o-Pleiadienequinones. Part 2.[1] Nucleophilic Substitution Reaction of *o*-Pleiadienequinone with Alcohols

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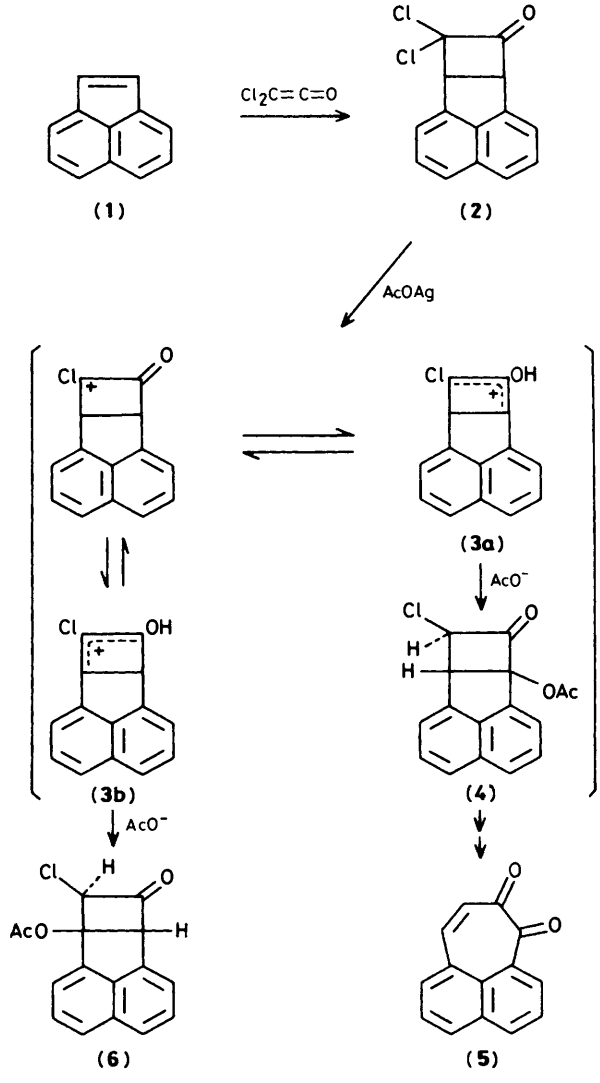
In the course of the synthesis of the title compound (**5**) by the hydrolysis of the dichloro ketone (**2**) the acetoxy chloro ketone (**6**) was formed and accounted for in terms of the unusual bridgehead cation (**3b**). The nucleophilic substitution reaction of the compound (**5**) with various alcohols afforded alkoxy quinones (**8**) and/or acetals (**7**). The mechanism of the formation is discussed. The full characterization of 1-, 3-, and 6-methoxy quinones (**8a**$_1$), (**8a**$_2$), and (**8a**$_3$) by spectroscopic and electrochemical methods is described. An attempt to effect the de-*O*-methylation of the methoxy quinones (**8a**), by the action of trimethylsilyl iodide, failed; dihydro quinones (**15a**), (**15b**), and (**15c**) resulted. The oxidative rearrangement of compound (**5**) to γ-lactone (**17**) in the reaction with iron(III) sulphate is described.

Although nonbenzenoid quinones have attracted attention because of their unique structures, few synthetic studies have been made. In particular, far less is known about their reactivity than about the reactivity of the better known cyclobutadiene- and acenaphthene-quinones. In Part 1, we reported the synthesis and some properties of *o*-pleiadienequinone (**5**) which although not having peripheral has cross-conjugation: it was thus placed in the second category of non-benzenoid quinones.[1]

Here we report (*a*) a new mechanistic observation on the synthesis of compound (**5**), (*b*) the nucleophilic substitution reaction of the compound (**5**) with various alcohols, (*c*) full characterization by spectroscopic and electrochemical methods of the methoxy quinones (**8**) so obtained, and (*d*) the results of an attempted synthesis of hydroxy-*o*-pleiadienequinones.

The quinone (**5**) was synthesized (62% yield) by hydrolysis of the dichloro ketene adduct (**2**) to give the acenaphthylene (**1**) using silver acetate in acetic acid as reported earlier;[1] an increased yield was obtained by increasing the quantity of reagent used in a slightly modified procedure. A small amount of the chloro acetoxy ketone (**6**) was also obtained as a minor product (0.6% yield); this shows characteristic absorption in its i.r. spectrum at 1 810 and 1 752 cm^{-1} as a result of the presence of four-membered ring carbonyl and acetoxy groups; there were also two singlet proton signals at δ 4.48 (1 H) and 4.83 (1 H) on its n.m.r. spectrum. By the n.O.e. technique and comparison of chemical-shift values with those of the compound (**2**) and 8-chloro-8,8a-dihydrocyclobut[*a*]acenaphthylen-7(6b*H*)-one[1] the former signal was assigned to the *endo*-8-H and the latter to the *exo*-6b-H. Consequently, the structure of the compound (**6**) was determined as shown in Scheme 1. It is interesting to note that the concurrent formation of unusual bridgehead cations (**3a**) and (**3b**) in acidic conditions seems to be implied in this experiment; the acetate (**4**) was not isolated but its intermediate formation is supported by a number of many related facts.[1,2]

When the quinone (**5**) is allowed to react with an excess of various primary and secondary alcohols in the presence of an organic or Lewis acid with or without benzene as solvent, 8,8-dialkoxy ketones (**7**) and an isomeric mixture of 1-, 3-, and 6-alkoxy quinones (**8**) were obtained (Scheme 2); the results are listed in Table 1. Some physical characteristics and the results of elemental analysis of the acetals (**7**) and the quinones (**8**) are given in Tables 2 and 3. The spectroscopic data for compounds (**7**) and (**8**) are given in Tables 4 and 5. When toluene-*p*-sulphonic acid is used as a catalyst, both the acetals (**7**) and the alkoxy quinones (**8**) were obtained for reactions with methanol, ethanol, propanol, isopropyl alcohol, butanol, and ethylene cyanohydrin, but only the monoacetals (**7**) were obtained with isopentyl alcohol, benzyl alcohol, allyl alcohol, prop-2-ynyl alcohol, and ethylene glycol. The reaction with t-butyl alcohol gave neither the acetal (**7**) nor the alkoxy quinone (**8**). When

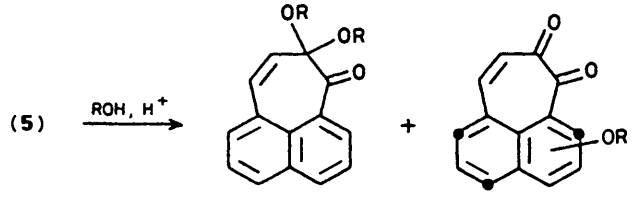


Scheme 1.

Table 1. Reaction of compound (5) with various alcohols

R in ROH	Catalyst or reagent	Refluxing time (h)	Products (% yield) Acetal		Alkoxy compound	
Me	*p*-TsOH	8	(7a)	56.2	(8a)	3.6
Me	$ZnCl_2$	8	(7a)	14.3	(8a)	32.3 (19:55:26)[b]
Me	H_2SO_4 $Fe_2(SO_4)_3$	2	(7a)	0	(8a)	83.9 (24:50:26)[b]
Me	$ZnCl_2$ $Fe_2(SO_4)_3$	2	(7a)	0	(8a)	80.0 (23:57:20)[b]
Et	*p*-TsOH	5	(7b)	10.0	(8b)	29.8 (1:1.4:1)[c]
Et	$ZnCl_2$	5	(7b)	5.5	(8b)	29.2
Pr	*p*-TsOH[a]	12	(7c)	25.5	(8c)	5.8
Pr^i	*p*-TsOH	6	(7d)	2.9	(8d)	4.4
Bu	*p*-TsOH[a]	12	(7e)	65.2	(8e)	Trace
$CN(CH_2)_2$	*p*-TsOH[a]	3	(7f)	44.1	(8f)	2.3
$PhCH_2$	*p*-TsOH[a]	2	(7g)	50.0	(8g)	0
Allyl	*p*-TsOH[a]	6	(7h)	38.3	(8b)	0
$HC{\equiv}CCH_2$	*p*-TsOH[a]	8	(7i)	25.7	(8i)	0
$HO(CH_2)_2$	*p*-TsOH[a]	8	(7j)	10.8	(8j)	0
Isopentyl	*p*-TsOH[a]	18	(7k)	30.0[d]	(8k)	0
Bu^t	*p*-TsOH	24	(7l)	0	(8l)	0

[a] Refluxed in dry benzene. [b] Ratio between alkoxy isomers; $(8a_1):(8a_2):(8a_3)$. [c] Ratio between alkoxy isomers; $(8b_1):(8b_2):(8b_3)$. [d] Not purified.



