Synthesis and Properties of Cyclohepta[*de*]naphthalene-7,8-dione, *o*-Pleiadienequinone

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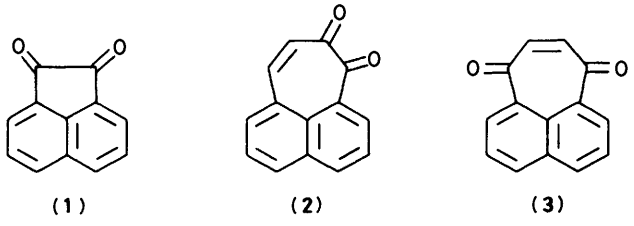
Cyclohepta[*de*]naphthalene-7,8-dione, *o*-pleiadienequinone (**2**), was synthesized by hydrolysis of the acenaphthylene–dichloroketene adduct (**5**); chloro(hydroxy)ketone (**6**) was the precursor. Compound (**2**) afforded the triacetate (**16**) by a Thiele–Winter-type reaction and a phenalene compound (**19**) by alkaline hydrolysis. Spectral data suggest that the dione (**2**) has contributions from such canonical forms as 2,3-(**2a**) and/or 4,5-benzotropolonate (**2b**) structures. The polarographic $E_{\frac{1}{2}}$ value of the dione (**2**) is −0.23 V at pH 5.28 which is between that of 1,2-naphthoquinone and anthraquinone.

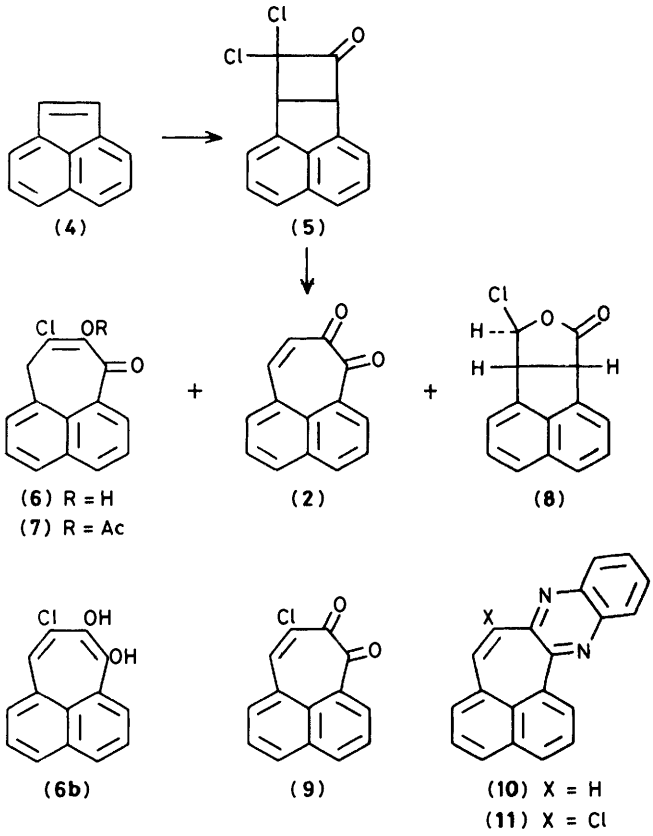
Non-benzenoid quinones can be classified into three categories; diones with peripheral conjugation, diones without peripheral but with cross-conjugation, and fulvalenediones.† Although many non-benzenoid quinones belonging to the first category ([4*n* + 2] or [4*n*]annulenediones) have been reported, not many quinones belonging to the second or third categories are known. Belonging to the first category‡ are cyclobutene-1,2-dione,[1] cyclo-octadecatetraenetetrayne-1,6- and -1,10-dione,[2] 1,6:8,13-propanediylidene[14]annulene-2,3- and -2,5-dione,[3] 2,5,7-cyclo-octa-2,5,7-triene-1,4-[4] and -1,2-dione,[5] 2,3,6,7-dibenzobicyclo[6.2.0]deca-2,6,8-trien-4-yne-9,10-dione and 2,3:6,7-dibenzobicyclo[6.2.0]deca-2,4,6,8(1)-tetraene-9,10-dione,[6] 8,13-dimethyl-2,9,11-trisdehydro[16]annulene-1,4-dione,[7] 9-methoxyheptalene-1,8- and -3,8-dione,[8] azulene-1,2-diones,[9] azulene-1,5- and -1,7-dione,[10] and acepleiadylene-5,6- and 5,8-dione;[11] belonging to the second are acenaphthenequinone (**1**) and cyclohepta[*de*]naphthalene-7,8- (**2**)[12] and -7,10-dione (**3**);[13] belonging to the third are sesquifulvalene-7,10-dione,[14] heptatriafulvalene-3,4-,[15] and -1,2-dione,[16] and heptafulvalene-3,4-dione.[17]



