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Intramolecular Cycloaddition of Two Acyl-1,4-benzoquinone Moieties on Photolysis

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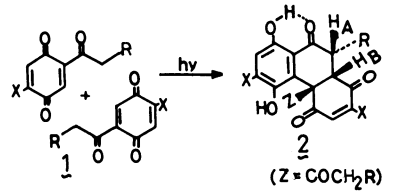
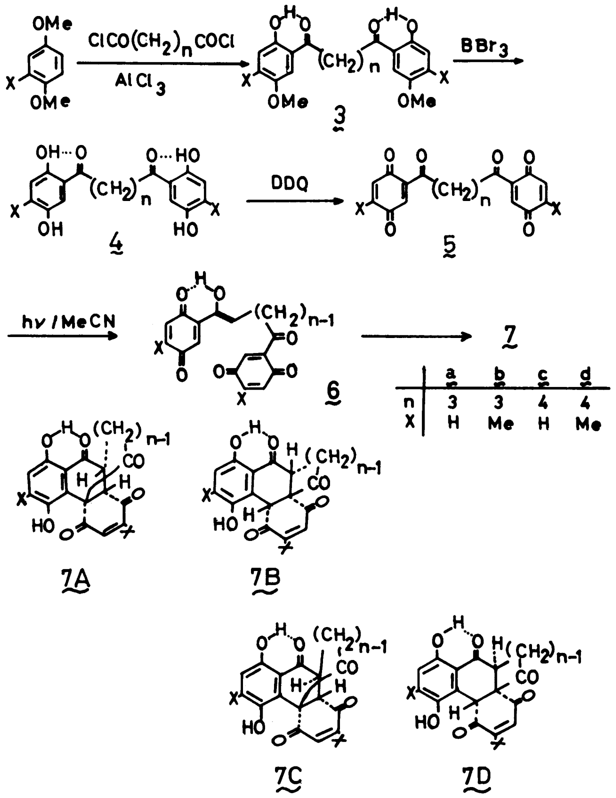
Upon irradiation a regio- and stereoselective cycloaddition occurred intramolecularly between two acyl-1,4-benzoquinone moieties connected by a polymethylene bridge. The regio- and stereoselectivities are different from those of the corresponding intermolecular cycloaddition; this was interpreted in terms of the Diels-Alder reaction between an acyl-1,4-benzoquinone moiety and a photochemically produced dienol.

In 1979 we reported[1)] that 2-alkanoyl-1,4-benzoquinones (**1**) underwent a regio- and stereoselective dimerization on photolysis to give racemic 4aα-acyl-10β-alkyl-5,8-dihydroxy-4aα,10aα-dihydro-1,4,9(10H)-phenanthrenetriones (**2**).[2)] We are interested in whether a similar cycloaddition can occur intramolecularly between two acylquinone moieties. If such reactions could proceed, we might obtain, by a simple procedure, a group of compounds which have characteristic structures and properties. Actually the substrates, 2,2′-(α,ω-dioxo-α,ω-alkanediyl)bis(1,4-benzoquinone)s (**5a—d**)[3)] prepared by the processs given in Scheme underwent the expected cycloaddition. When a degassed solution of **5** in acetonitrile[4)] (0.05 mol dm^{-3}) was irradiated through Pyrex filter by a high pressure mercury-arc lamp, an intramolecular addition product of the substrate was obtained as the sole product in the yield of 25—30%. The yield of the product raised to 54% when the lower initial concentration of **5c** (0.002 mol dm^{-3}) was used.[5)] Without light, a degassed solution of **5** had remained unchanged on standing at room temperature over a week.





	a	b	c	d
n	3	3	4	4
X	H	Me	H	Me

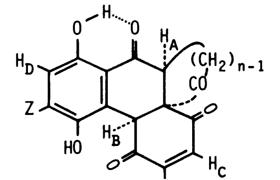
Scheme 1.