Scheme 2.

zinc chloride was used as a catalyst,* the methoxy quinone (**8a**) was obtained in better yield but the yield of ethoxy quinone (**8b**) changed little. The ratio of the formation of the acetal (**7b**) and the alkoxy quinone (**8b**) was examined in the reaction of the quinone (**5**) (20 mmol) with ethanol (100 ml). The amount of toluene-*p*-sulphonic acid added was changed from 0.0026 mmol to 1.1 mmol in five independent experiments and zinc(II) chloride from 0.2 to 2 mmol in two. The ratio of the acetal (**7b**)/alkoxy quinone (**8b**) changed from 1.8/10 to 3.8/10 for toluene-*p*-sulphonic acid and from 3.0/10 to 3.3/10 for zinc(II) chloride, that is, increased amounts of catalysts brought decrease of the formation of alkoxy quinone (**8b**). As a typical case, the reaction of the quinone (**5**) with methanol and the structural determination of the reaction products are described below.

Upon refluxing the quinone (**5**) with methanol and toluene-*p*-sulphonic acid for 8 h, the acetal (**7a**) and the methoxy quinone (**8a**) were obtained in the ratio of *ca.* 1:2. The methoxy quinone (**8a**) was a *ca.* 1:2:1 mixture of 1-, 3-, and 6-methoxy quinones ($8a_1$), ($8a_2$), and ($8a_3$). Further treatment of the acetal (**7a**) or the methoxy quinone (**8a**) with methanol in a similar way gave only recovery of the starting materials. The acetal (**7a**) has an i.r. absorption peak at 1 685 cm^{-1} for the naphthoyl carbonyl group and two doublets at δ 5.95 (9-H) and 7.05 (10-H) (*J* 12 Hz) in the ^1H n.m.r. spectrum, indicating that the acetal (**7a**) has an olefinic linkage on a seven-membered ring skeleton. That compound ($8a_3$) does not show its lowest field signal for aromatic protons near δ 9, is an indication that the methoxy group is at the 6-position where the effect of the magnetic anisotropy from the carbonyl group at 7-position is greatest; compounds ($8a_1$) and ($8a_2$) have signals for double doublets at δ 8.94 (6-H) and 9.17 (6-H) respectively, indicating there is a methoxy group at the 1-, 2-, or 3-positions. In consideration of the fact that for the quinone (**5**) the signals of the naphthalene ring protons appear in the order of 6-, 4-, 3-, 1-, and 2- from low field, a pair of doublets at δ 8.56 and 8.28 for compound ($8a_1$) and similar ones at δ 8.18 and 7.83 for compound ($8a_2$) can be ascribed to protons at the 3- and 2-positions, and 1- and 2-positions respectively. Therefore compound ($8a_1$) is 1-methoxy-*o*-pleiadienequinone and compound ($8a_2$) is 3-methoxy-*o*-pleiadienequinone. The ^{13}C n.m.r. spectra of the carbonyl carbons at 7-C for ($8a_1$) and ($8a_2$) and that at 8-C for the quinone ($8a_3$) showed signals at δ 184.9, 185.3, and 184.6 respectively; these values are those of ordinary quinones. The signals of the carbonyl carbons at 8-C of the quinones ($8a_1$) and ($8a_2$), and that at 7-C of the quinone ($8a_3$) appeared at δ 166.5, 166.8, and 167.0 respectively, suggesting that these are aromatic ester carbonyl carbons. These observations indicate that a methoxy group and one of the two carbonyl groups are linked by double bonds to form a vinylogue of a methyl ester group. The i.r. absorption maxima at 1 653, 1 673, and 1 650 cm^{-1} were assigned to the carbonyl groups at the 7-, 7-, and 8-positions for the quinones ($8a_1$), ($8a_2$), and ($8a_3$) respectively. The other absorption maxima at 1 714, 1 718, and 1 717 cm^{-1}, were assigned to carbonyl groups at the 8-, 8-, and 7-positions of the quinones ($8a_1$), ($8a_2$), and ($8a_3$), respectively. These can be most reasonably interpreted as ester carbonyl group absorption in agreement with the ^{13}C n.m.r. spectra. Comparing the i.r. data for the C-7 carbonyl group and the ^1H n.m.r. chemical shift value of 6-H for compound ($8a_1$)

* Since tropolone and tropone are known to form complexes with divalent metal ions,[3] the possibility of complex formation with these ions was investigated for the quinone (**5**) which has contributions from polar structures.[1] The ether extracts from the aqueous layer of a mixture of a solution of the quinone (**5**) in chloroform and aqueous copper(II) chloride, cobalt(II) chloride, or zinc chloride[4] showed new weak absorption maxima in their i.r. spectra at 1 730 and 1 710 cm^{-1}; these were relatively strong for the zinc(II) chloride reaction.

Table 2. Elemental analysis, appearance, m.p., and *m/z* of the acetals (7)

Compound	Appearance	M.p. (°C)[a]	Molecular formula	Analytical data[b] C (%), H (%)	*m/z* (%)[c] (Relative abundance)
(7a)	Pale yellow needles	113—114 (hexane)	$C_{16}H_{14}O_3$	C 75.5 (75.57) H 5.6 (5.55)	*254* (17), 195 (35), 180 (23), 164 (78), 152 (100), 151 (35)[d]
(7b)	Colourless needles	133—144 (hexane)	$C_{18}H_{18}O_3$	C 76.55 (76.57) H 6.45 (6.43)	*282* (5), 209 (11), 180 (100), 166 (9), 152 (40), 151 (14)[d]
(7c)	Colourless cubes	74—75 (hexane)	$C_{20}H_{22}O_3$	C 77.35 (77.39) H 7.0 (7.14)	*310* (3), 269 (23), 268 (11), 253 (18), 226 (24), 224 (14), 209 (10), 184 (78), 192 (46), 167 (27), 166 (21), 165 (11), 155 (27), 154 (100), 153 (48), 152 (20)[e]
(7d)	Pale yellow crystals	81—82 (hexane)	$C_{20}H_{22}O_3$	C 77.55 (77.39) H 7.05 (7.14)	*310* (1), 268 (5), 223 (7), 209 (15), 181 (100), 153 (7), 152 (10)[f]
(7e)	Yellow cubes	63—64 (hexane)	$C_{22}H_{26}O_3$	C 78.15 (78.07) H 7.75 (7.74)	*338* (1), 182 (14), 181 (10), 180 (100), 165 (7), 153 (13), 152 (38)[d]
(7f)	Colourless cubes	169—170 (benzene)	$C_{20}H_{16}N_2O_3$	C 72.4 (72.28) H 4.85 (4.85) N 8.35 (8.43)	*332* (2), 234 (5), 207 (20), 181 (53), 180 (36), 165 (12), 164 (18), 153 (23), 152 (100), 151 (30), 150 (14)[d]
(7g)	Pale yellow needles	148—149.5 (hexane)	$C_{28}H_{22}O_3$	C 82.8 (82.73) H 5.8 (5.45)	*406* (2), 298 (10), 272 (10), 271 (25), 270 (17), 182 (10), 181 (45), 180 (14), 152 (6), 108 (39), 107 (13), 92 (14), 91 (100)[h]
(7h)	Pale brown needles	73—74 (benzene–hexane)	$C_{20}H_{18}O_3$	C 78.3 (78.41) H 6.0 (5.92)	*306* (2), 266 (14), 265 (55), 249 (14), 223 (19), 222 (66), 221 (100), 203 (16), 202 (64), 192 (31), 180 (33), 179 (47), 178 (11), 166 (13), 152 (10)[h]
(7i)	Colourless needles	107—108.5 (hexane)	$C_{20}H_{14}O_3$	C 79.2 (79.45) H 4.75 (4.67)	*302* (2), 264 (17), 248 (15), 223 (19), 222 (81), 221 (38), 202 (10), 193 (13), 192 (78), 191 (100), 190 (15), 182 (49), 181 (81), 179 (26), 166 (14), 153 (11), 152 (72)[g]
(7j)	Pale yellow plates	131.5—132 (benzene–hexane)	$C_{16}H_{12}O_3$	C 75.95 (76.18) H 4.9 (4.80)	*252* (11), 181 (34), 180 (86), 179 (11), 165 (12), 164 (13), 153 (13), 152 (100), 151 (16)[d]
(7k)	Oil	120/200 Pa			*366* (2), 279 (15), 209 (13), 182 (46), 181 (100), 180 (25), 165 (13), 153 (21), 152 (59), 151 (16)[d]

[a] Solvents in parentheses were used for recrystallization. [b] Numerals in parentheses indicate calculated values. [c] Parent molecular ion shown in italics. [d] 75 eV. [e] 35 eV. [f] 30 eV. [g] 25 eV. [h] 5 eV.