In the present paper we report the synthesis, some reactions, and physico-chemical properties of the title compound, *o*-pleiadienequinone (**2**),[12] which belongs to the second category and can be regarded as a higher analogue of acenaphthenequinone (**1**). Although dione (**1**) has been known for a long time and was studied by Trost to compare it with pyracyloquinone,[18] comparison of the characteristics of dione (**2**) with those of dione (**1**) reveals the essential features of these systems. The isomer of compound (**2**), cyclohepta[*de*]naphthalene-7,10-dione (**3**) was recently reported.[13]

In the course of our study of the reaction mechanism of Stevens' tropolone synthesis,[19,20a] we anticipated that hydrolysis of the dichloroketene–acenaphthylene adduct (**5**) would afford dione (**2**) if Bartlett's explanation of the formation of seven-membered rings was correct.[19,21]

† These quinones can be considered as being related to the corresponding parent hydrocarbons in the same way that benzoquinone is related to benzene.



Scheme 1.

A variety of different temperatures has been used for the addition of the apparently unstable compound dichloroketene to olefins using dichloroacetyl chloride–triethylamine (from −10 °C for 5 min to refluxing in toluene for 24 h).[19,20] The addition reaction of dichloroketene to acenaphthylene (**4**) was repeated more than fifty times under different conditions to optimize the reaction conditions. The yield was raised to 10% by the simultaneous addition of dichloroacetyl chloride and

‡ Cyclohepta-3,6-diene-1,2,5-trione (S. Ito, Y. Shoji, H. Takeshita, M. Hirama, and K. Takahashi, *Tetrahedron Lett.*, 1975, 1075) and cyclohepta-4,6-diene-1,2,3-trione (M. Hirama and S. Ito, *Tetrahedron Lett.*, 1975, 1071) can also be classified as belonging to the first category since their reduced forms, hydroxytropolones, are aromatic.

