ONE-STEP SYNTHESIS OF 2,3-DIHYDROANTHRA[2,3-*b*]FURAN-4,11-DIONES AND 1*H*-NAPHTH[2,3-*f*]INDOLE-4,11-DIONES BY [2+3] PHOTOADDITION OF 2-HYDROXY- OR 2-AMINO-1,4-ANTHRACENEDIONE WITH CYCLIC AND ACYCLIC ALKENES[1]

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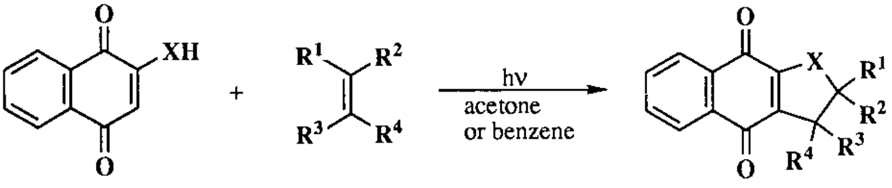
Abstract —— A one-step formation of 2,3-dihydroanthra[2,3-*b*]furan-4,11-diones in 32~78% yields by a [2+3] type regioselective photoaddition of 2-hydroxy-1,4-anthracenedione with a variety of alkenes is reported. An analogous one-step formation of 1*H*-2,3-dihydronaphth[2,3-*f*]indole-4,11-dione in 53% yield by the [2+3] type regioselective photoaddition of 2-amino-1,4-anthracenedione with isobutene is also described. The photoannelation of 2-amino-1,4-anthracenedione with 2-methoxypropene under the same conditions as with isobutene resulted in the formation of 2-methyl-1H-naphth[2,3-*f*]indole-4,11-dione (55%) *via* a spontaneous elimination of methanol from the intially formed [2+3] photoadduct.

In a recent paper[2] we reported a one-step exclusive formation of 2,3-dihydronaphtho[2,3-*b*]furan-4,9-diones (**3a**) in good yields by a new [2+3] type regioselective photoaddition of 2-hydroxy-1,4-naphthoquinone (**1a**) with a variety of alkenes (**2**). The dihydronaphthofurandiones, thus obtained, could readily be transformed into naphtho[2,3-*b*]furan-4,9-diones including a natural quinone, maturinone.[2] In our subsequent paper[3] we also disclosed a one-step synthesis of 1*H*-benz[*f*]indole-4,9-diones (**3b**) by a regioselective [2+3] photoaddition of 2-amino-1,4-naphthoquinone (**1b**) with various alkenes (**2**).[3] These photoannelations are outlined in Scheme 1.



1a X=O
1b X=NH

2
R^1-R^4; H, alkyl, OR, OAc, COOMe etc.

3a X=O
3b X=NH

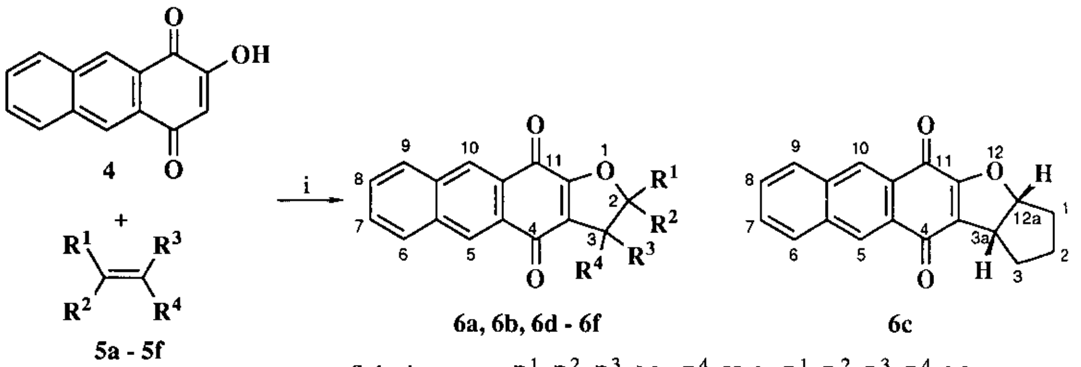
Scheme 1

In this paper we report on an application of these photoannelations to a one-step synthesis of 2,3-dihydroanthra[2,3-*b*]furan-4,11-diones as well as their nitrogen analogues, 1*H*-naphth[2,3-*f*]indole-4,11-diones.