TABLE 1. ^{1}H NMR DATA OF **7B** (THE PHOTO-PRODUCT DERIVED FROM **5**): δ (acetone-d_6)

7B	OH[a)]	OH	H$_D$	H$_{D'}$	H$_C$	H$_{C'}$	H$_B$	H$_A$	Me$_D$	Me$_C$	$-(\mathrm{CH_2})_{n-1}$
a[b)]	11.83	9.69	7.02	6.78[c)]	6.43	6.97[d)]	4.27	3.67	—	—	i
			(ABq, 9.3 Hz)		(ABq, 10.6 Hz)		(s[e)])	(m)			
b	12.02	7.49	6.73	—	6.24	—	4.32	3.53	2.01	2.24	2.3—2.6
			(s)		(q, 1.5 Hz)		(s)	(m)	(s)	(d, 1.5 Hz)	(m)
c	12.13	8.22	7.25	6.65[d)]	6.29	6.97[d)]	4.58	3.27	—	—	2.3—2.7
			(ABq, 8.8 Hz)		(ABq, 10.2 Hz)		(dd[f)])	(dd[g)])			(m)
d	12.11	7.50	6.75	—	6.40	—	4.68	3.22	2.20	1.99	2.3—2.6
			(s)		(q, 1.5 Hz)		(s)	(dd[h)])	(s)	(d, 1.5 Hz)	(m)

a) Chelated. b) In DMSO-d_6. c) The half wing of the AB quartet broadened by coupling with H$_B$. d) The each signal of the half wing of the AB quartet spiked to a doublet in coupling with H$_B$; J=1.8 (H$_{C'}$: **a**), 1.4 (H$_{C'}$: **c**), and 1.2 Hz (H$_{D'}$: **c**). e) A broad singlet; see footnote c and d. f) J=1.4 and 1.2 Hz; see footnote d. g) J=4.9 and 10.7 Hz. h) J=4.9 and 11.2 Hz. i) Behind the signals of residual protons of DMSO.

	a	b	c	d
Y	H$_{C'}$	Me$_C$	H$_{C'}$	Me$_C$
Z	H$_{D'}$	Me$_D$	H$_{D'}$	Me$_D$
n	3	3	4	4



7Ba-d

The ^{1}H NMR data of the products (Table 1) were similar to those of **2**, suggesting a compound either of the structures **7A—D**.[6] While the signals of **2** at about δ 4.1 due to H_B were doublets ($J\simeq4$ Hz), the corresponding signals of the products derived from **5a**,[7] **5b**, and **5d** were singlets and that of the product from **5c** was a double doublet (J=1—2 Hz). The double resonance technique revealed that the atoms coupling with the atom giving the double doublet were an olefinic and an aromatic protons,[8] but not the proton corresponding to H_A of **2**. This fact exclude the possibilities of **7A** and **7C**, which should show a doublet due to the atom corresponding to H_B of **2**. The structure of the product derived from **5d** was unequivocally established as (4a*RS*,8a*SR*,13b*SR*)-10,13-dihydroxy-2,12-dimethyl-6,7,8,8a-tetrahydro-1,4,5,9(13b*H*)-benz[*e*]anthracenetetrone (**7Bd**) by the X-ray structural analysis. The perspective view of a molecule of **7Bd** is given in Fig. 1.

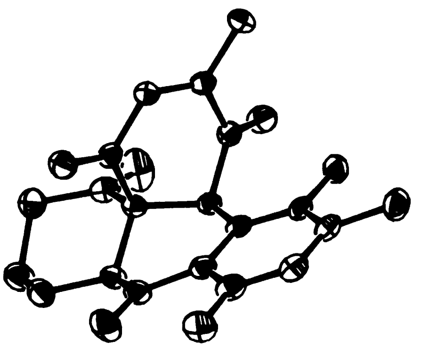
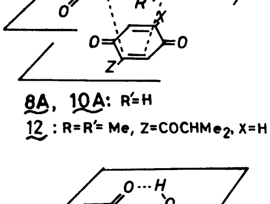


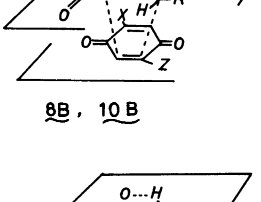
Fig. 1. Perspective view of (4a*R*,8a*S*,13b*S*)-10,13-dihydroxy-2,12-dimethyl-6,7,8,8a-tetrahydro-1,4,5,9-(13b*H*)benz[*e*]anthracenetetraone (**7Bd**).