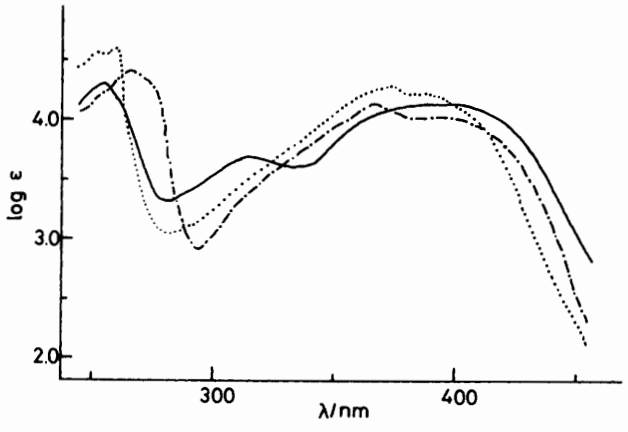


Figure 1. Electronic spectra of methoxy quinones: —— (**8a**$_1$); - - - - (**8a**$_2$); — — — — (**8a**$_3$) (solution in chloroform).

with those for compound (**8a**$_2$), the carbonyl group at C-7 of the latter seems to be more polarized than the former. If the u.v. spectral longest- and shorter-wavelength absorptions of compound (**5**) are considered to result from the longitudinal and transverse excitation respectively, the effect of the introduction of a methoxy group at the 1-, 3-, and 6-positions seems to be reflected reasonably in the absorption maxima of the compounds (**8a**$_1$), (**8a**$_2$), and (**8a**$_3$) (Figure 1).

The mass spectra (Figure 2) show that the major process of fragmentation for the 3-alkoxy quinones (**8a**$_1$), (**8a**$_2$), and (**8a**$_3$) is first the loss of an alkoxy group followed by two successive eliminations of carbon monoxide. A minor process is first the

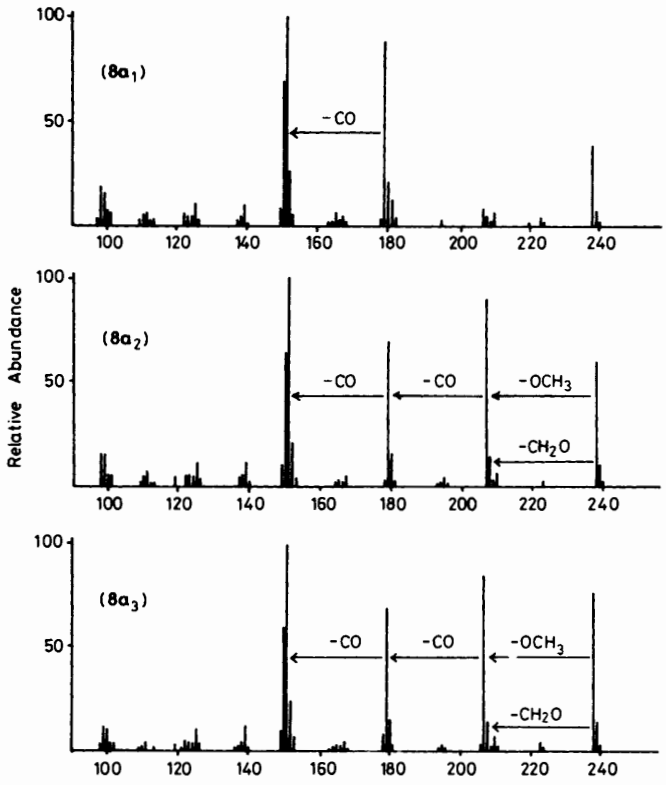


Figure 2. Mass spectra (75 eV) of alkoxyquinones (**8a**$_1$), (**8a**$_2$), and (**8a**$_3$).

Table 3. Elemental analysis, appearance, m.p., and *m/z* of the alkoxy quinones (**8**)

Compound	Appearance	M.p. (°C)[a]	Molecular formula	Analytical data[b] C (%), H (%)	*m/z* (%)[c,d] (Relative abundance)
(**8a**$_1$)	Yellow needles	158.5—159 (hexane)	$C_{15}H_{10}O_3$	C 75.35 (75.62) H 4.1 (4.23)	240 (1), 239 (7), *238* (38), 208 (4), 207 (6), 179 (88), 151 (100), 150 (69)
(**8a**$_2$)	Pale yellow needles	166.5—167 (hexane)	$C_{15}H_{10}O_3$	C 75.85 (75.62) H 4.45 (4.23)	240 (2), 239 (11), *238* (60), 208 (14), 207 (89), 179 (69), 151 (100), 150 (63)
(**8a**$_3$)	Yellow needles	116—117 (hexane)	$C_{15}H_{10}O_3$	C 75.5 (75.62) H 4.35 (4.23)	240 (3), 239 (14), *238* (77), 208 (14), 207 (85), 179 (69), 151 (100), 150 (60)
(**8b**$_1$)	Lemon-yellow needles	109.5–110.5 (hexane)	$C_{16}H_{12}O_3$	C 76.45 (76.18) H 4.9 (4.79)	254 (2), 253 (9), *252* (45), 224 (18), 207 (61), 196 (8), 179 (36), 168 (6), 151 (100), 150 (55)
(**8b**$_2$)	Yellow scales	127—128 (hexane)	$C_{16}H_{12}O_3$	C 76.35 (76.18) H 5.0 (4.79)	254 (5), 253 (15), *252* (53), 224 (17), 207 (100), 196 (8), 179 (62), 151 (100), 150 (67)
(**8b**$_3$)	Yellow needles	103—104 (hexane)	$C_{16}H_{12}O_3$	C 76.3 (76.18) H 5.0 (4.79)	254 (2), 253 (16), *252* (87), 224 (18), 207 (61), 196 (8), 179 (25), 168 (5), 151 (58), 150 (34)
(**8d**$_2$)	Yellow needles	135—136 (hexane)	$C_{17}H_{14}O_3$	C 76.4 (76.68) H 5.2 (5.30)	268 (2), 267 (13), *266*, (59), 224 (100), 207 (41), 196 (29), 179 (38), 168 (14), 151 (87), 150 (45)

[a] Solvents in parentheses were used for recrystallization. [b] Numerals in parentheses indicate calculated values. [c] Parent molecular ion shown in italics. [d] 75 eV.

