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Linearly Condensed *peri*-Hydroxy Aromatic Compounds Derived from the Cycloaddition Reaction of Homophthalic Anhydrides with Dienophiles

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Thermal treatment of homophthalic anhydrides (**1** and **2**) with various dienophiles (**3**—**12**) caused cycloaddition with spontaneous extrusion of carbon dioxide to give the corresponding linearly condensed *peri*-hydroxy aromatic compounds (**13**—**23**) in considerable yields. A possible mechanism for these reactions is proposed.

Keywords——cycloaddition; homophthalic anhydride; thermal reaction; carbon dioxide extrusion; regiocontrolled reaction; linearly condensed phenolic compound; *peri*-hydroxy aromatic compound; tetracyclic compound

Although homophthalic anhydrides (1,3-isochromanediones) have been shown to react with polar double bonds such as azomethines (Schiff base or cyclic imines)[1,2] or aromatic aldehydes[2] regiospecifically to afford the corresponding heterocycles and have been used as versatile synthons for the synthesis of natural products,[3] no reactions of these anhydrides with carbon-carbon multiple bonds were known until we recently reported in a brief communication that homophthalic anhydride (**1**) can react with carbon-carbon multiple bonds ($C=C$ and $C\equiv C$) to give linearly condensed phenolic compounds regioselectively in a single stage.[4] This paper describes these interesting cycloaddition reactions of homophthalic anhydrides (**1** and **2**) and the reaction mechanism, including a full account of the work mentioned in the previous communication.[4]

Cycloaddition Reaction of Homophthalic Anhydrides (1 and 2)

The reaction was generally carried out by employing homophthalic anhydride (**1**) and 1.0—2.0 equivalents of dienophile (**3**—**11** or **12**) in refluxing toluene, bromobenzene, or dichlorobenzene. In the case of the reaction of **1** with a volatile dienophile such as dialkyl acetylenedicarboxylate (**3** or **4**) or alkyl propiolate (**5** or **6**), the reaction was performed in a sealed tube. The presence of a base such as triethylamine or potassium carbonate in the reaction mixture had no great effect. A typical experimental procedure is as follows for the reaction of **1** with dimethyl acetylenedicarboxylate (**3**). A solution of **1** and **3** in toluene was heated at 150 °C for 1 d in a sealed tube, and the mixture was concentrated. Purification of the residue by a usual silica gel column chromatography gave the naphthol (**13**). In a similar fashion, the anhydride **1** reacted with various types of carbon-carbon multiple bonds (**4**—**12**) to give linearly condensed *peri*-hydroxy aromatic compounds (**14**—**21**) in moderate yields. 8-Methoxyhomophthalic anhydride (**2**)[5] also reacted with these dienophiles (**7** and **11**) to give the corresponding regiocontrolled cycloadducts (**22** and **23**). The attractive feature of these reactions is that the *peri*-hydroxy aromatic compounds (**13**—**23**) were obtained regioselectively in a single stage: as can be seen in Table I, the anhydride **1** was treated with methyl propiolate (**5**), ethyl propiolate (**6**), 3-bromojuglone (**11**), and 3-bromo-5-methoxy-1,4-