The above finding indicates that the regio- and stereoselectivities of the intramolecular addition are different from those of the intermolecular one. The stereochemistry of the reactions is explicable in terms of the Diels-Alder reaction between an acylquinone moiety and a photochemically produced dienol moiety. For the intramolecular addition reaction, four orientations, **8A-D** corresponding to **7A-D**, may be possible. In **8C** and **8D** the access of two molecular planes is sterically hindered by the polymethylene chain existing inside the *cis*-dienol form. Such hindrance may not be exerted either in **8A** nor in **8B**. Though **8B** may be less favorable than **8A** because of steric hindrance caused by folding the polymethylene chain of **8B**, the chain (n=3 and 4) is not long enough to construct **8A**. Consequently the reaction to give **7B** may proceed preferentially. Second, for the intermolecular addition of **1** with the dienol **9**, orientations **10A—D** can be drawn. In **10C**, **D** the access of the molecular planes are hindered by a process similar to that explained for **8C**, **D**. **10B** is sterically hindered by the overlapping of the alkyl and acyl groups. Because of the least steric hindrance of **10A**, the selective formation of **2** is feasible.

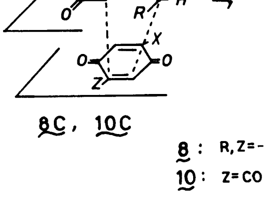


8A, **10A**: R′=H

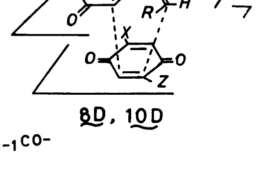
12: R=R′= Me, Z=COCHMe$_2$, X=H



8B, **10B**



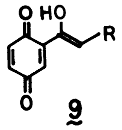
8C, **10C**



8D, **10D**

8: R,Z=-(CH$_2$)$_{n-1}$CO-

10: Z=COCH$_2$R



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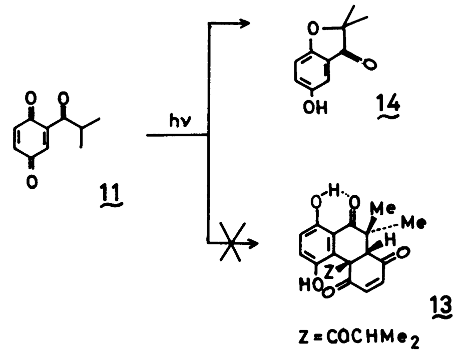

TABLE 2. Final atomic coordinates (×10^4) of the non-hydrogen atoms of **7Bd** with their estimated standard deviations in parentheses[12]

C(1)	1300(3)	1101(5)	5321(5)
C(2)	1757(3)	2110(5)	4701(5)
C(3)	2121(3)	3004(5)	5410(4)
C(4)	2059(3)	3068(5)	6805(5)
C(4a)	1635(3)	1972(5)	7464(4)
C(5)	2210(3)	878(5)	7745(5)
C(6)	2811(3)	1137(6)	8798(6)
C(7)	2390(4)	1469(7)	10033(6)
C(8)	1884(3)	2653(6)	9825(5)
C(8a)	1294(3)	2417(5)	8739(5)
C(9)	780(3)	3550(5)	8499(5)
C(9a)	291(3)	3549(5)	7317(5)
C(10)	-273(3)	4501(5)	7136(5)
C(11)	-766(3)	4466(6)	6071(6)
C(12)	-694(3)	3488(5)	5196(5)
C(13)	-144(3)	2538(5)	5379(5)
C(13a)	357(3)	2547(4)	6412(4)
C(13b)	966(3)	1485(5)	6589(4)
C(2-Me)	1803(3)	2040(6)	3273(5)
C(12-Me)	-1221(3)	3438(7)	4004(6)
O(1)	1229(2)	30(3)	4869(4)
O(4)	2340(2)	3954(4)	7388(3)
O(5)	2164(3)	-130(4)	7192(5)
O(9)	742(3)	4443(4)	9260(4)
O(10)	-370(2)	5471(4)	7969(4)
O(13)	-83(2)	1569(4)	4491(3)

To examine the above steric effect towards the access of the molecular planes, we investigated the photolysis of 2-isobutyryl-1,4-benzoquinone (**11**). The cycloaddition through the corresponding orientation, **12**, may be unfavorable because a methyl group locates inside the *s-cis* dienol form. On irradiation, **11** did not afford the corresponding dimer **13**, but gave 2,2-dimethyl-5-hydroxy-3(2*H*)-benzofuranone (**14**), an intramolecularly cyclized product in 20% yield.