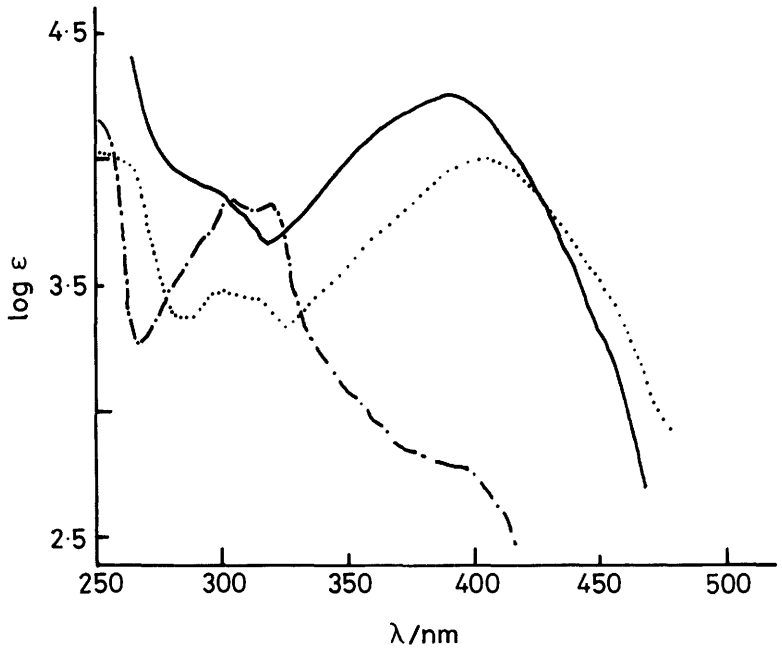
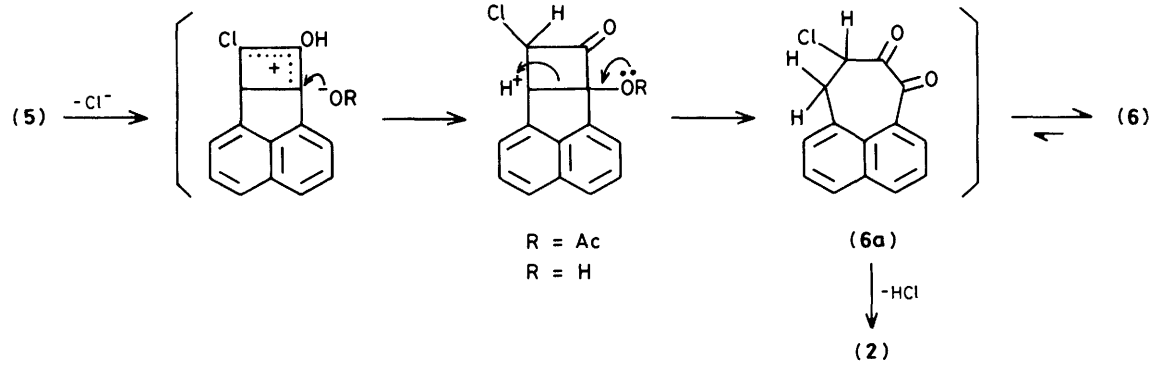


Figure. Electronic spectra of diones: ——— (**2**); ····· (**9**); —·—·—(**1**) (solutions in chloroform)



Scheme 2.

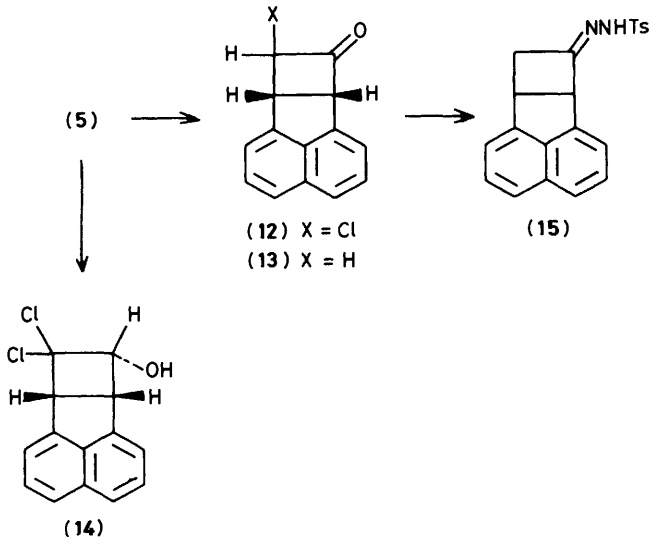
triethylamine at constant equimolar rates during a 12 h period to a stirred solution of acenaphthylene (**4**) in dry hexane at room temperature. The hydrolysis of the adduct (**5**), either with sodium acetate in hot acetic acid or with triethylamine in acetic acid at room temperature, afforded three products; hydroxyketone (**6**) (9% yield), *o*-pleiadienequinone (**2**) (52% yield), and γ-lactone (**8**) (2% yield) (Scheme 1).