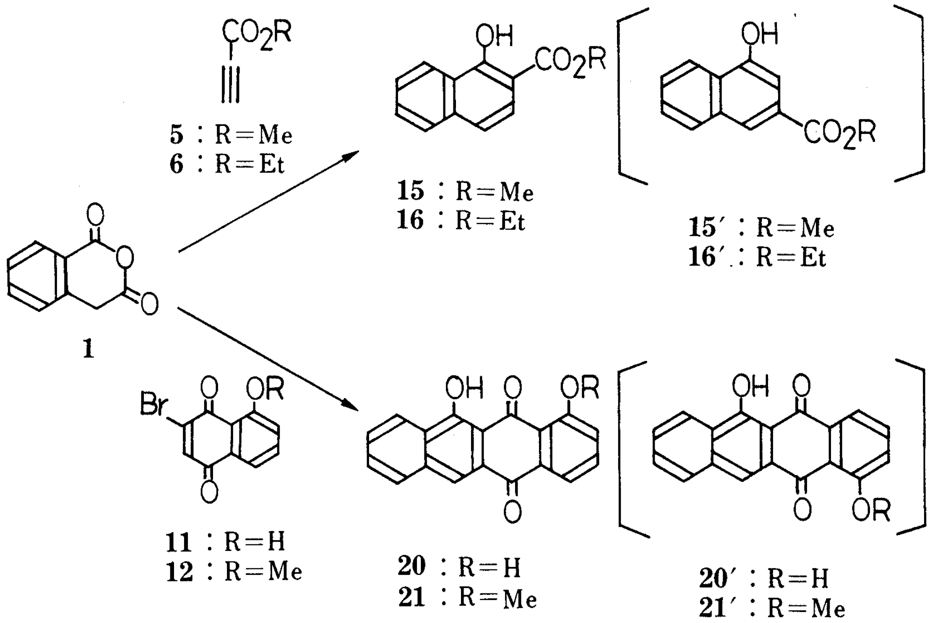
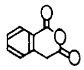
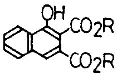
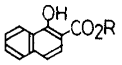
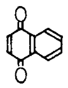
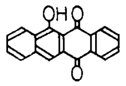
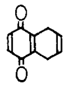
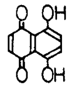
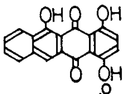
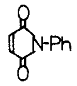
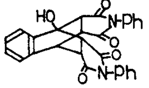
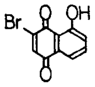
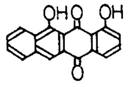
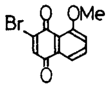
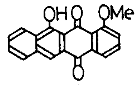
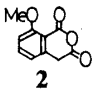
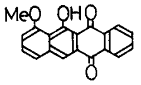
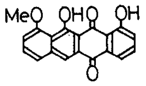


Chart 1

Table I. Cycloaddition Reactions of Homophthalic Anhydrides (1 and 2) with Various Dienophiles (3—12)

Homophthalic anhydride	Dienophile	Reaction conditions	Product		Yield$^{a)}$ (%)
 **1**	$RO_2CC{\equiv}CCO_2R$	**3**: R=Me in toluene at 150 °C for 24 h$^{b)}$		**13**: R=Me	65
		4: R=Et in toluene at 150 °C for 24 h$^{b)}$		**14**: R=Et	63
	$HC{\equiv}CCO_2R$	**5**: R=Me in toluene at 150 °C for 24 h$^{b)}$		**15**: R=Me	9
		6: R=Et in toluene at 150 °C for 24 h$^{b)}$		**16**: R=Et	19
		**7** in dichlorobenzene at 200 °C for 7 h		**17**	44
		**8** in dichlorobenzene at 200 °C for 15 h		**17**	27
		**9** in dichlorobenzene at 200 °C for 7 h		**18**	38
		**10** in dichlorobenzene at 200 °C for 20 h		**19**$^{c)}$	48
		**11** in bromobenzene at 120 °C for 1 h		**20**	41
		**12** in bromobenzene at 120 °C for 1 h		**21**	39
 **2**	**7**	in dichlorobenzene at 180 °C for 7 h		**22**	42
	11	in bromobenzene at 120 °C for 0.5 h		**23**	25

a) Isolated yields based on homophthalic anhydride (**1** or **2**).
b) The reaction was carried out in a sealed tube.
c) Although a single isomer was obtained, the stereochemistry was not determined.

naphthoquinone (**12**) to give the corresponding isomers as sole products. The structures were assigned as **15**, **16**, **20**, and **21** (not as **15′**, **16′**, **20′** and **21′**) on the basis of spectral evidence (see the experimental section) and finally confirmed by comparison of the products with authentic specimens.$^{6-9)}$ The reaction conditions, products and yields are summarized in Table I.

Consideration of Reaction Mechanism

There are three possible routes for the formation of the linearly condensed adducts (**13**—**23**) from homophthalic anhydrides (**1** and **2**) and dienophiles (**3**—**12**), *i.e.* (i) [4+2]cycloaddition of the conjugated dienol isomer (**1a**) to the dienophile followed by spontaneous extrusion of carbon dioxide (route A), (ii) Michael reaction of the enol isomer (**1b**) to the dienophile followed by spontaneous extrusion of carbon dioxide (route B), and (iii) [4+2]cycloaddition of the *ortho*-xylylene intermediate (**24**) generated by the initial extrusion of carbon dioxide to the dienophile (route C). Route A has been observed in the thermal cycloaddition of indene$^{10)}$ or glutaconic anhydride$^{11)}$ and in the acid-catalyzed cycloaddition of phthalan$^{12)}$ to active dienophiles. Route B has been observed in the reaction of metallated phthalide$^{13)}$ with various dienophiles and also in the reaction of anhydride (**1**) with ethyl chlorocarbonate or diazomethane, which gives the product through the 3-hydroxyisocoumarin form (**1b**).$^{14)}$ Poute C has been well documented in the pyrolysis or photolysis of benzocyclobutene$^{15)}$ or isochromanone,$^{16)}$ and the formation of the *ortho*-xylylene intermediate (**24**) from **1** was also reported at high temperature (over 500 °C) in a stream of nitrogen.$^{17)}$