If the above cycloadditions proceed through the dienols, **6** and **9**,[9] they should be trapped with another dienophile present in the reaction solution. As stated previously,[1] however, no such adducts were obtained and **2** was still the only isolable product when the photolysis of **1** was effected in the presence of maleic anhydride, *N*-phenylmaleimide, or dimethyl acetylenedicarboxylate. A similar result was obtained for the intramolecular reaction. When a solution of **5c** in acetonitrile (0.002 mol dm^{-3}) was irradiated in the presence of maleic anhydride (0.2 mol dm^{-3}), no adducts between them were obtained and **7Bc** was isolated in a yield of 57%, a comparable yield with the reaction in the absence of maleic anhydride (*vide supra*).

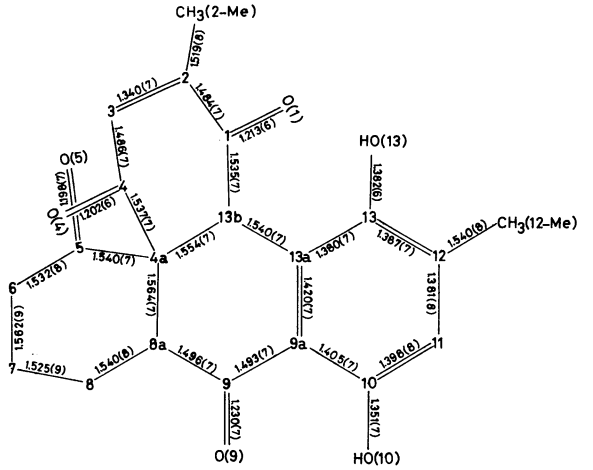

Fig. 2. Bond distances (l/Å) and atomic labelling numbers of **7Bd**.

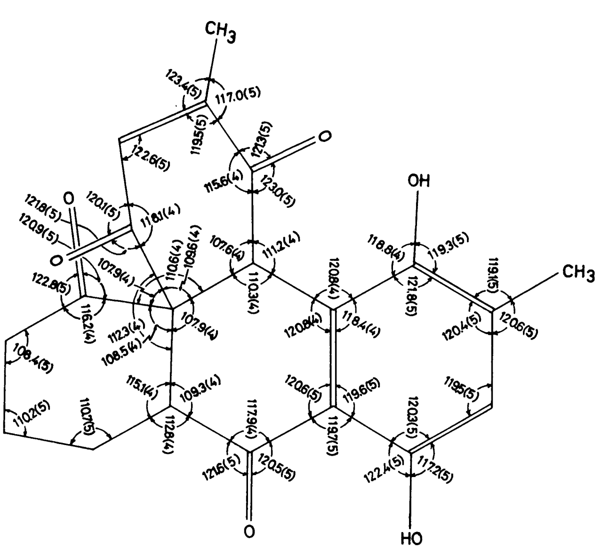

Fig. 3. Bond angles (ϕ/°) of **7Bd**.

Experimental

All new compounds gave satisfactory results in mass spectrometry. ^{1}H NMR spectra were measured by a JEOL JNM FX-100 and FX-90Q spectrometers.

α,ω-Bis(2,5-dihydroxyphenyl)-α,ω-alkanediones (4).[10] Glutaryl or adipoyl dichloride (0.05 mol) was added dropwise to a suspension of $AlCl_3$ (0.1 mol) in a solution of *p*-dimethoxybenzene or 2,5-dimethoxytoluene (0.1 mol) in 1,2-dichloroethane (100 cm^3) with stirring. After further stirring under refluxing for 8 h and subsequent addition of ice water and concentrated hydrochloric acid (10 cm^3), the reaction mixture was extracted with diethyl ether. The concentrated residue of the extract gave, after recrystallization from ethanol, a yellow solid of α,ω-bis(2-hydroxy-5-methoxyphenyl)-α,ω-alkanedione (**3**), which contained a small amount of α,ω-bis(2,5-dimethoxyphenyl)-α,ω-alkanedione. This crude product was treated with BBr_3 in dichloromethane in the usual manner to give a yellow solid of α,ω-bis(2,5-dihydroxyphenyl)-α,ω-alkanedione (**4**), which was recrystallized from ethanol.

1,5-Bis(2,5-dihydroxyphenyl)-1,5-pentanedione (4a). Yield 80%. Mp 211—213 °C. Found: C, 64.31; H, 5.10%. Calcd for $C_{17}H_{16}O_6$: C, 64.55; H, 5.10%.