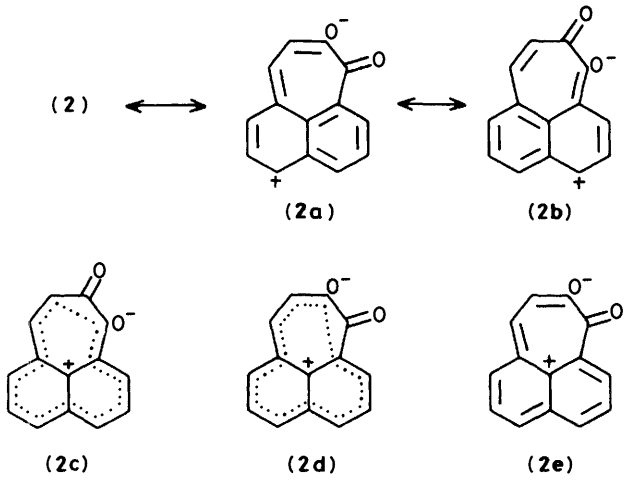
Compound (**2**) is very stable after purification and was obtained in 90% yield from hydroxyketone (**6**) under similar reaction conditions and therefore compound (**6**) is the precursor of dione (**2**). By treating compound (**6**) with acetic anhydride, the acetate (**7**) was obtained. However, in chloroform solution or in the solid state compound (**6**) does not have the pleiadiene diol form (**6b**) (no OH group signal was observed in the i.r. and ^{1}H n.m.r. spectra). This suggests that in the diol (**6b**) the resonance energy acquired by assuming the conjugated pleiadiene structure is smaller than the strain energy caused by the seven-membered skeleton. The hydrolysis of the adduct (**5**) with silver acetate in acetic acid afforded exclusive formation of dione (**2**), though the yield was rather poor (37%). Oxidation of compound (**6**) with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in dry benzene afforded 9-chloropleiadiene-7,8-dione (**9**) in 39% yield. Compound (**2**) has an i.r. absorption peak at 1 661 cm^{-1} for the carbonyl groups and two doublets at δ 6.56 (9-H) and 7.59 (10-H), *J* 13.1 Hz, in the ^{1}H n.m.r. spectrum. These facts suggest that the dione (**2**) has an olefinic linkage on a seven-membered skeleton. The mass spectrum of the dione (**2**) showed a weak (*M* + 2) peak, characteristic for a quinone,[18] and suggests that it is decomposed through phenalenone and acenaphthylene successively. The u.v. spectra of compounds (**2**) and (**9**) are shown in the Figure together with that of compound (**1**). On refluxing with *o*-phenylenediamine in methanol, diones (**2**) and (**9**) afforded the corresponding quinoxaline derivatives (**10**) and (**11**) respectively. These are the first known heterocyclic compounds containing the pleiadiene skeleton, confirming the α-diketone structures. The reaction sequence of the formation of dione (**2**) is shown in Scheme 2. Dechlorination of the dichlorocyclobutanone (**5**) would generate a cation, which on attack by an acetate ion would form the acetate; this would then hydrolyse to form the chlorodiketone (**6a**), from which elimination of hydrogen chloride would yield the quinone (**2**). This reaction could be explained partly by applying Bartlett's mechanism[21] for Stevens' tropolone synthesis (hydrolysis of the dichloroketene–cyclopentadiene adduct) but not by Kitahara's.[19,21,22]