Results

Synthesis of 2,3-Dihydroanthra[2,3-*b*]furan-4,11-diones.

Irradiation of 2-hydroxy-1,4-anthracenedione (**4**)[4] and an excess olefin (2-methyl-2-butene, 2,3-dimethyl-2-butene, cyclopentene, α-methylstyrene, vinyl acetate, or methyl methacrylate) in acetone with a 500 W high-pressure Hg arc through a Pyrex filter for 0.8~1.5 h gave a corresponding single [2+3] type photoadduct, respectively, in 54~78% yields, as outlined in Scheme 2. These photoadditions were completely regioselective.



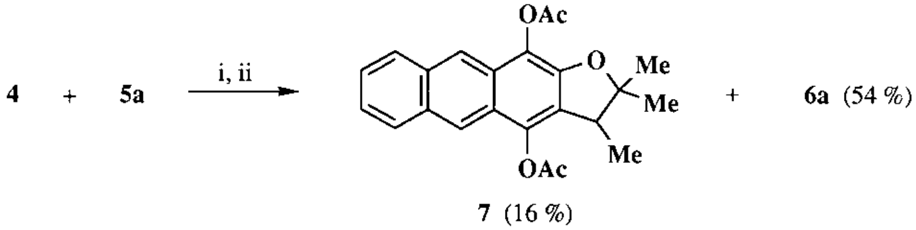
4 + 5a - 5f → 6a, 6b, 6d - 6f; 6c

i) hν - acetone

Substituents **a**: $R^1=R^2=R^3=Me, R^4=H$; **b**: $R^1=R^2=R^3=R^4=Me$;
c: $R^1,R^3=(CH_2)_3, R^2=R^4=H$; **d**: $R^1=Ph, R^2=Me, R^3=R^4=H$;
e: $R^1=OAc, R^2=R^3=R^4=H$; **f**: $R^1=COOMe, R^2=Me, R^3=R^4=H$

Scheme 2

Moreover, while the photoadducts can be obtained in benzene as the solvent as well, we found that the yield of the photoadduct was generally lower and that photoannelation in benzene required a much longer time than in acetone. Thus, while the photoaddition of 2-hydroxyanthraquinone (**4**) with five equivalents of α-methylstyrene (**5d**) in acetone came to completion in 1 h to give an exclusive photoadduct (**6d**) in 71% yield, photoaddition in benzene required 7.5 h and gave the photoadduct in only 32% yield. As in the case of the photoaddition of 2-hydroxy-1,4-naphthoquinone (**1a**) with olefins, a hydroquinone intermediate could be isolated in the form of the diacetate (**7**) in the photoaddition of 2-hydroxyquinone (**4**) with olefin (**5a**) by treating the product with acetic anhydride immediately after the photoaddition was completed (Scheme 3). The results together with the regioselectivity and the effect of the solvent on the yield of the products in this photoaddition (which are products parallel to those in the photoaddition of 2-hydroxy-1,4-naphtoquinone (**1a**) with alkenes recently reported by us) indicated that the pathway for the formation of 2,3-dihydroanthra[2,3-*b*]furan-4,11-diones involves a reaction path parallel to the one for the photoannelation of 2-hydroxynaphthoquinone proposed by us in a previous paper.[2]