Table 4. Spectroscopic data of acetals (**7**)

Compound	$\lambda_{max.}$/nm (log ε)	$\nu_{max.}$/cm^{-1}	δ (60 MHz)
(**7a**)	322 (3.77), 340sh (3.71)	1 685, 1 170, 1 056	3.20 (6 H, s, 2 CH_3), 5.95 (1 H, d, *J* 12 Hz, 9-H), 7.05 (1 H, d, *J* 12 Hz, 10-H), 7.40—8.13 (6 H, m, ArH)
(**7b**)	324—325.5 (3.94), 339sh (3.90), 357sh (3.74)	1 691, 1 156, 1 077	0.95 (6 H, t, 2 CH_3), 3.55 (4 H, q, CH_3), 6.08 (1 H, d, *J* 12 Hz, 9-H), 7.08 (1 H, d, *J* 12 Hz, 10-H), 7.30—8.10 (6 H, m, ArH)
(**7c**)	320 (3.92), 336sh (3.86), 360sh (3.73)	1 694, 1 160, 1 072	0.53 (6 H, t, 2 CH_3), 1.35 (4 H, sex, 2 CH_2), 3.35 (4 H, t, 2 CH_2), 5.92 (1 H, d, *J* 12 Hz, 9-H), 6.82 (1 H, d, *J* 12 Hz, 10-H), 7.18—8.02 (6 H, m, ArH)
(**7d**)	316 (3.94), 336 (3.84)	1 696, 1 148, 1 056	0.82 (6 H, d, 2 CH_3), 1.18 (6 H, d, 2 CH_3), 3.94 (2 H, sep, 2 CH), 6.07 (1 H, d, *J* 12 Hz, 9-H), 7.00 (1 H, d, *J* 12 Hz, 10-H), 7.36—8.07 (6 H, m, ArH)
(**7e**)	320 (3.92), 330sh (3.80)	1 694, 1 152, 1 064	0.50—1.53 (14 H, m, 2 $CH_2CH_2CH_3$), 3.45 (4 H, m, 2 CH_2), 5.97 (1 H, d, *J* 12 Hz, 9-H), 6.92 (1 H, d, *J* 12 Hz, 10-H), 7.30—8.07 (6 H, m, ArH)
(**7f**)	320 (3.92), 336 (3.91), 354 (3.83)	2 250, 1 674, 1 156, 1 074	2.37 (4 H, m, 2 CH_2CN), 3.75 (4 H, m, 2 CH_2O), 5.93 (1 H, d, *J* 12 Hz, 9-H), 7.07 (1 H, d, *J* 12 Hz, 10-H), 7.33—8.10 (6 H, m, ArH)
(**7g**)	320 (3.95), 336sh (3.91)	1 686, 1 146, 1 084	4.48 (4 H, s, 2 CH_2), 6.05 (1 H, d, *J* 12 Hz, 9-H), 6.62—7.06 (11 H, m, 2 PhH and 10-H), 7.31—8.07 (6 H, m, ArH)
(**7h**)	317 (3.91), 336sh (3.86)	1 680, 1 154, 1 064	3.93 (4 H, d, 2 CH_2O), 4.77 (4 H, m, 2 CH_2), 5.76 (2 H, qui, 2 CH), 5.91 (1 H, d, *J* 12 Hz, 9-H), 6.89 (1 H, d, *J* 12 Hz, 10-H), 7.27—7.96 (6 H, m, ArH)
(**7i**)	322 (3.92), 336 (3.90), 354 (3.83)	2 116, 1 688, 1 154, 1 060	2.18 (2 H, bs, 2 CH), 4.08 (4 H, bs, 2 CH_2), 5.76 (1 H, d, *J* 12 Hz, 9-H), 6.78 (1 H, d, *J* 12 Hz, 10 Hz), 7.12—7.85 (6 H, m, ArH)
(**7j**)	322 (3.94), 336sh (3.92), 364sh (3.74)	1 664, 1 160, 1 028	3.87 (2 H, m, CH_2), 3.98 (2 H, m, CH_2), 6.16 (1 H, d, *J* 12 Hz, 9-H), 7.01 (1 H, d, *J* 12 Hz, 10-H), 7.40—8.22 (6 H, m, ArH)
(**7k**)	320 (3.92), 336sh (3.84), 356sh (3.68)	1 678, 1 142, 1 064 ($CHCl_3$)	0.40—1.0 (12 H, m, 4 CH_3), 1.0—1.60 (6 H, m, 2 CH and 2 CH_2), 3.10—3.73 (4 H, m, 2 CH_2), 6.03 (1 H, d, *J* 12 Hz, 9-H), 7.00 (1 H, d, *J* 12 Hz, 10-H), 7.27—8.15 (6 H, m, ArH)

loss of alkene followed by two successive eliminations of carbon monoxide. This is similar to the major process for general aryl alkyl ethers, where the alkene is eliminated to form the corresponding hydroxyaryl compound.* For methylaryl compounds the sequential elimination of a methyl group and two successive carbon monoxides is a general feature* but for these methoxy quinones (**8a**$_2$) and (**8a**$_3$) the sequential elimination of a methoxy radical and two carbon monoxides is a major path. The loss of formaldehyde seems to be a minor process* and practically no elimination of a methyl group was recorded. In contrast to the methoxy quinones (**8a**$_2$) and (**8a**$_3$) only a very weak ion ($M^{+\cdot}$ − OMe) was observed for the methoxy quinone (**8a**$_1$), indicating that at least under the conditions of measurement the stereochemical repulsion between 10-H and 1-OMe of the compound (**8a**$_1$) is larger than and different from that between 4-H and 3-OMe of the quinone (**8a**$_2$) and that between 7-CO and 6-OMe of the quinone (**8a**$_3$).

* Loss of a formaldehyde and a methoxy group from the molecular ion is noted in some derivatives of methoxyaryl compounds.[5]

The spectral data for the ethoxy quinones, (**8b**$_1$), (**8b**$_2$), and (**8b**$_3$) are similar to those of the methoxy quinones (**8a**$_1$), (**8a**$_2$) and (**8a**$_3$), respectively.

The electrochemical reduction of the quinones (**8a**$_1$), (**8a**$_2$), and (**8a**$_3$) as well as that of a series of reference compounds was examined by cyclic voltammetry and the formal potentials are listed in Table 6. The quinone (**5**) has almost the same potential values, E_1 and E_2, as the isomeric 9,10-anthraquinone. As expected, the 9-chloro-*o*-pleiadienequinone (**9**) showed a higher potential value than the quinone (**5**). All the voltammograms of the methoxy quinones (**8a**$_1$), (**8a**$_2$), and (**8a**$_3$) showed good reversibility. While the E_1 values, which are the indicator of the ease of formation of anion radicals, are in the order (**8a**$_1$) > (**8a**$_3$) > (**8a**$_2$), the E_2 values for the formation of dianions are in the reverse order of (**8a**$_2$) > (**8a**$_3$) > (**8a**$_1$). From stereomodels, the *peri* interaction between 10-H and 1-OMe seems to be larger than that between 4-H and 3-OMe, a situation reflected perhaps in electrochemical potential differences between (E_1 + E_2) and (E_1 − E_2) for compounds (**8a**$_1$) and (**8a**$_2$). The voltammometric reversibility of the

Table 5. Spectroscopic data of the alkoxy quinones (**8**)