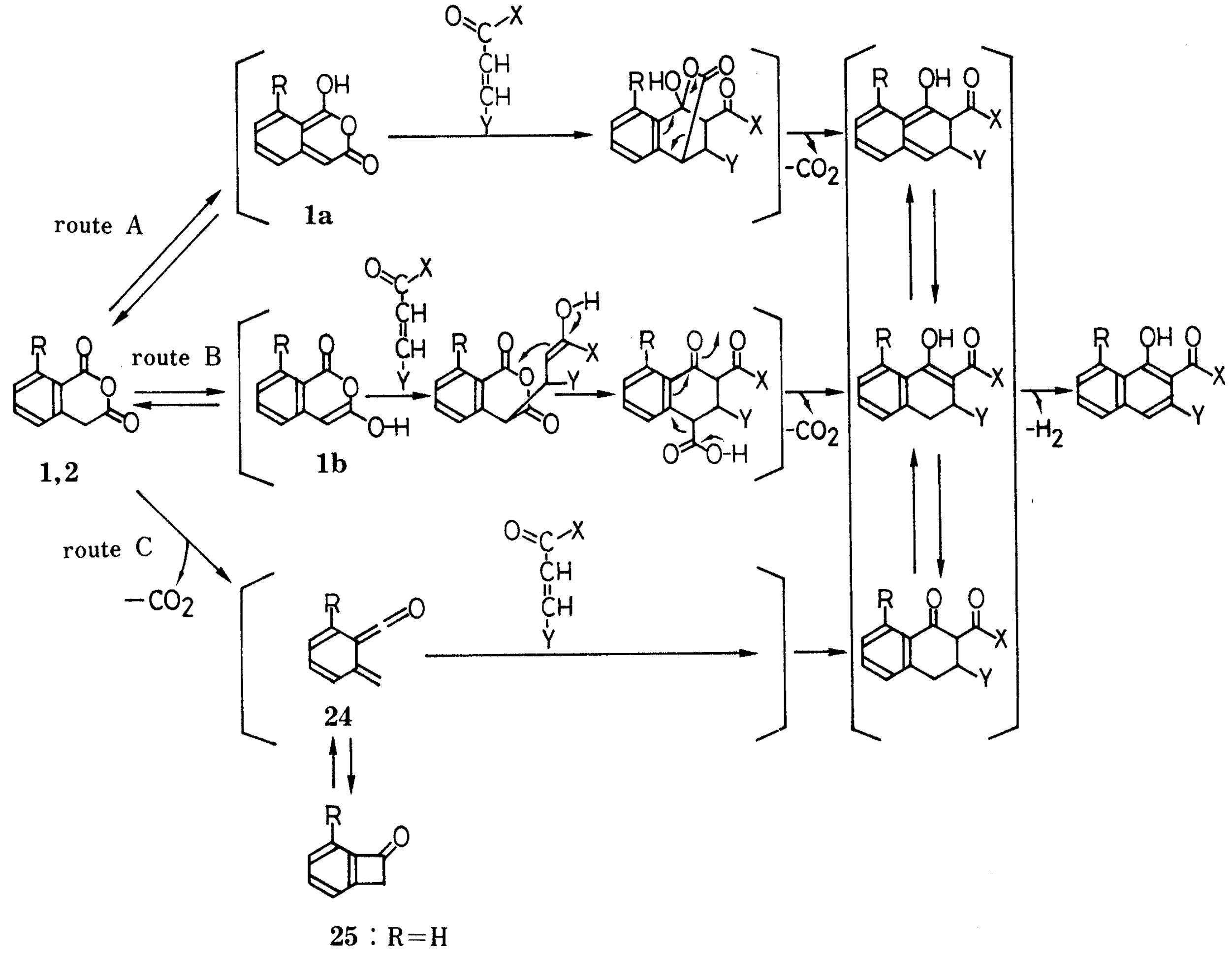


Chart 2

Although we could not obtain definite evidence, route A seems most likely for the thermal cycloaddition of **1** or **2** to dienophiles. Route C was ruled out on the basis of the following two results. i) Prolonged heating of **1** in dichlorobenzene did not give benzocyclobuten-1(2*H*)-one (**25**) or fulveneallene at all, and **1** was recovered unchanged. If the *ortho*-xylylene (**24**) is generated in the reaction medium, benzocyclobutenone (**25**) or fulveneallene should be obtained.[17] ii) The yields of the adduct obtained from **1** or **25** with the dienophile (**3**) under the same conditions were quite different: the benzocyclobutenone (**25**), prepared by the reported method[18] reacted with **3** to give only an 8% yield of **13**, although **1** reacted with **3** to give a 65% yield of **13** under the same conditions. The isolation of the 1 : 2 adduct (**19**) as a main product from the reaction of **1** and **10** strongly supports the formation of the dienol isomer (**1a**) (route A), since **19** is presumably formed by cycloaddition of **10** to an active conjugated enol intermediate (**26**), which is analogous to the dienol intermediate (**1a**).