1,5-Bis(2,5-dihydroxy-4-methylphenyl)-1,5-pentanedione (4b). Yield 80%. Mp 202—203 °C. Found: C, 66.49; H, 5.90%. Calcd for $C_{19}H_{20}O_6$: C, 66.27 H, 5.85%.

1,6-Bis(2,5-dihydroxyphenyl)-1,6-hexanedione (4c). Yield 85%. Mp 236—238 °C. Found: C, 65.25; H, 5.55%. Calcd for $C_{18}H_{18}O_6$: C, 65.44; H, 5.49%.

1,6-Bis(2,5-dihydroxy-4-methylphenyl)-1,6-hexanedione (4d). Yield 85%. Mp 137—139 °C (recrystallized from EtOH-THF (1:1)). Found: C, 67.08; H, 6.19%. Calcd for $C_{20}H_{22}O_6$: C, 67.02; H, 6.19%.

The ^{1}H NMR and IR data of **4** are presented for **4d**; δ (acetone-d_6)=1.81 (4H, m, $(\text{-COCH}_2\text{C}\underline{\text{H}_2})_2$, 2.23 (6H, broad s, 2ArMe), 3.05 (4H, m, $(\text{-COC}\underline{\text{H}_2}\text{CH}_2)_2$), 6.72 (2H, broad s, 2ArH), 7.31 (2H, s, 2ArH), 7.97 (2H, s, 2OH), 11.85 (2H, s, 2 chelated OH); ν (KBr) 3480 (broad and strong), 3080, 2980, 2920, 2880, 1660, 1610, 1600 cm^{-1}.

2,2′-(1,5-Dioxo-1,5-pentanediyl)bis(1,4-benzoquinone) (5a) and 2,2′-(1,5-Dioxo-1,5-pentanediyl)bis(5-methyl-1,4-benzoquinone) (5b). A solution of DDQ (4 mmol) in dry acetone (5 cm^3) was added to a solution of **4a** or **4b** (2 mmol) in dry acetone (30 cm^3) under a dry atmosphere. After about 0.5 h the solvent was evaporated under 10^{-4} mmHg (1 mmHg=133.322 Pa). The solid residue was extracted with hot benzene. The crystals which deposited on cooling were recrystallized from benzene.

5a: Mp 108—110 °C, Yield 80%. Found: C, 65.28; H, 3.81%. Calcd for $C_{17}H_{12}O_6$: C, 65.38; H, 3.87%. ^{1}H NMR ($CDCl_3$): δ=2.04 (2H, quintet, J=7.0 Hz, $(\text{-COCH}_2)_2\text{C}\underline{\text{H}_2}$), 2.96 (4H, t, J=7.0 Hz, $(\text{-COC}\underline{\text{H}_2})_2\text{CH}_2$), 6.8—7.0 (6H, m, ArH). IR (KBr): ν 3060, 2960, 2920, 2880, 1700, 1660, 1610 cm^{-1}. UV (MeCN): λ_{max} (ε) 246 (3.64 × 10^4), 300 (980) (sh), 450 (73) nm.

5b: Mp 148—150 °C, Yield 80%. Found: C, 66.92; H, 4.74%. Calcd for $C_{19}H_{16}O_6$: C, 67.05; H, 4.75%. ^{1}H NMR ($CDCl_3$): δ= 1.98 (2H, quint, J=7.0 Hz, $(\text{-COCH}_2)_2\text{C}\underline{\text{H}_2}$), 2.07 (6H, t, J= 1.0 Hz, 2ArMe), 2.93 (4H, t, J=7.0 Hz, $(\text{-COC}\underline{\text{H}_2})_2\text{CH}_2$), 6.57 (2H, q, J=1.0 Hz, 2ArH), 6.88 (2H, s, 2ArH). IR (KBr): ν 3060, 2980, 2910, 2890, 1710, 1660, 1605 cm^{-1}. UV (MeCN): λ_{max} (ε) 250 (3.50 × 10^4), 314 (1.30 × 10^3) (sh), 450 (100) nm.