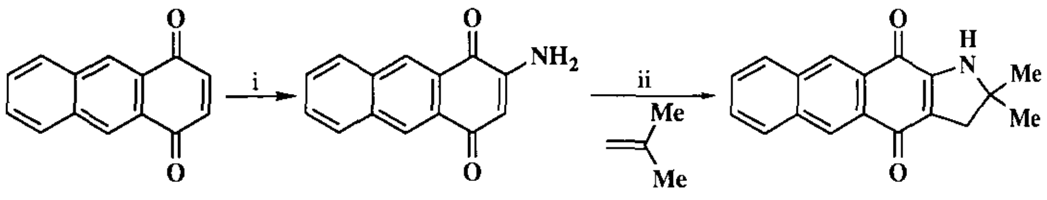


i) hν - acetone; ii) Ac_2O - Py

Scheme 3

Synthesis of 1*H*-Naphth[2,3-*f*]indole-4,11-diones

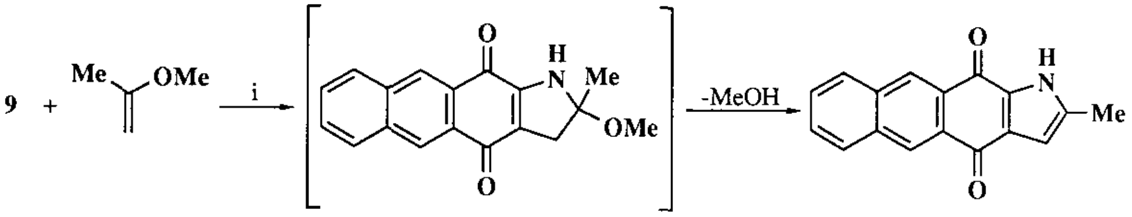
Analogous photoannelation can be achieved with 2-amino-1,4-anthracenedione (**9**). 2-Aminoquinone (**9**) could be readily prepared by the reaction of 1,4-anthracenedione (**8**)[5] with sodium azide according to a method by Fieser and Hartwell.[6] The irradiation of aminoquinone (**9**) with excess isobutene in benzene for 1.5 h under the same conditions as for the photoaddition of the hydroxy analogue (**4**) gave exclusively 2,3-dihydro-2,2-dimethyl-1*H*-naphth[2,3-*f*]indole-4,11-dione (**10**) in 53% yield. The photoaddition was completely regioselective as in the case of the photoaddition of 2-amino-1,4-naphthoquinone previously reported by us[3] (Scheme 4). The analogous photoaddition of aminoquinone (**9**) with 2-methoxypropene (**11**) in benzene, however, gave 2-methyl-1*H*-naphth[2,3-*f*]indole-4,11-dione (**13**) (55%), which was apparently formed by a spontaneous elimination of MeOH from the initial [2+3] type adduct (**12**) during the course of the reaction or during the workup stage. While the formation of the photoadducts (**10**) and (**12**) involves air oxidation of a hydroquinone intermediate, we were unsuccessul to isolate these intermediates as their diacetate, as in the case of the photoaddition of the oxygen analogues (**4**) mentioned above. The hydroquinone intermediate seems to be more susceptible to air oxidation than does that formed in the annelation of 2-hydroxyquinone (**4**).



8 **9** **10**

i) NaN$_3$ - AcOH, 70 $^{\circ}$C; ii) hν - acetone or benzene

Scheme 4



11 **12** **13**

i) hν - benzene

Scheme 5

It is very likely that the path of the photoaddition of **9**, which involves the initial formation of the hydroquinone derivatives as an intermediate, is analogous to that we previously proposed for the photoaddition of 2-aminonaphthoquinone (**1b**).[3]

Conclusion

The results reported in the foregoing part indicate that the unprecedented regioselective formation of [2+3] photoadducts is general in the photoaddition between 2-hydroxy- or 2-aminoquinone system and alkenes and can be extended to the photoannelation of 2-hydroxy- and 2-amino-1,4-anthracenedione. 2,3-Dihydroanthra[2,3-*b*]furan-4,11-diones and 1*H*-naphth[2,3-*f*]indole-4,11-diones, thus obtained, may have potential utility for the synthesis of a variety of heteroaromatic compounds.

EXPERIMENTAL

General Method.

For the instruments used and the precedure of the photolysis see refs. 2 and 3.