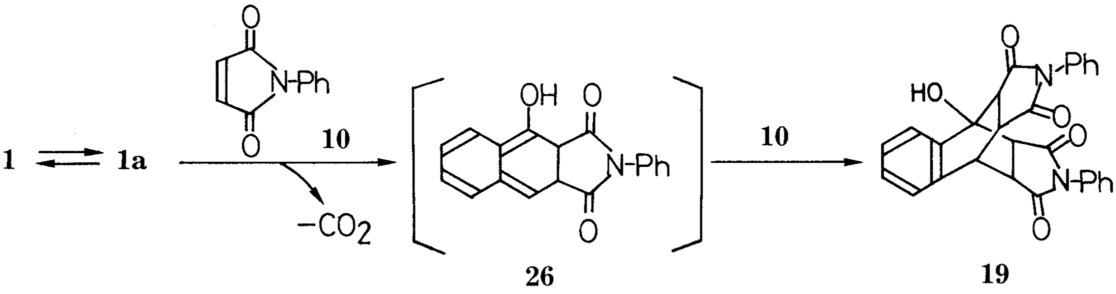


Chart 3

Furthermore, we investigated the reaction of homophthalic anhydride (**1**) with a 3-bromo-1,4-naphthoquinone derivative (**11** or **12**). Since the nucleophilic end of the diene usually reacts at the unsubstituted olefinic site of the bromonaphthoquinone (**11** or **12**) in the Diels–Alder reaction,[19] route A (Diels–Alder reaction of **1a** to **11** or **12**) is expected to involve reaction at the unsubstituted olefinic carbon to give the adduct (**20** or **21**). On the other hand, route B (Michael reaction of **1b** to **11** or **12**) is expected to involve reaction at the adjacent carbon to the bromine atom to give the isomeric adduct (**27** or **28**), since Michael reactions of β-halovinylketones are known to proceed by an addition–elimination sequence.[20] The fact that thermal treatment of **1** with the bromonaphthoquinone (**11** or **12**) in bromobenzene gave the single adduct (**20** or **21**) regioselectively[21] is quite consistent with route A; however, not enough is known about the Michael receptor properties of the bromoquinone (**11** or **12**) to rule out the Michael reaction (route B).