2,2′-(1,6-Dioxo-1,6-hexanediyl)bis(1,4-benzoquinone) (5c) and 2,2′-(1,6-Dioxo-1,6-hexanediyl)bis(5-methyl-1,4-benzoquinone) (5d). A solution of **4c** or **4d** and DDQ was prepared as above. On standing for about 0.5 h a yellow solid crystallized out; this was recrystallized from dry acetone, with care taken to avoid contact with moisture.

5c: Mp 146—151 °C, Yield 70%. Found: C, 66.34; H, 4.36%.

Calcd for $C_{18}H_{14}O_6$: C, 66.25; H, 4.32%. ^{1}H NMR ($CDCl_3$): δ=1.71 (4H, m, $(\text{-COCH}_2\text{C}\underline{\text{H}}_2)_2$), 2.90 (4H, m, $(\text{-COC}\underline{\text{H}}_2\text{CH}_2)_2$), 6.8—6.9 (6H, m, ArH). IR (KBr): ν 3060, 2960, 2920, 2880, 1700, 1650, 1610 cm^{-1}. UV (MeCN): 246 (3.29×10^4), 300 (960) (sh), 445 (67) nm.

5d: Mp 145—149 °C, Yield 75%. Found: C, 67.75; H, 5.05%. Calcd for $C_{20}H_{18}O_6$: C, 67.79; H, 5.12%. ^{1}H NMR ($CDCl_3$): δ= 1.62 (4H, m, $(\text{-COCH}_2\text{C}\underline{\text{H}}_2)_2$, 2.08 (6H, d, J=1.5 Hz, 2ArMe), 2.90 (4H, m, $(\text{-COC}\underline{\text{H}}_2\text{CH}_2)_2$), 6.61 (2H, q, J=1.5 Hz, 2ArH), 6.93 (2H, s, 2ArH). IR (KBr): ν 3050, 2960, 2910, 2880, 1710, 1660, 1610 cm^{-1}. UV (MeCN): λ_{max} (ε) 250 (3.55×10^4), 315 (1.24×10^3) (sh), 435 (75) nm.

Photolysis of 5. A Pyrex glass tube containing a dry acetonitrile solution of **5** (0.05 or 0.002 mol dm^{-3}) was sealed after having been degassed by the thaw-freeze-pump method and irradiated by a 300 W high pressure mercury-arc lamp for 5 h (the yield of **7B** was not increased by prolonged irradiation). Because **7B** was decomposed by silica gel, its isolation and purification could not be performed by column chromatography, but were effected as described in the following to give **7B** in the yield of 25—30%. The yields did not seem to vary much with **5** but did depend on the isolation, because it was decomposed with a trace amount of water contained in solution and sometimes even with moisture in the isolation procedure. No other products except tar were found. Remaining **5** could not be recovered (it was also decomposed by silica gel and water).

The concentrated residue of the irradiated solution of **5a** was washed with ethyl acetate and dissolved in hot dry acetone. Yellow crystals of **7Ba** were obtained by allowing the solution to stand after addition of petroleum ether.

The concentrated residue of the irrradiated solution of **5c** was repeatedly extracted with hot benzene. The concentrated residue of the combined extract was recrystallized from dry acetone to give yellow needles of **7Bc**, which contained acetone as crystal-solvent. These were dried at about 60 °C under 10^{-4} mmHg.

The concentrated residue of the irradiated solutions of **5b** and **5d** were repeatedly extracted with hot benzene. The concentrated residues of the extract were dissolved in a small amount of hot benzene. Yellow crystals of **7Bb** and **7Bd** were obtained by allowing the solutions to stand after an addition of petroleum ether. The crystals of **7Bd** containing benzene as crystal-solvent were dried at about 60 °C under 10^{-4} mmHg.

*(4a*RS,*7a*SR,*12b*SR*)-9,12-Dihydroxy-6,7-dihydro-1,4,5,8(7a*H,*12b*H*)-cyclopenta*[k]*phenanthrenetetrone (7Ba).* Decomposed at *ca.* 207 °C. Found: C, 65.29; H, 3.84%. Calcd for $C_{17}H_{12}O_6$: C, 65.38; H, 3.87%. IR (KBr): ν 3400, 3060, 2980, 2910, 2880, 1755, 1720, 1685, 1660, 1620, 1600 cm^{-1}. UV (MeCN): λ_{max} (ε) <220, 260 (7.00×10^3) (sh), 373 (5.05×10^3) nm.