2-Hydroxy-1,4-anthracenedione (4).
This quinone was prepared according to the reported procedure.[4]

2,3-Dihydro-2,2,3-trimethylanthra[2,3-*b*]furan-4,11-dione (6a).
A solution of **4** (50 mg, 0.22 mmol) and 2-methyl-2-butene (310 mg, 4.5 mmol) in acetone (32 ml) was irradiated through a Pyrex filter for 1.5 h. After evaporation of the solvent, purification of the residue by preparative tlc on silica gel using chloroform gave **6a** (54 mg, 78%): mp 211~213°C (hexane- ether-chloroform); ir 1674, 1646, 1611 cm^{-1}; ^1H nmr (90 MHz) δ 1.36 (3H, d, *J*=7.25 Hz, 3-Me), 1.52 and 1.54 (6H, 2s, 2-Me), 3.32 (1H, q, *J*=7.25 Hz, 3-H), 7.55~7.75 (2H, m, 7- and 8-H), 7.95~8.1 (2H, m, 6- and 9-H), 8.55 and 8.61 (2H, 2s, 5- and 10-H); ms (rel. intensity) *m/z* 292 (M^+, 100). *Anal.* Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 78.21; H, 5.47.

2,3-Dihydro-2,2,3,3-tetramethylanthra[2,3-*b*]furan-4,11-dione (6b).
Irradiation of a solution of **4** (50 mg, 0.22 mmol) and **5b** (380 mg, 4.5 mmol) in acetone (32 ml) for 1 h was carried out in a similar fastion as above to give **6b** (37 mg, 73 %); mp 186~186.5°C (hexane-ether); ir 1680, 1645, 1613 cm^{-1}; ^1H nmr (90 MHz) δ 1.42 (6H, s, 3-Me), 1.47 (6H, s, 2-Me), 7.5~7.7 (2H, m, 7- and 8-H), 7.9~8.1 (2H,

m, 6- and 9-H), 8.53 and 8.60 (2H, 2s, 5- and 10-H); ms (rel. intensity) *m/z* 306 (M^+, 100). Calcd for $C_{20}H_{18}O_3$; M, 306.1255. Found: *m/z* 306.1255.

cis-2,3,3a,12a-Tetrahydro-1*H*-anthra[2,3-*b*]cyclopenta[*d*]furan-4,11-dione (6c).

The photoreaction of **4** (30 mg, 0.13 mmol) and cyclopentene (**5c**) (0.18 g, 2.7 mmol) in acetone (19 ml) for 50 min gave **6c** (21 mg, 54%): mp 215.5~217°C (hexane-ether-chloroform); ir 1672, 1650, 1614 cm^{-1}; ^1H nmr (400 MHz) δ 1.5~1.65 (1H, m), 1.75~1.95 (2H, m) 2.05~2.15 (1H, m), 2.55~2.35 (1H, m), 4.00 (1H, ddd, *J*=8.30, 7.33, 1.80 Hz, 3a-H), 5.51 (1H, dd, *J*=8.30, 5.37 Hz, 12a-H), 7.65~7.70 (2H, m, 7- and 8-H), 8.0~8.05 (2H, m, 6- and 9-H), 8.56 and 8.62 (2H, 2s, 5- and 10-H); ms (rel. intensity) *m/z* 290 (M^+, 100). *Anal.* Calcd for $C_{19}H_{14}O_3$: C, 78.61; H, 4.86. Found: C, 78.26; H, 4.75.

2,3-Dihydro-2-methyl-2-phenylanthra[2,3-*b*]furan-4,11-dione (6d).