Compound	$\lambda_{max.}$/nm (log ε)	$\nu_{max.}$/cm^{-1}	δ (90 MHz), *J* (Hz) 1-H	2-H	3-H	4-H	5-H	6-H	9-H	10-H	Others
(**8a**$_1$)	254 (4.30), 312—320 (3.67), 396 (4.11)	1 714, 1 653, 1 281, 828, 774	—	8.32	8.58	7.75	7.62	8.95	6.68	7.73	4.05 (3 H, s, CH_3)
			J_{23} 7.8, J_{45} 7.3, J_{46} 2, J_{56} 7.3, J_{910} 9.7								
(**8a**$_2$)	252 (4.35), 260 (4.37), 370 (4.23)	1 718, 1 637, 1 265, 870, 825, 775	8.18	7.83	—	8.54	7.70	9.17	6.72	7.67	4.05 (3 H, s, CH_3)
			J_{12} 7.8, J_{45} 7.4, J_{46} 1.5, J_{56} 8.5, J_{910} 10.2								
(**8a**$_3$)	266 (4.36), 363 (4.10), 368 (3.74), 388—392sh (3.99)	1 717, 1 650, 1 296, 1 270, 1 255, 826, 767	8.16	7.74	8.61	8.02	8.02	—	6.77	8.73	4.05 (3 H, s, CH_3)
			J_{12} 8, J_{13} 1.8, J_{23} 8, J_{910} 10.2								
(**8b**$_1$)	256 (4.15), 309—313 (3.61), 324sh (3.59), 352sh (3.67), 366.5 (3.82), 390.5—400 (3.74)	1 715, 1 642, 1 262[a]	—	8.20	8.44	7.57	7.57	8.85	6.59	7.60	1.47 (3 H, t, *J* 7, CH_3), 4.49 (2 H, q, *J* 7, CH_2)
			J_{23} 7.8, J_{46} 2.8, J_{56} 7, J_{910} 9.7								
(**8b**$_2$)	253 (4.35), 265 (4.36), 368—372 (4.23), 385sh (4.19)	1 710, 1 641, 1 262[a]	8.07	7.50	—	8.25	7.75	9.12	6.65	7.55	1.47 (3 H, t, *J* 7, CH_3), 4.48 (2 H, q, *J* 7, CH_2)
			J_{12} 7.5, J_{45} 7.1, J_{46} 1, J_{56} 9.0, J_{910} 9.7								
(**8b**$_3$)	267 (4.46), 346sh (3.94), 351sh (3.97), 362.5 (4.12), 392—395 (3.99)	1 720, 1 710, 1 642, 1 260[a]	8.01	7.70	8.47	7.86	7.86	—	6.65	8.61	1.46 (3 H, t, *J* 7, CH_3), 4.47 (2 H, q, *J* 7, CH_2)
			J_{12} 6, J_{13} 1, J_{23} 6, J_{910} 10.5								
(**8c**$_2$)	252 (4.36), 260 (4.40), 368 (4.24)	1 710, 1 640, 1 252, 855, 820, 778	8.27	7.85	—	8.67	7.79	9.30	6.81	7.70	1.09 (3 H, t, *J* 7, CH_3), 1.90 (2 H, m, CH_2), 4.43 (2 H, t, *J* 6.6, CH_2)
			J_{12} 7.6, J_{45} 7.5, J_{46} 0.8, J_{56} 8.5, J_{910} 10								
(**8d**$_2$)	364 (3.95)	1 706, 1 642, 1 256, 1 108, 1 098, 855, 818, 778	8.10	7.83	—	8.52	7.70	9.21	6.68	7.81	1.46 (6 H, d, *J* 6.3, 2 CH_3). 5.33 (1 H, sep, *J* 6.3, CH)
			J_{12} 7.5, J_{45} 7.3, J_{46} 1.1, J_{56} 8.4, J_{910} 10								

[a] $CHCl_3$ solution.

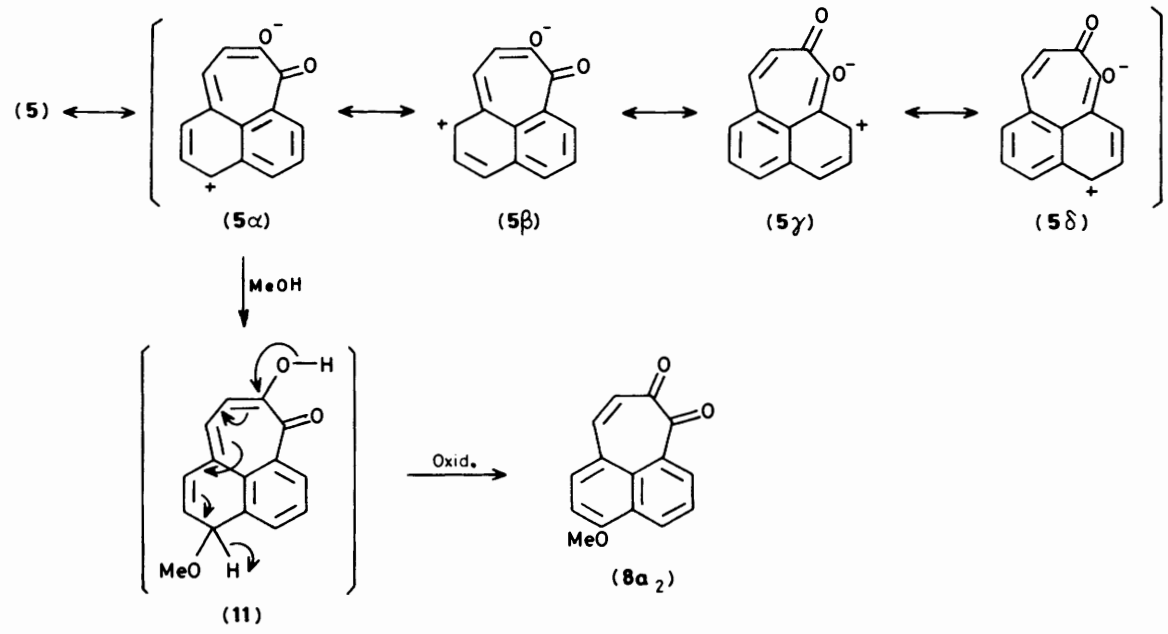
Table 6. Electrochemical reduction potentials of *o*-pleiadienequinones (**8a**$_1$), (**8a**$_2$), (**8a**$_3$), (**5**), and (**9**), and reference compounds[a]

Compound	E_1	E_2	$E_1 - E_2$	$E_1 + E_2$
Ferrocene[b]	0.48			
1,4-Naphthoquinone	−0.59	−1.40	0.81	−1.99
9-Chloro-*o*-pleiadienequinone (**9**)	−0.69	−1.42	0.73	−2.11
1-Methoxy-*o*-pleiadienequinone (**8a**$_1$)	−0.81	−1.53	0.72	−2.34
6-Methoxy-*o*-pleiadienequinone (**8a**$_3$)	−0.82	−1.45	0.63	−2.27
9,10-Anthraquinone	−0.83	−1.53	0.70	−2.36
o-Pleiadienequinone (**5**)[c]	−0.83	−1.55	0.72	−2.38
Acenaphthenequinone (**10**)	−0.85	−1.11	0.26	−1.96
3-Methoxy-*o*-pleiadienequinone (**8a**$_2$)	−0.85	−1.41	0.56	−2.26

[a] At 27.0 ± 0.5 °C in dry dimethylformamide as described in the text. Potentials relative to Ag/AgCl/sat. NaCl electrode. [b] G. Gritzner and J. Kuta, *Pure Appl. Chem.*, 1984, **56**, 462. [c] Ref. 1.

quinone (**5**) and the 9-chloro quinone (**9**) is poorer than that for the methoxy quinones (**8a**$_1$), (**8a**$_2$), and (**8a**$_3$) especially for oxidation; this indicates that the anion radicals or dianions of the former are less stable. This fact seems to be supported by the result from the catalytic hydrogenation of the quinone (**5**) with 5% Pd/C in methanol, where although the characteristic yellow colour of the quinone (**5**) disappears after absorption of 1 molar equiv. amount of hydrogen, after purification a small amount of the quinone (**5**) is recovered and unidentified products were obtained. The E_1 value for the quinone (**5**) is slightly higher than that of acenaphthenequinone (**10**) but the E_2 values for the former is much lower than that of the latter; the latter, therefore, more easily forms a dianion than the former. This suggests that the latter has a five-membered ring which favours electron attachment while the former has a seven-membered ring which disfavours the minus charge.

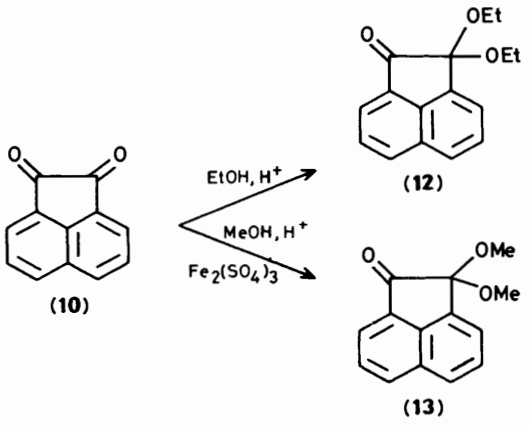
The mechanism for formation of the methoxy quinone (**8a**$_2$) is shown in Scheme 3. From an ^{1}H n.m.r. study of the quinone (**5**) it was proposed that the quinone (**5**) has contributions from such canonical structures as the benzotropolonate ions, (**5**α), (**5**β), (**5**γ), and (**5**δ), in acidic solution. If methanol attacks the ion (**5**α) by 1,8-addition, the adduct (**11**) must be formed, which would be converted into the methoxy quinone (**8a**$_2$) by the successive oxidation process. In this process, the quinone (**5**) itself must be working as the oxidizing agent in view of the yield of the methoxy quinone (**8a**) which never exceeded 50% without the addition of an oxidizing agent. The yield increased to 84% with iron(III) sulphate as oxidizing agent (Table 1), supporting the above explanation. The other methoxy quinones (**8a**$_1$) and (**8a**$_3$) must be formed similarly. Since the ratio between the products *via* the benzotropolonate ions (**5**α) and (**5**β) and that *via* the benzotropolonate ion (**5**γ) is 2 to 1, the former ions may