*(4a*RS,*7a*SR,*12b*SR*)-9,12-Dihydroxy-2,11-dimethyl-6,7-dihydro-1,4,5,8,(7a*H,*12b*H*)-cyclopenta*[k]*phenanthrenetetrone (7Bb).* Mp 212—217 °C. Found: C, 66.81; H, 4.69%. Calcd for $C_{19}H_{16}O_6$: C, 67.05; H, 4.75%. IR (KBr): ν 3410, 3080, 3000, 2970, 2930, 2840, 1745, 1710, 1670, 1640, 1580 cm^{-1}. UV (MeCN): λ_{max} (ε) 234 (2.07×10^4), 268 (7.07×10^3) (sh), 361 (4.97×10^3) nm.

*(4a*RS,*8a*SR,*13b*SR*)-10,13-Dihydroxy-6,7,8,8a-tetrahydro-1,4,5,9-(13b*H*)-benz*[e]*anthracenetetrone (7Bc).* Mp 189—192 °C. Found: C, 66.43; H, 4.23%. Calcd for $C_{18}H_{14}O_6$: C, 66.25; H, 4.32%. IR (KBr): ν 3420, 3080, 2970, 2880, 2860, 1735, 1705, 1680, 1650, 1620, 1600 cm^{-1}. UV (MeCN): λ_{max} (ε) <220, 257 (5.49×10^3) (sh), 371 (4.88×10^3) nm.

*(4a*RS,*8a*SR,*13b*SR*)-10,13-Dihydroxy-2,12-dimethyl-6,7,8,8a-tetrahydro-1,4,5,9(13b*H*)-benz*[e]*anthracenetetrone (7Bd).* Mp 214—216 °C. Found: C, 67.95; H, 5.18%. Calcd for $C_{20}H_{18}O_6$: C, 67.79; H, 5.12%. IR (KBr): ν 3450, 3040, 2980, 2950, 2920, 2860, 2850, 1720, 1670, 1640, 1610, 1580 cm^{-1}. UV (MeCN): λ_{max} (ε) 236 (1.97×10^4), 255 (7.12×10^3) (sh), 363 (5.46×10^3) nm.

Isobutyryl-1,4-benzoquinone (11). A mixture of *p*-dimethoxybenzene (5 g), isobutyric acid (5 g), and polyphosphoric acid (70 g) was stirred for 5 h at 60 °C. The reaction mixture was diluted with excess water and extracted with diethyl ether. The concentrated residue of the washed and dried extract was distilled under reduced pressure to give 2′, 5′-dimethoxyisobutyrophenone in the yield of 55%. Bp 120—121 °C/2 mmHg. Found: C, 69.08; H, 7.61%. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74%. ^{1}H NMR ($CDCl_3$): δ=1.10 (6H, d, J=6.7 Hz, $\text{CH}\underline{\text{Me}}_2$), 3.40 (1H, hept, J=6.7 Hz, $\text{C}\underline{\text{H}}\text{Me}_2$), 3.67 (3H, s, OMe), 3.72 (3H, s, OMe), 6.7—6.9 (3H, m, ArH).

The treatment of 2′,5′-dimethoxyisobutyrophenone with BBr_3 in the usual manner gave a yellow liquid of isobutyryl hydroquinone in the yield of 80%. Bp 137—138 °C/2 mmHg. Found: C, 66.81; H, 6.84%. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71%. ^{1}H NMR (acetone-d_6): δ=1.15 (6H, d, J= 6.5 Hz, $\text{CH}\underline{\text{Me}}_2$), 3.37 (1H, hept, J=6.5 Hz, $\text{C}\underline{\text{H}}\text{Me}_2$), 6.7—7.1 (3H, m, ArH), 8.90 (1H, s, OH), 11.85 (1H, s, chelate OH). A solution of isobutyrylhydroquinone in benzene was stirred with an excess of Ag_2O and $MgSO_4$ for 0.5 h.[1] The concentrated residue of the filtered solution was sublimed *in vacuo* to give a yellow solid of isobutyryl-1,4-benzoquinone (**11**) in the yield of 70%. Mp 27—28 °C. Found: C, 67.21; H, 5.72%. Calcd for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66%. ^{1}H NMR ($CDCl_3$): δ=1.10 (6H, d, J=6.8 Hz, $\text{CH}\underline{\text{Me}}_2$), 3.11 (1H, hept, J=6.8 Hz, $\text{C}\underline{\text{H}}\text{Me}_2$), 6.67 (3H, s, ArH). IR (KBr): ν 3060, 3000, 2960, 2920, 2880, 1700, 1670, 1600 cm^{-1}. UV (MeCN): λ_{max} (ε) 246 (1.90×10^4), 300 (461) (sh), 450 (30) nm.