The photoreaction of **4** (30 mg, 0.13 mmol) and α-methylstyrene (**5d**) (79 mg, 0.67 mmol) in acetone (18 ml) for 1 h gave **6d** (32 mg, 71%): mp 219~220.5°C (hexane-ether-chloroform); ir 1681, 1649, 1615, 1592 cm^{-1}; ^1H nmr (90 MHz) δ 1.90 (3H, s, 2-Me), 3.36 (1H, d, *J*=19.53 Hz, 3-H), 3.60 (1H, d, *J*=19.53 Hz, 3-H), 7.2~7.75 (7H, m), 7.95~8.1 (2H, m, 6- and 9-H), 8.56 and 8.65 (2H, 2s, 5- and 10-H); ms (rel intensity) *m/z* 340 (M^+, 74), 118 [$(CH_2CMePh)^+$, 100]. Calcd for $C_{23}H_{16}O_3$: M, 340.1099. Found: *m/z* 340.1105.

The reaction in benzene (same scale) for 7.5 h gave 14 mg (32%) of **6d**.

2-Acetoxy-2,3-dihydroanthra[2,3-*b*]furan-4,11-dione (6e).

The photoreaction of **4** (30 mg, 0.13 mmol) and vinyl acetate (**5e**) (0.23 g, 2.7 mmol) in acetone (19 ml) for 50 min. gave **6e** (26 mg, 63 %): mp 219.5~222°C; ir 1759, 1679, 1655, 1626 cm^{-1}; ^1H nmr (90 MHz) δ 2.14 (3H, s, OAc), 3.20 (1H, dd, *J*=18.68, 3.08 Hz, 3-H), 3.54 (1H, dd, *J*=18.68, 7.03 Hz, 3-H), 7.03 (1H, dd, *J*=7.03, 3.08 Hz, 2-H), 7.6~7.8

(2H, m, 7- and 8-H), 7.95~8.15 (2H, m, 6- and 9-H), 8.60 and 8.65 (2H, 2s, 5- and 10-H); ms (rel. intensity) *m/z* 308 (M^+, 9.4), 248 [$(M\text{-}AcOH)^+$, 40], 238 [$(M\text{-}CH_2CO)^+$, 100]. Calcd for $C_{18}H_{12}O_5$: M, 308.0684. Found: *m/z* 308.0681.

Methyl 2,3-Dihydro-2-methyl-4,11-dioxoanthra[2,3-*b*]furan-2-carboxylate (6f).

The photoreaction of **4** (45 mg, 0.20 mmol) and methyl methacrylate (0.40 g, 4.0 mmol) in acetone (29 ml) for 3 h gave **5f** (35 mg, 54 %): mp 213~214°C (hexane-ether-chloroform); ir 1735, 1683, 1655, 1641, 1618, 1591 cm^{-1}; ^1H nmr (90 MHz) δ 1.82 (3H, s, 2-Me), 3.14 (d, 1H, *J*=17.58 Hz, 3-H), 3.69 (1H, d, *J*=17.58 Hz, 3-H), 3.83 (3H, s, COOMe), 7.55~7.75 (2H, m, 7- and 8-H), 7.95~8.2 (2H, m, 6- and 9-H), 8.55 and 8.61 (2H, 2s, 5- and 10-H); ms (rel.intensity) *m/z* 322 (M^+, 15), 263[$(M\text{-}COOMe)^+$, 100]. Calcd for $C_{19}H_{14}O_5$: M, 322.0842. Found: *m/z* 322.0817.

Isolation of a Hydroquinone Derivative as Its Diacetate, 4,11-Diacetoxy-2,3-dihydro-2,2,3-trimethylanthra[2,3-*b*]furan (7) in the Photoaddition of 2-Hydroxy-1,4-anthracenedione (4) with Alkene (5a).