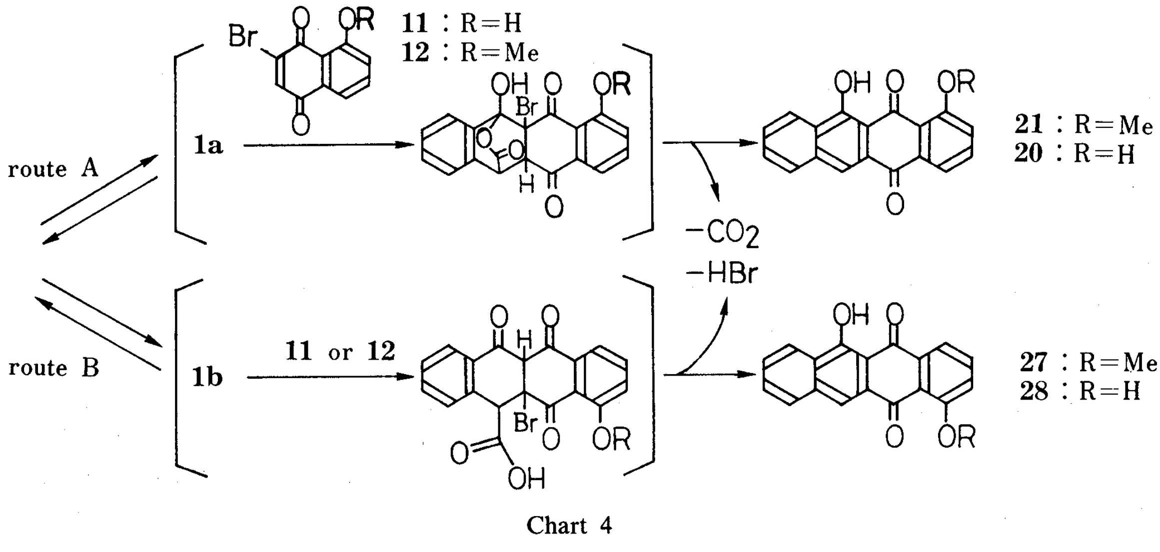


Chart 4

Experimental

All melting points are uncorrected. Infrared (IR) absorption spectra were recorded on a JASCO IRA-1 spectrometer, and nuclear magnetic resonance (NMR) spectra on a Hitachi R-20A or a Hitachi R-22 (90 MHz) spectrometer (with tetramethylsilane as an internal standard). Low- and high-resolution mass spectra (MS) were obtained with a JEOL JMS D-300 instrument, with a direct inlet system. Column chromatography was carried out on Merck silica-gel 60.

The starting 3-bromojuglone (**11**) was prepared by the reported method.[22,23] 3-Bromojuglone methyl ether (**12**) was directly prepared from **11** by methylation with methyl iodide and silver oxide.

3-Bromo-5-methoxy-1,4-naphthoquinone (12)——A suspension of 3-bromojuglone (**11**) (88.9 mg, 0.35 mmol) in chloroform (9 ml) was shaken vigorously with silver oxide (300 mg, 1.29 mmol) and methyl iodide (0.22 ml, 3.5 mmol) for 1 h. Two further additions of silver oxide (150 mg, 0.65 mmol) and methyl iodide (0.12 ml, 1.9 mmol) were made at intervals of 1 h with shaking. Stirring was continued at room temperature overnight, then the mixture was filtered, and the residue was extracted with chloroform (20 ml). The combined extracts were concentrated *in vacuo* and the residue was subjected to column chromatography on silica gel (with benzene as an eluting solvent) to give an 88% yield (82.3 mg) of **12**. Recrystallization from ethyl acetate–pet. ether gave pure **12**, mp 154—156 °C (lit.[23] 154—155°C, lit.[24] 150—153°C). IR $\nu_{max}^{CHCl_3}$ cm^{-1}; 1670, 1650. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 4.00 (3H, s, OMe), 7.28 (1H, m, ArH), 7.38 (1H, s, CH=), 7.6—7.8 (2H, m ArH).

General Procedure for the Cycloaddition of Homophthalic Anhydrides (1 and 2) to Dienophiles (3—12)——A mixture of homophthalic anhydride (**1** or **2**) (1 mmol) and dienophile (1—2 mmol) in toluene (2 ml), *ortho*-dichlorobenzene (2 ml) or bromobenzene (2 ml) was heated under the conditions indicated in Table I. The solvent was removed under reduced pressure and the residue was subjected to column chromatography on silica gel with benzene or chloroform as an eluting solvent to give the adduct. By means of this procedure, the following compounds (**13**—**23**) were prepared.

Dimethyl 1-Hydroxynaphthalene-2,3-dicarboxylate (13)——i) From 1: This was prepared from **1** (50 mg, 0.31 mmol) and **3** (90 mg, 0.62 mmol). Recrystallization from benzene–hexane gave pure **13**, mp 102—103.5 °C (lit.[6] 102—108 °C). IR $\nu_{max}^{CDCl_3}$ cm^{-1}: 1715, 1655. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 3.88 (3H, s, OMe), 3.92 (3H, s, OMe), 7.37 (1H, s, ArH), 7.3—7.85 (3H, m, ArH), 8.34 (1H, m, ArH), 11.82 (1H, s, OH).

ii) From 25: This was prepared from **25** (50 mg, 0.42 mmol) and **3** (119 mg, 0.84 mmol). Purification by column chromatography on silica gel (with benzene as an eluting solvent) gave pure **13**, which was identical with an authentic sample obtained in i).