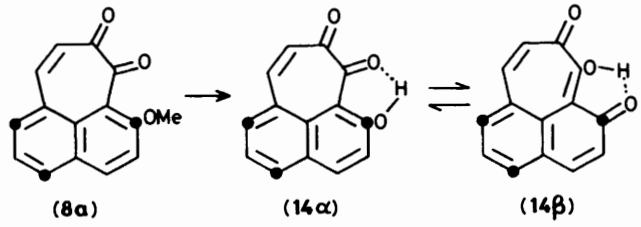
Scheme 3.

be more stable than the latter. It is noted that the product *via* the ion (5δ) was not observed in spite of a careful search. This suggests that the benzotropolonate-type ions (5γ) and (5δ) may not be good contributors but the formation of 6-methoxy-quinone (**8a**$_3$) can result from the transitional formation of a hydrogen bond between the carbonyl group at the 7-position and a methanol molecule. For comparison, acenaphthene-quinone (**10**), a lower analogue of compound (**5**), was refluxed with absolute ethanol in the presence of toluene-*p*-sulphuric acid or with absolute methanol in the presence of sulphuric acid and iron(III) sulphate to afford the mono-acetal (**12**) (85%) or (**13**) (72%) but no ethoxy or methoxy-acenaphthenequinone; this indicated that *o*-pleiadiene-quinone (**5**) can give rise to the stabilized cationic forms shown in Scheme 3, while acenaphthenequinone (**10**) cannot [1] (Scheme 4).

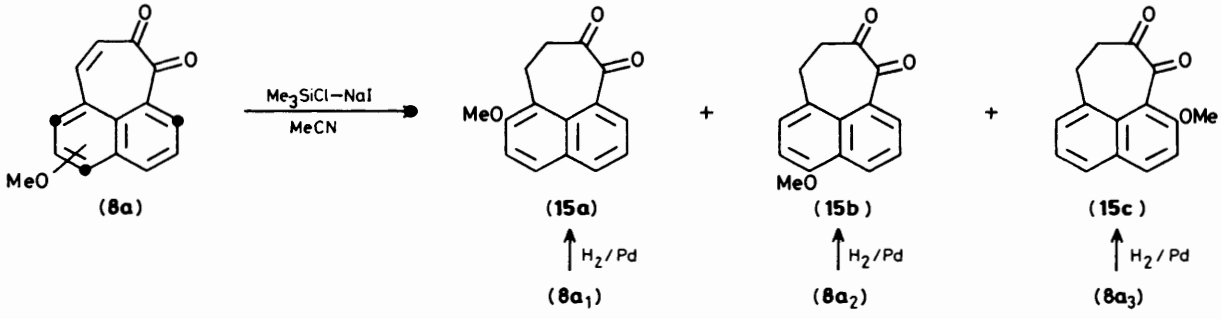
Replacement of the methoxy group by a hydroxy group, was thought to be of interest in order to see which form of the molecule, (**14**α) or (**14**β) (the former has a naphthol and the latter a tropolone structure), would be the more stable (Scheme 5). Accordingly, the methoxy quinone (**8a**) was treated



Scheme 4.

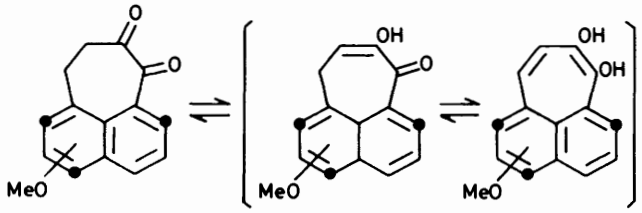


Scheme 5.

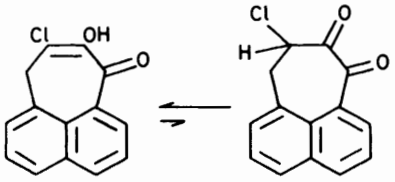


Scheme 6.

first with hydrogen bromide in boiling acetic acid but afforded only resinous materials which failed to give a positive iron(III) chloride colour test, and then with a 1 equimolar quantity of boron tribromide initially at −70 °C and then at room temperature in dichloromethane; there was a 79% recovery of starting material. By the reaction with trimethylsilyl iodide generated from trimethylsilyl chloride and sodium iodide no de-*O*-methyl compound was obtained* but, unexpectedly, a mixture of 9,10-dihydromethoxy diones (**15a**), (**15b**), and (**15c**) was obtained (20% yield) in the ratio of 1.6:2.4:1. These were separated by silica-gel column chromatography but structure assignment was impossible from the usual spectroscopic data. Consequently, each methoxy quinone (**8a**$_1$), (**8a**$_2$), or (**8a**$_3$) was independently reduced on 5% Pd/C with hydrogen to afford the corresponding dihydromethoxy quinones (**15a**), (**15b**), or (**15c**) (16% yield). These are reasonably stable (Scheme 6). On the basis of ^{1}H n.m.r. spectroscopy these compounds (**15a**), (**15b**), and (**15c**) existed only in the diketo form. It is interesting that the dione (**15**) takes neither the 'aromatized' form (**15β**) nor the enol ketone structure (**15α**); this contrasts with the chlorohydroxy-ketone (**16α**), which is more stable than its diketo form (**16β**)[1] (Scheme 7).



(15) (15α) (15β)

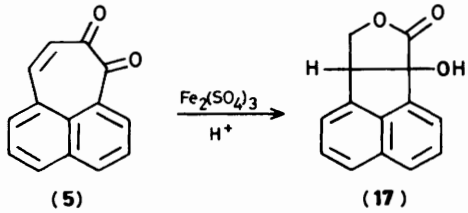


(16α) (16β)

Scheme 7.

The attempted reaction of the methoxy quinone (**8a**) with *o*-phenylenediamine in boiling methanol in the presence of acid catalysis gave only recovery of starting material; this behaviour differs from that of compound (**5**) which gives a quinoxaline derivative,[1] a reflection of the inner strain in this molecule.

Finally, in order to obtain hydroxy-*o*-pleiadienequinone (**14**) directly, compound (**5**) was treated with a mixture of iron(III) sulphate, sulphuric acid, and aqueous dioxane; unexpectedly, the γ-lactone (**17**) was obtained (30%) (Scheme 8). The u.v.



(5) (17)

Scheme 8.

* The generation of a β-iodo ketone from an α,β-unsaturated ketone by reaction with trimethylsilyl iodide has been reported but the formation of the exhaustively reduced unsaturated ketone has not.[7]

spectrum of the compound (**17**) showed similar absorption curve as 7-*exo*-chloro-6b,9a-dihydroacenaphtho[1,2-*c*]furan-9(7*H*)-one[1] and i.r. absorption maxima appear at 1 766 cm^{-1} for a γ-lactone moiety and at 3 350 and 3 010 cm^{-1} for the tertiary hydroxy group, the existence of which was also supported by the very slow deuterium-proton exchange (60 min) of the broad signal at δ 4.35 (1 H) on its ^{1}H n.m.r. spectrum. A typical ABX signal appears for the protons (7β-H (δ 2.40), 7α-H (δ 3.50), and 6b-H (δ 5.60), the assignment of which was carried out by the double resonance technique. The coupling constants, *J* 18 Hz for the geminal protons, 7α-H and 7β-H, and *J* 1.5 and 8 Hz indicate the dihedral angles between 6b-H and 7α-H are 129° and 8° between 6b-H and 7β-H calculated by the Karplus equation. These do not contradict the proposed structure. Upon treatment with aqueous sodium hydroxide, compound (**5**) is known to rearrange into 1-hydroxyphenalene-1-carboxylic acid[1] and cyclohepta[*de*]-naphthalene-1,4-dione is known to rearrange into 3-(dimethoxymethyl)phenalenone when treated with sulphuric acid and methanol.[8] Both examples are rearrangements from a seven-membered ring to a six-membered ring, while in this case, interestingly, the rearrangement occurred from a seven-membered ring to a five-membered ring. We are currently investigating the mechanism.