The solvent was removed immediately after a solution of **4** (40 mg, 0.18 mmol) and **5a** (0.25 g, 3.6 mmol) in acetone (26 ml) was irradiated for 1.5 h under the same conditions as described above. The residue was treated with acetic anhydride (1 ml) in pyridine (1 ml) at 50°C for 2 h. Excess reagents were removed in vacuo to give a residue, which was purified by preparative tlc on silica gel (chloroform) to afford **7** (28 mg, 16 %) and **6a** (28 mg, 54 %). **7**: an oil ; Rf 0.14; ir (neat) 1774, 1660 cm^{-1}; ^1H nmr (90 MHz) δ 1.30 (3H, d, *J*=7.25 Hz, 3-Me), 1.39 (3H, s, 2-Me), 1.51 (3H, s, 2-Me), 2.51 and 2.54 (6H, 2s, OAc), 3.34 (1H, q, *J*=7.25 Hz, 3-H), 7.3~7.7 (2H, m), 7.8~8.0 (2H, m, 6- and 9-H), 8.20 and 8.23 (2H, 2s, 5- and 10-H); ms (rel. intensity) *m/z* 378 (M^+, 21), 336 [$(M\text{-}CH_2CO)^+$, 36] 294 ($[M\text{-}2CH_2CO]^+$, 100). Calcd for $C_{23}H_{22}O_5$: M, 378.1468. Found: *m/z* 378.1454.

2-Amino-1,4-anthracenedione (9).

To a stirred solution of 1,4-anthracenedione (**8**) (330 mg, 1.59 mmol) in acetic acid (2.5 ml) under an atmosphere of nitrogen was added sodium azide (170 mg, 2.62 mmol) dissolved in 0.5 ml of water. The mixture was stirred at 70°C for 2 h, and cooled. The precipitated solids were filtered, washed with water and recrystallized from ethanol to give pure aminoquinone (**9**) (166 mg, 50 %): mp 282~285°C; ir 3380, 3260, 1686, 1618, 1585, 1542 cm^{-1}; ^1H nmr (90 MHz) δ 5.0~5.4 (2H, br s, NH_2), 6.13 (1H, s, 3-H), 7.55~7.75 (2H, m, 6- and 7-H), 7.9~8.1 (2H, m, 5- and 8-H), 8.58 and 8.61 (2H, 2s, 9-, 10-H); ms (rel. intensity) *m/z* 223 (M^+, 100). Calcd for $C_{14}H_9NO_2$: M, 223,0633. Found: *m/z* 223.0624.

2,3-Dihydro-2,2-dimethyl-1*H*-naphth[2,3-*f*]indole-4,11-dione (10).

The photoreaction of **9** (50 mg, 0.22 mmol) and isobutene (0.62 g, 1.1 mmol) in benzene (32 ml) for 1.5 h followed by separation by preparative tlc on silica gel (dichloromethane) gave **10** (32 mg, 53 %): mp 250°C (dec.)(hexane-ether-dichloromethane); ir 3324, 1665, 1630, 1609, 1587 cm^{-1}; ^1H nmr (90 MHz) δ 1.43 (6H, s, 2-Me), 2.97 (2H, s, 3-H), 5.0~5.3 (1H, br s, N-H), 7.45~7.65 (2H, m, 7- and 8-H), 7.8~8.05 (2H, m, 6- and 9-H), 8.50 and 8.53 (2H, 2s, 5- and 10-H); (rel. intensity) *m/z* 277 (M^+, 38), 262 [(M-Me),$^+$ 100]. Calcd for $C_{18}H_{15}NO_2$: M, 277.1103. Found: *m/z* 277.1082.

2-Methyl-1*H*-naphth[2,3-*f*]indole-4,11-dione (13).

The photoaddition of **9** (50 mg, 0.22 mmol) and 2-methoxypropene (**11**) (0.32 g, 4.5 mmol) in benzene (32 ml) for 1.5 h gave **13** (32 mg, 55 %): mp > 300°C; ir 3202, 3130, 1662, 1616, 1590 cm^{-1}; ^1H nmr (90 MHz, DMSO-d_6) δ 2.34 (3H, s, 2- Me), 6.49 (1H, s, 3-H), 7.6~7.8 (2H, m, 7- and 8-H), 8.1~8.3 (2H, m, 6- and 9-H), 8.63 and 8.65 (2H, 2s, 5- and 10-H), 8.7~9.2 (1H, br s, N-H): ms (rel. intensity) *m/z* 261 (M^+, 100). Calcd for $C_{17}H_{11}NO_2$: M, 261.0790. Found: *m/z* 261.0784.

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Received, 26th September, 1991