Dichloroketone (**5**) was reduced with zinc in acetic acid to the

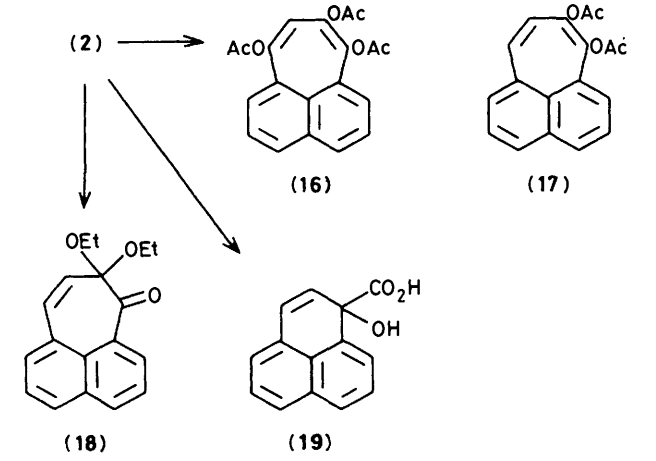
Table. ^{1}H N.m.r. parameters of the dione (**2**) (δ values, internal standard $SiMe_4$), with J values in Hz

	1-H	2-H	3-H	4-H	5-H	6-H	9-H	10-H
δ ($CDCl_3$)	7.84	7.60	8.09	8.23	7.73	8.43	6.56	7.59
	$J_{1,2}$ 7.6, $J_{1,3}$ 1.5, $J_{1,10}$ 1.1, $J_{2,3}$ 7.8, $J_{4,5}$ 7.5, $J_{4,6}$ 1.2, $J_{5,6}$ 7.5, $J_{9,10}$ 12.8							
δ (CF_3CO_2H)	8.11	7.76	8.31	8.45	7.86	8.75	6.91	8.03
	$J_{1,2}$ 7.5, $J_{1,3}$ 1.0, $J_{2,3}$ 7.5, $J_{4,5}$ 8.0, $J_{4,6}$ 1.2, $J_{5,6}$ 8.0, $J_{9,10}$ 12.5							
δ ($CDCl_3$) − δ (CF_3CO_2H)	−0.27	−0.16	−0.22	−0.22	−0.13	−0.32	−0.35	−0.44





Scheme 4.



Scheme 3.

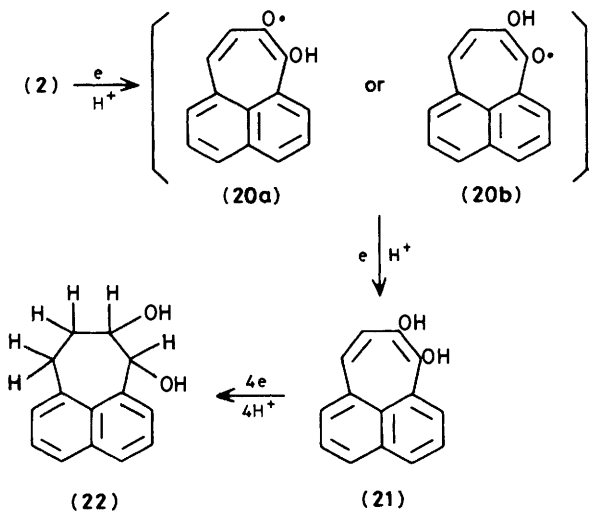
monochloroketone (**12**) (the configuration of 8-H was not clear), and further to the monoketone (**13**) in high yield. With sodium borohydride compound (**5**) was reduced exclusively to the α-hydroxyketone (**14**). The hydroxy group must therefore have the *syn*-configuration. From the cyclobutanone (**13**), the tosylhydrazone (**15**) was obtained quantitatively. It was decomposed in the presence of sodium methoxide at 160 °C for 2 h in anhydrous bis(2-methoxyethyl) ether but gave only unidentified products, contrary to the expectation that cyclohepta[*de*]naphthalene (pleiadiene) might be produced. Perhaps the conditions used were too severe.