Photolysis of 11. A solution of **11** in actonitrile (0.1 mol dm^{-3}) was irradiated in degassed condition by a 300 W high pressure mercury-arc lamp for 10 h. The concentrated residue of the solution was submitted to column chromatography on silica gel with an eluent of petroleum ether–diethyl ether (2 : 1) to give 2,2-dimethyl-5-hydroxy-3(2*H*)-benzofuranone (**14**) in the yield of 20%. No other products except tar were found and no unreacted **11** was recovered. **14**: Mp 158—159 °C (recrystallized from benzene). Found: C, 67.24; H, 5.72%. Calcd for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66%. ^{1}H NMR ($CDCl_3$): δ=1.45 (6H, s, 2Me), 6.20 (1H, s, OH), 6.9—7.3 (3H, m, ArH). IR (KBr): ν 3280 (broad and strong), 3020, 2980, 2920, 1710, 1630 cm^{-1}. UV (EtOH): λ_{max} (ε) 253 (7.67×10^3), 370 (4.48×10^3) nm.

X-Ray Structural Analysis. The compound of **7Bd** was crystallized from toluene to give crystals containing solvent molecules. A single crystal of an approximate size, $0.1\times0.5\times0.8$ mm, was used for the intensity measurement. The crystal data were: monoclinic, $P2_1/a$, a=17.537(1), b= 10.358(1), c=10.588(1) Å, β=91.942(7)°, V=1922.2(2) Å^3, Z= 4, D_m=1.378 g cm^{-3} (by floatation method with petroleum ether–carbon tetrachloride solution), D_c=1.382 as $C_{20}H_{18}O_6\cdot1/2(C_6H_5CH_3)$. The unit-cell dimensions were obtained by means of the least-squares technique with the values of 35 reflections. The intensities of 2543 independent reflections were collected in the range of $\sin\theta/\lambda\leqq0.65$ by a θ—2θ scan mode (2°/min) on a Rigaku four-circle diffractometer with Ni-filtered Mo $K\alpha$ radiation. The crystal structure was solved by MULTAN. Refinement was effected by the constraint full matrix least-squares method[11] because of the disorder of solvent molecule. The difference Fourier synthesis after the anisotropic refinement of the nonhydrogen atoms revealed all the hydrogen atoms except the methyl and hydroxyl hydrogen atoms. The final refinement, including the contribution of hydrogen atoms, reduced the R factor to 0.088 without $|F_{obsd}|=0$. The final atomic parameters[12] are given in Table 2. The bond distances and bond angles are shown in Figs. 2 and 3 respectively.

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2) A enantiomer, **2**, is shown for the convenience of drawing the corresponding intermediate, **10**.

3) The UV spectra of **5** were similar to that of 1,4-benzoquinone (see Experimental section).

4) When benzene was used as solvent, **7B** was obtained in a similar yield as in acetonitrile.

5) The increased yield of **7Bc** in a reaction using a lower initial concentrationof **5c** suggests that polymeric compounds may be formed by intermolecular reactions between **5c**.

6) A enantiomer of each pair is shown.

7) A broad singlet. See footnote e in Table 1.

8) See footnotes d and f in Table 1. This fact is indicative of a W-letter arrangement of H_B and $H_{C'}$.

9) No direct evidences for the intervention of the dienols, **6** and **9**, could be obtained by following the reactions with ^1H NMR and IR spectroscopic methods. In frozen 2-MeTHF, **1** showed a complexed fluorescence spectrum, which could not be straightfowardly interpreted because **2** showed a complexed one. **5** showed no fluorescent bands in frozen 2-MeTHF.

10) **3** was prepared by following the method described for the synthesis of 1,16-bis(2,5-dimethoxyphenyl)-1,16-hexadecanedione; K. Yoshihira, S. Sasaki, H. Ogawa, S. Natori, *Chem. Pharm. Bull.*, **16**, 2383 (1968).

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12) Table of the anisotropic thermal factors of non-hydrogen atoms are kept at the Chemical Society of Japan. Document No. 8411.