), 7.39(2H, d, J=8Hz), 7.6-7.9(4H, m), 8.0-8.3(2H, m). UV max(EtOH)(logc):425(2.52), 405(2.77), 331(3.48), 275(4.17), 252(4.48), 247(4.44). Calcd for C\(_{20}\)H\(_{16}\)O\(_4\): C,74.99;H,5.04. Found:C,74.82;H,5.04.

2-Methoxy-2-(2'-thienyl-2-oxo)ethyl-1,4-naphthoquinone(\(\text{g}_\text{c}\)): orange-yellow needles(from ethanol), mp 90.0-93.0°. m/e:312(M\(^+\)). IR(KBr):1665. NMR(CDC\(_1\)\(_3\)): \(\delta\) 4.08(3H, s), 4.20(2H, s), 7.0-7.2(1H, m).
7.5-8.1(6H,m). Calcd for C_{17}H_{12}O_{4}S:C,65.37;H,3.87;S,10.27. Found:C,65.39;H,3.82;S,10.21.

4-Phenynaphtho[2,3-d][1,3]dioxepin-6,11-dione(9a): red needles (from methylene chloride), mp 168.0°.

m/e:304(M^{+}). IR(KBr):1660, 1580, 1560. NMR(CDC1_{3}):δ 7.75(2H,s), 6.91(1H,s), 7.3-8.0(7H,m), 8.1-8.3(2H,m). 13C-NMR(CDC1_{3}):δ 94.0(t), 95.0(d), 123.6, 125.6, 126.3, 128.5, 130.0, 131.3, 131.6, 133.8, 134.3, 155.5, 163.1, 178.0, 183.5. UV max(EtOH)(loge):462(3.74), 307(4.36), 224(4.11). Calcd for C_{17}H_{12}O_{4}:C,65.37;H,3.87;S,10.27. Found:C,65.39;H,3.82;S,10.21.

4-Phenyl-4,5-dihydronaphtho[2,3-d][1,3]dioxepin-6,11-dione was recrystallized from ethanol-methylene chloride as yellow needles (yield:60 %), mp 162.0-163.0°. m/e:306(M^{+}). IR(KBr):1670, 1560, 1295. NMR(CDC1_{3}):δ 2.42(3H,s), 5.67(2H,s), 6.91(1H,s), 7.32(2H,d,J=8Hz), 7.6-7.9(4H,m), 8.1-8.3(2H,m). UV max(EtOH)(loge):472(3.72), 311(4.61), 237(4.04). Calcd for C_{20}H_{14}O_{4}:C,74.45;H,4.60. Found:C,74.30;H,4.49.

Chemical reactivity of 9a (Scheme 6).

Step (a): Hydrogenation of 9a was performed in the ethanol solution with Pd-charcoal as catalyst for 6 h (under the hydrogen pressure of 5 kg/cm^{2}). 4-Phenyl-4,5-dihydronaphtho[2,3-d][1,3]dioxepin-6,11-dione was recrystallized from ethanol-methylene chloride as yellow needles (yield:60 %), mp 162.0-163.0°. m/e:306(M^{+}). IR(KBr):1670, 1560, 1295. NMR(CDC1_{3}):δ 2.96(1H,dd,J=9,16 Hz), 3.66(1H,dd,J=2,16Hz), 4.65(1H,dd,J=2,9Hz), 5.04(1H,d,J=7Hz), 5.67(1H,dd,J=7Hz), 7.2-7.5(5H,m), 7.5-7.8(2H,m), 7.9-8.2(2H,m). UV max(MeOH)(loge):420(2.54), 330(3.63), 273(4.13), 250(4.29), 244(4.30). Calcd for C_{19}H_{14}O_{4}:C,74.45;H,4.60. Found:C,74.30;H,4.49.

Step (b): The acetic anhydride solution(10ml) of 9a(152 mg) and zinc powder(1 g) was refluxed for 30 min and the reaction mixture was poured into water. 6,11-Diacetoxy-4-phenynaphtho[2,3-d][1,3]dioxepin was isolated as colorless crystals (from ethanol)(yield:82%), mp 175.0-176.0°. m/e:390(M^{+}). IR(KBr):1750, 1370, 1200. NMR(CDC1_{3}):δ 2.46(3H,s), 2.51(3H,s), 5.58(2H,s), 6.24(1H,s), 7.2-7.8(9H,m). UV max(MeOH)(loge):341(2.54), 291(4.37), 284(4.38), 257(4.13), 241(4.18), 233(4.26), 226(4.33). Calcd for C_{23}H_{18}O_{6}:C,70.76;H,4.65. Found:C,70.88;H,4.80.

Step (c): The ethanol solution (20 ml) of 9a (152 mg) was treated with hydrobromic acid (48%, 10 drops) in the presence of 2,4-dinitrophenylhydrazine. Purification of the reaction mixture by column chromatography on silica gel gave 2-hydroxy-3-(2-phenyl-2-oxo)ethy-1,4-naphthoquinone and 2,4-dinitrophenylhydrazone of formaldehyde.
References and Notes

   f) W. B. Manning and D. J. Wilber, ibid., 45, 733 (1980).
4) Preliminary reports on the present photochemical reaction: see (2j) and (2k).
7) 2-Bromo-3-ethoxy-1,4-naphthoquinone undergoes the similar photochemical reaction with 1-tri-
methylsilyloxyethylene, resulting in the formation of 2-(2-aryl-2-oxo)ethyl-3-ethoxy-1,4-naphtho-
quinone and 4-aryl-2-methylnaphtho[2,3-d][1,3]dioxepin-6,11-dione in reasonable yields. Cf.(2j).
8) 8a was synthesized by methylation of 2-hydroxy-3-(2-phenyl-2-oxo)ethyl-1,4-naphthoquinone, which was derived from 2-hydroxy-1,4-naphthoquinone and phenylacetaldehyde.
9) The starting materials are all compatible with their spectral data.
10) The reaction mixture was deoxygenated by bubbling with the commercially available nitrogen gas without further purification.
11) Addition of pyridine (equimolar to 1a) was helpful to keep the reacting mixture clean.
12) 2-Hydroxy-3-(2-phenyl-2-oxo)ethyl-1,4-naphthoquinone is an intermediate for the independent synthesis of 8. Cf. (8).

Received, 20th July, 1981

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