Experimental

M.p.s were determined with a Mitamura air-bath apparatus and are not corrected. ^{1}H and ^{13}C N.m.r. spectra (tetramethylsilane as internal standard) were determined with a JEOL-PMX-60si and/or a JEOL-JNM-FX90Q spectrometers. I.r. spectra were determined with a JASCO A-2 instrument, electronic spectra (u.v. and vis.) with a Hitachi 340 spectrophotometer, and mass spectra with a JEOL-01SG-2 spectrometer. Unless otherwise stated the spectra were taken in the following solvents/media: u.v. and visible, $CHCl_3$; i.r., KBr; ^{1}H and ^{13}C n.m.r., $CDCl_3$. The cyclic voltammogram was recorded in the usual manner with a Yanagimoto polarographic analyser P-1100. The progress of most reactions was followed by t.l.c. using Kieselgel 60 G (Merck). Preparative column chromatography was carried out using Kieselgel 60 (Merck 70—230 mesh). Ether refers to diethyl ether.

Cyclic Voltammetry.—All measurements were performed at 27.0 ± 0.5 °C in dry dimethylformamide with 0.1M-tetrabutylammonium perchlorate as supporting electrolyte. Substrates were present at 0.1mM, and the reduction potentials were determined under a nitrogen atmosphere in a standard three-electrode cell equipped with a silver–silver chloride electrode as reference. Voltammograms were recorded at a scan rate of 100 mV s^{-1}.

Cyclohepta[de]*naphthalene-7,8-dione* (o-*Pleiadienequinone*) (**5**) and 8a-exo-*Acetoxy*-8-exo-*chloro*-8,8a-*dihydrocyclobut*[a]-*acenaphthylen*-7-(6bH)-*one* (**6**).—A mixture of dichlorocyclobutanone (**2**)[1] (7.89 g, 0.03 mol), silver acetate (20.02 g, 0.12 mol), and acetic acid (300 ml) was refluxed for 12 h with vigorous stirring in the dark. The reaction mixture was filtered and the filtrate poured into a large volume of water and extracted with dichloromethane; the extract was washed with water, dried ($MgSO_4$), and evaporated. The residue was chromatographed on a silica gel (700 g) column with benzene as eluant to give recovered dichlorocyclobutanone (**2**) (2.142 g, 27.1%). Subsequent elution with dichloromethane afforded the *acetoxychlorocyclobutanone* (**6**) (52 mg, 0.6%) as colourless needles, m.p. 169.5—170.0 °C (from hexane); *m/z* (30 eV) 223 ($M^{+\cdot}$ − CO − ^{35}Cl, 8%), 181 ($M^{+\cdot}$ − CO − ^{35}Cl − CH_2CO, 100), and 152 (acenaphthylene$^{+\cdot}$, 61) (Found: C, 67.3; H, 4.05;

Cl, 12.5. $C_{16}H_{11}ClO_3$ requires C, 67.03; H, 3.87; Cl, 12.36%); $\lambda_{max.}$ 287sh (log ε 3.85), 297.5 (3.92), 311sh (3.71), and 331sh nm (2.91); $\nu_{max.}$ 1 810, 1 752, and 1 207 cm^{-1}; δ 2.39 (3 H, s, CH_3), 4.48 (1 H, s, 8a-H), 4.83 (1 H, s, 6b-H), and 7.00—7.79 (6 H, m, ArH); and the quinone (**5**) (3.85 g, 61.8%) as yellow needles, m.p. 115—116 °C (from hexane).[1] Neither the use of more silver acetate nor a longer reaction time raised the yield of compound (**5**).

General Procedure for Reaction of Alcohols with the Quinone (**5**).—Although in the following, methanol is used, the method is generally applicable to other alcohols.

(*a*) A mixture of the quinone (**5**) (408 mg, 2 mmol), toluene-*p*-sulphonic acid monohydrate (30 mg, 0.16 mmol), and anhydrous methanol (150 ml) was refluxed for 8 h in a Soxhlet extractor containing molecular sieve 3A in a filter paper thimble. The contents were poured into water and extracted with benzene and the organic layer was washed with aqueous sodium hydrogen carbonate and water, dried ($MgSO_4$), and evaporated. The residue was chromatographed on a silica gel (60 g) column with dichloromethane to give the *acetal* (**7a**) (280 mg, 56.2%) as colourless needles, m.p. 113—114 °C (from hexane); and the methoxy quinone (**8a**) (17 mg, 3.6%).

(*b*) A mixture of the quinone (**5**) (2.00 g, 9.62 mmol), zinc chloride (140 mg, 1.02 mmol), and anhydrous methanol (200 ml) was refluxed in a manner similar to that described in experiment (**a**). After removal of the solvent, the residue was chromatographed on a silica gel (180 g) column with dichloromethane to give the acetal (**7a**) (250 mg, 10.2%), m.p. 112—114 °C, and a mixture of three methoxy quinones (**8a**), which was repeatedly chromatographed on a silica gel (330 g) column with benzene to give 1-, 3-, and 6-methoxy quinones, (**8a**$_1$), (**8a**$_2$), and (**8a**$_3$), successively; (**8a**$_1$) (120 mg, 5.2%), yellow needles, m.p. 155—156 °C (from hexane); (**8a**$_2$) (346 mg, 15.1%), yellow needles, m.p. 166—167 °C (from hexane); (**8a**$_3$) (164 mg, 7.2%), m.p. 116—117 °C (from hexane).

(*c*) A mixture of the quinone (**5**) (198 mg, 0.95 mmol), concentrated sulphuric acid (3 ml), iron(III) sulphate (800 mg, 2 mmol), and anhydrous methanol (50 ml) was refluxed. The reaction mixture was poured into aqueous sodium hydrogen carbonate and extracted with chloroform and the organic layer washed with water, dried ($MgSO_4$), and evaporated. The residue was chromatographed on a silica gel (60 g) column with dichloromethane as eluant to give the methoxy quinones (**8a**) (190 mg, 83.9%) as a mixture. The ratio of the isomers was determined by l.c. (detector, λ 254 nm) as (**8a**$_1$):(**8a**$_2$):(**8a**$_3$) = 24:50:26.

(*d*) Under conditions similar to those described in (*c*) above but using zinc chloride (30 mg) instead of concentrated sulphuric acid as catalyst, the methoxy quinone (**8a**) (202 mg, 80%) was obtained in the ratio of (**8a**$_1$):(**8a**$_2$):(**8a**$_3$) = 23:57:20 determined by l.c. (detector, λ 254 nm).

2,2-*Diethoxyacenaphthylen*-1(2H)-*one* (**12**).—A mixture of acenaphthenequinone (**10**) (379 mg, 2.07 mmol), toluene-*p*-sulphonic acid (30 mg) and ethanol (50 ml) was refluxed under the conditions of method (*a*) above for 5 h to give the title compound (**12**) (446 mg, 85.0%) as colourless crystals, m.p. 66—66.5 °C (from hexane), $\lambda_{max.}$ 316 (log ε 3.69) and 336 nm (3.67); $\nu_{max.}$ 1 723, 1 200, 1 090, and 1 064 cm^{-1}; δ 1.29 (6 H, t, *J* 7.6 Hz, $2CH_3$), 3.90 (4 H, m, $2CH_2$), and 7.38—8.00 (6 H, m, ArH).

2,2-*Dimethoxyacenaphthylen*-1(2H)-*one* (**13**).—A mixture of acenaphthenequinone (**10**) (183 mg, 1.01 mmol), iron(III) sulphate (800 mg, 2 mmol), and methanol (80 ml) was refluxed for 2 h under the conditions of method (*c*) above to give the title compound (**13**) (169 mg, 71.9%) as colourless crystals, m.p. 125—126 °C (from hexane); $\nu_{max.}$ 1 726, 1 200, 1 092, and 1 062 cm^{-1}; δ 3.63 (6 H, s, $2CH_3$) and 7.50—8.10 (6 H, m, ArH).

Trial Conversion of the o-*Methoxy quinone* (**8a**) *into the Hydroxy quinone* (**14**).—(*a*) A mixture of the methoxy quinone (**8a**$_2$) (100 mg, 0.42 mmol), hydrogen bromide (47%; 1 ml), and acetic acid (3 ml) was refluxed for 8 h. The reaction mixture was poured into aqueous sodium hydrogen carbonate and extracted with ether to give only carbonaceous materials.