Diethyl 1-Hydroxynaphthalene-2,3-dicarboxylate (14)——This was prepared from **1** (100 mg, 0.62 mmol) and **4** (211 mg, 1.24 mmol). Recrystallization from *n*-hexane gave pure **14**, mp 54—54.5 °C (lit.[25] bp 163—164 °C/0.05 mmHg). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1715, 1650. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 1.41 (6H, t, $J=7$ Hz, $2\times CH_2C\underline{H}_3$), 4.37 (2H, q, $J=7$ Hz, $C\underline{H}_2CH_3$), 4.41 (2H, q, $J=7$ Hz, $C\underline{H}_2CH_3$), 7.36 (1H, s, ArH), 7.4—7.85 (3H, m, ArH), 8.37 (1H, m, ArH), 11.97 (1H, s, OH).

Methyl 1-Hydroxy-2-naphthoate (15)——This was prepared from **1** (50 mg, 0.31 mmol) and **5** (52 mg, 0.62 mmol). Recrystallization from methanol gave pure **15**, mp 74.5—76 °C (lit.[6] 76—77 °C). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1660, 1635. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 3.97 (3H, s, OMe), 7.20 (1H, d, $J=8.5$ Hz, ArH), 7.3—7.8 (3H, m, ArH), 7.69 (1H, d, $J=8.5$ Hz, ArH), 8.2—8.45 (1H, m, ArH), 11.79 (1H, s, OH).

Ethyl 1-Hydroxy-2-naphthoate (16)——This was prepared from **1** (100 mg, 0.62 mmol) and **6** (122 mg, 1.24 mmol). Recrystallization from *n*-hexane gave pure **16**, mp 40.5—41 °C (lit.[7] 48—49 °C). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1640. ^{1}H-NMR (10% solution in $CDCl_3$) δ:1.45 (3H, t, $J=7$ Hz, $CH_2C\underline{H}_3$), 4.42 (2H, q, $J=7$ Hz, $C\underline{H}_2CH_3$), 7.22 (1H, d, $J=9$ Hz, ArH), 7.4—7.75 (3H, m, ArH), 7.74 (1H, d, $J=9$ Hz, ArH), 8.37 (1H, m, ArH), 12.00 (1H, s, OH).

6-Hydroxynaphthacene-5,12-dione (17)——i) From the Reaction of 1 and 7: This was prepared from **1** (100 mg, 0.62 mmol) and **7** (200 mg, 1.23 mmol). Recrystallization from chloroform gave pure **17**, mp 262—264°C (lit.[26] 268—270 °C). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1665, 1620, 1610. MS *m/z*: 274 (M^+). Acetylation of this dione with acetic anhydride in pyridine under the standard conditions followed by recrystallization from benzene gave the pure acetate of **17**, mp 228—230 °C. *Anal.* Calcd for $C_{20}H_{12}O_4$: C, 75.94; H, 3.82. Found: C, 75.86; H, 3.72. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1760, 1700, 1665. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 2.61 (3H, s, OAc), 7.5—7.85 (4H, m, ArH), 7.9—8.4 (4H, m, ArH), 8.76 (1H, s, ArH); MS *m/z*: 316 (M^+).

ii) From the Reaction of 1 and 8: This was prepared from **1** (160 mg, 1 mmol) and **8** (320 mg, 2 mmol). Recrystallization from chloroform gave pure **17**, which was identical with an authentic sample obtained in i).

1,4,6-Trihydroxynaphthacene-5,12-dione (18)——This was prepared from **1** (81 mg, 0.5 mmol) and **9** (95 mg, 0.5 mmol). Recrystallization from chloroform gave pure **18**, mp 290—292 °C (lit.[27] 294 °C). Acetylation of this dione with acetic anhydride in pyridine under the standard conditions followed by recrystallization from chloroform gave the pure triacetate of **18**, mp 269—272 °C. Exact mass Calcd for $C_{24}H_{16}O_8$: 432.0843. Found: 432.0837. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1770, 1680, 1620, 1580. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 2.38 (3H, s, OAc), 2.43 (3H, s, OAc), 2.54 (3H, s, OAc), 7.35 (2H, s, ArH), 7.5—7.8 (2H, m, ArH), 7.9—8.2 (2H, m, ArH), 8.59 (1H, s, ArH).