(*b*) A mixture of the methoxy quinone (**8a**$_2$) (100 mg, 0.42 mmol), boron tribromide (105 mg, 0.42 mmol), and dichloromethane (0.5 ml) was stirred for 6 h at −70 °C after which the reaction temperature was raised to room temperature during 12 h. Upon work-up, the methoxy quinone (**8a**$_2$) (79 mg, 79%) was recovered.

1-, 3-, *and* 6-*Methoxy*-9,10-*dihydrocyclohepta*[de]*naphthalene*-7,8-*diones* (**15a**), (**15b**), *and* (**15c**).—(*a*) To a stirred solution of the methoxy quinone (**8a**) (100 mg, 0.42 mmol) and sodium iodide (132 mg, 0.85 mmol) in acetonitrile (2 ml) trimethylsilyl chloride (91 mg, 0.84 mmol) was added dropwise. The reaction mixture was stirred for 4 h, refluxed for 20 h, and poured into water and extracted with ether. The ethereal extracts were washed with aqueous sodium thiosulphate and water, dried (Na_2SO_4), and evaporated. The residue was chromatographed on a silica gel (75 g) column with dichloromethane as eluant to afford the *title compound* (**15**) (20 mg, 19.8%), which was further separated into the three isomeric compounds in the following order using a Lobar column size A (Merck): (**15a**) (6.5 mg, 6.5%), yellow needles, m.p. 105.0—105.5 °C (from hexane); *m/z* (75 eV) 240 ($M^{+\cdot}$, 42%), 209 ($M^{+\cdot}$ − OCH_3, 36.5), 210 ($M^{+\cdot}$ − CH_2O, 7.6), 181 ($M^{+\cdot}$ − OCH_3 − CO, 6.7), and 150 ($C_{12}H_6^{+\cdot}$, 100); $\lambda_{max.}$ 256—259 (log ε 4.42) and 344—347 nm (3.86); $\nu_{max.}$($CHCl_3$) 1 718, 1 693, 1 279, and 1 098 cm^{-1}; δ (90 MHz) 2.99 (2 H, m, 9-CH_2), 3.45 (2 H, m, 10-CH_2), 4.03 (3 H, s, CH_3), 7.49 (1 H, dd, *J* 8 Hz, *J* 2 Hz, 5-H), 7.60 (1 H, t, *J* 8 Hz, 4-H), 8.20 (2 H, s, 2-H and 3-H), and 8.74 (1 H, dd, *J* 8.1 Hz, 6-H); (**15b**) (9.4 mg, 9.4%), pale yellow needles, m.p. 113—114 °C (from hexane); *m/z* (75 eV) 240 ($M^{+\cdot}$, 78), 210 ($M^{+\cdot}$ − CH_2O, 14), 209 ($M^{+\cdot}$ − OCH_3, 85), 181 ($M^{+\cdot}$ − OCH_3 − CO, 65), 182 ($M^{+\cdot}$ − CH_2O − CO, 11), and 150 ($C_{12}H_6^{+\cdot}$, 100); $\lambda_{max.}$ 271—278.5 (log ε 3.34), 280sh (3.36), 284sh (3.39), 289sh (3.41), 323 (4.01), and 339 nm (3.98); $\nu_{max.}$($CHCl_3$) 1 711, 1 687,1 282, 1 267, and 1 111 cm^{-1}; δ 2.98 (2 H, m, 9-CH_2), 3.46 (2 H, m, 10-CH_2), 4.01 (3 H, s, CH_3), 7.47 (1 H, d, *J* 8 Hz, 1-H), 7.71 (1 H, t, *J* 8 Hz, 5-H), 8.19 (1 H, d, *J* 8 Hz, 2-H), 8.25 (1 H, dd, *J* 8 Hz, 2 Hz, 4-H), and 9.23 (1 H, dd, *J* 1 Hz, 6-H); (**15c**) (4 mg, 4%), colourless needles, m.p. 129.5—130.0 °C (from hexane); *m/z* (75 eV) 240 ($M^{+\cdot}$, 97%), 210 ($M^{+\cdot}$ − CH_2O, 9), 209 ($M^{+\cdot}$ − OCH_3, 54), 182 ($M^{+\cdot}$ − CH_2 − CO, 17), 181 ($M^{+\cdot}$ − OCH_3 − CO, 100), and 150 ($C_{12}H_6^{+\cdot}$, 68); $\lambda_{max.}$ 247 (log ε 4.39), 313 (3.65), and 344—348 nm (3.54); $\nu_{max.}$($CHCl_3$) 1 705, 1 705sh, 1 263, 1253, and 1 112 cm^{-1}; δ 2.99 (2 H, t, *J* 6.3 Hz, 9-H), 3.06 (2 H, t, *J* 6.3 Hz, 10-H), 3.95 (3 H, s, CH_3), 7.15 (1 H, q, *J* 9.3 Hz, 7.3 Hz, 2-H), 7.24 (2 H, s, 4- and 5-H), 7.93 (1 H, d, *J* 7.3 Hz, 1-H), and 8.71 (1 H, d, *J* 9.3 Hz, 3-H).

(*b*) Catalytic hydrogenation of the methoxy quinone (**8a**) (500 mg, 2.1 mmol) in methanol (80 ml) in the presence of 5% Pd/C (100 mg) was carried out. After the mixture had absorbed 46 ml of hydrogen gas (49 ml, calc.), the catalyst was filtered off and the methanol was evaporated. The residue was chromatographed on a silica gel column with dichloromethane as eluant to give the *title compound* (**15**) (78 mg, 15.5%) and a small amount of recovered methoxyquinone (**8a**).

Miscellaneous Reactions of the 3-*Methoxy quinone* (**8a**$_2$).—(*a*) A mixture of 3-methoxy quinone (**8a**$_2$) (100 mg, 0.42 mmol), toluene-*p*-sulphonic acid (15 mg), and absolute methanol (50

ml) was refluxed for 8 h to give upon work-up recovered (**8a**$_2$) (96 mg, 96%).

(*b*) A mixture of the 3-methoxy quinone (**8a**$_2$) (100 mg, 0.42 mmol), *o*-phenylenediamine (45 mg, 0.42 mmol), and methanol (15 ml) was refluxed for 2 h. After removal of the solvent column-chromatographic purification of the residue with dichloromethane as eluant gave recovery of the quinone (**8a**$_2$) (95 mg, 95%).

9a-*Hydroxy*-6b,9a-*dihydroacenaphtho*[1,2-c]*furan*-9(7H)-*one* (**17**).—A mixture of *o*-pleiadienequinone (**5**) (200 mg, 0.96 mmol), iron(III) sulphate (800 mg, 2 mmol), concentrated sulphuric acid (3 ml), dioxane (30 ml), and water (15 ml) was refluxed for 2 h. The reaction mixture was poured into aqueous sodium hydrogen carbonate and extracted with chloroform. The organic layer was washed with water, dried ($MgSO_4$), and evaporated and the residue chromatographed on a silica gel column with a mixture of dichloromethane and ethyl acetate (1:3) as eluant to give the *title compound* (**17**) (66 mg, 30.4%) as colourless crystals, m.p. 158—159 °C (from hexane–benzene) (Found: C, 74.45; H, 4.55. $C_{14}H_{10}O_3$ requires C, 74.33; H, 4.46%); *m*/*z* (75 eV) 226 ($M^{+\cdot}$, 4%), 198 ($M^{+\cdot}$ − CO, 36), 168 (28), 155 (12), 154 (26), 153 (100), 152 ($C_{12}H_8^{+\cdot}$, 30), 151 (10), and 149 (11); $\lambda_{max.}$ 292 nm (log ε 4.10); $\nu_{max.}$($CHCl_3$) 3 550, 3 010, 1 766, and 1 270 cm^{-1}; δ 2.40 (1 H, dd, *J* 18 and 1.5 Hz, 7-*exo*-H), 3.50 (1 H, dd, *J* 18 and 8 Hz, 7-*endo*-H), 4.35 (1 H, br s, exchangeable with D_2O, 9a-OH), 5.60 (1 H, dd, *J* 8 and 1.5 Hz, 6b-H), and 7.13—7.90 (6 H, m, ArH).

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Received 3rd *January* 1986; *Paper* 6/017