1 : 2 Adduct (19) from 1 and 10——This was prepared from **1** (160 mg, 1.0 mmol) and **10** (360 mg, 2.0 mmol).

Recrystallization from chloroform–*n*-hexane gave pure **19**, mp 232—234 °C. *Anal.* Calcd for $C_{28}H_{20}N_2O_5$: C, 72.40; H, 4.34; N, 6.03. Found: C, 72.45; H, 4.27; N, 6.15. IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 1770, 1715, 1705, 1640. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 3.09 (1H, d, $J=9$ Hz, CH), 3.15 (1H, d, $J=9$ Hz, CH), 3.3—3.8 (3H, m, 2×CH and OH), 4.37 (1H, t, $J=9$ Hz, CH), 6.8—7.9 (14H, m, ArH).

1,11-Dihydroxynaphthacene-5,12-dione (20)——This was prepared from **1** (65 mg, 0.40 mmol) and **11** (50 mg, 0.198 mmol). Recrystallization from toluene gave pure **20**, mp 277—279 °C (lit.[8] 276—278 °C, lit.[9] 281—283 °C). IR $\nu_{\max}^{KCl}$ cm^{-1}: 1660 (non-chelated quinone carbonyl band), 1610, 1590, 1570.

1-Methoxy-11-hydroxynaphthacene-5,12-dione (21)——This was prepared from **1** (60 mg, 0.37 mmol) and **12** (50 mg, 0.187 mmol). Recrystallization from toluene gave pure **21**, mp 272—273 °C (lit.[9] 263—266 °C). IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 1670 (non-chelated quinone carbonyl band), 1620, 1585. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 4.05 (3H, s, OMe), 7.2—7.45 (1H, m, ArH), 7.5—7.8 (2H, m, ArH), 7.8—8.1 (2H, m, ArH), 8.19 (1H, s, ArH), 8.35—8.6 (2H, m, ArH), 14.93 (1H, s, OH). Demethylation of this dione with BBr_3 gave **20** exclusively, as follows. A solution of BBr_3 (1.5 g, 0.57 mmol) in methylene chloride (1 ml) was added dropwise to a solution of the methyl ether (**21**) (16 mg, 0.0526 mmol) in methylene chloride (8 ml) at −78 °C under argon. The mixture was stirred at −50 °C for 1 h, allowed to warm to room temperature, stirred for 2 h, poured into a mixture of crushed ice and sat. $NaHCO_3$, and extracted with chloroform. The extract was washed with saturated aqueous sodium chloride, dried over Na_2SO_4, and concentrated. The residue was subjected to column chromatography on silica gel (with benzene as an eluting solvent) to give an 85% (13 mg) yield of **20**. Recrystallization from toluene gave pure **20**, mp 280.5—281 °C, which was identical with the sample obtained from the reaction of **1** and **11**.

6-Hydroxy-7-methoxynaphthacene-5,12-dione (22)——This was prepared from **2** (50 mg, 0.26 mmol) and **7** (50 mg, 0.32 mmol). Recrystallization from chloroform gave pure **22**, mp 260.5—261.5 °C. *Anal.* Calcd for $C_{19}H_{12}O_4$: C, 74.99; H, 3.97. Found: C, 75.05; H, 3.79. IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 1665, 1615, 1580. ^{1}H-NMR (10% solution in $CDCl_3$) δ: 4.04 (3H, s, OMe), 6.98 (1H, dd, $J=6$ and 2 Hz, ArH), 7.4—7.8 (4H, m, ArH), 8.10 (1H, s, ArH), 8.2—8.45 (2H, m, ArH), 15.67 (1H, s, OH).

1,11-Dihydroxy-10-methoxynaphthacene-5,12-dione (23)——This was prepared from **2** (80 mg, 0.42 mmol) and **11** (70 mg, 0.28 mmol). Recrystallization from benzene gave pure **23**, mp 265—266 °C. Exact mass Calcd for $C_{19}H_{12}O_5$: 320.0685. Found: 320.0697. IR $\nu_{\max}^{KCl}$ cm^{-1}: 1660, 1610, 1600, 1565.

Benzocyclobuten-1(2*H*)-one (25)——This was prepared from anthranilic acid in four steps by the reported method.[18]

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