Compound (**2**) was treated with acetic anhydride in the presence of a catalytic amount of mineral acid (conditions of the Thiele–Winter reaction) to give the expected triacetate (**16**). However, using acetic anhydride from old stock gave a mixture of compound (**16**) and the diacetate (**17**), while a mixture of acetic anhydride and acetic acid afforded only the triacetate (**16**). Treatment of compound (**2**) with absolute ethanol and acid gave the diethyl acetal (**18**), and with 1 M sodium hydroxide a rearranged product, 1-hydroxyphenalene-1-carboxylic acid (**19**), was obtained (Scheme 3).

The Diels–Alder reaction of compound (**2**) with cyclopentadiene (reflux for 4 h at 80 °C in benzene), cycloheptatriene (reflux for 46 h at 118 °C), furan (for 114 h at room temperature), or anthracene (reflux for 63 h at 150 °C in tetralin) did not yield any adducts.

By comparing the ^{1}H n.m.r. chemical shift differences (△δ 0.85—1.40 p.p.m.) of the aromatic protons between pleiadiene ($CDCl_3$)[23] and compound (**2**) with those (0.45—0.56 p.p.m.) between acenaphthylene (**4**) ([$^2H_6$]DMSO) and dione (**1**) ([$^2H_6$]DMSO), it was established that the ene-dione group attached to the *peri* position of naphthalene ring is significantly more electron-attracting than the dione group. As shown in the Table the proton chemical-shift differences of the naphthalene ring protons between acidic and neutral conditions are appreciably larger for compound (**2**) [δ($CDCl_3$) − δ(CF_3CO_2H) = −0.13 to −0.32 p.p.m.] than those for compound (**1**) [δ([$^2H_6$]DMSO) − δ(CF_3CO_2H) = −0.05 to + 0.1 p.p.m.],[18] indicating that in trifluoroacetic acid solution the electron density on the naphthalene ring is more decreased for compound (**2**) than for compound (**1**). These facts suggest that compound (**2**) has some contribution from canonical structures like 2,3- (**2a**) and/or 4,5-benzotropolonate (**2b**) ions, since 1,2-(**2c**) or 1,10-homophenalenium (**2d**), or [12]annulenone (**2e**) structures can be discounted (Scheme 4).

The electrochemical reduction of compound (**2**) was examined by polarography. The half-wave reduction potential was obtained in aqueous ethanol at pH 5.28; E_1 = −0.23 V (one electron), E_2 = −0.40 V (one electron), and E_3 = −1.14 V (four electrons). The E_1 value of compound (**2**) is much higher than that of dione (**1**) (−0.74 V)[24] and is between that of 1,2-



Scheme 5.

naphthoquinone (−0.06 V) [25] and 9,10-anthraquinone (−0.50 V).[26,*] As shown in Scheme 5, the electrochemical reduction of compound (**2**) could proceed through an intermediary generation of semiquinone radical (**20a**) or (**20b**) and hydroquinone (**21**) successively, and finally form the diol (**22**).

The ^{13}C n.m.r. data for the carbonyl carbons of compound (**2**), δ_C 191.6 and 192.6 p.p.m. show the intermediate value of ordinary quinones [27] and α-dicarbonyl carbons or conjugated carbonyl carbons.

All these data indicate that compound (**2**) has considerable quinonoid character.

Experimental

M.p.s were determined with a Mitamura air-bath apparatus and are not corrected. ^1H N.m.r. spectra (tetramethylsilane as internal standard) were determined with a Varian A-60 D spectrometer. I.r. spectra were determined with a JASCO A-2 instrument, electronic spectra (u.v.) with a Hitachi 340 spectrophotometer, and mass spectra with a JEOL-01SG-2 spectrometer. The spectra were taken in the following solvents/media unless otherwise stated: u.v., $CHCl_3$; i.r., KBr; ^1H n.m.r., $CDCl_3$. The DC polarogram was taken with a Yanagimoto P-8 polarograph. Preparative column chromatography was carried out using Kieselgel 60 (Merck 70—230 mesh). Ether refers to diethyl ether.

8,8-*Dichloro*-8,8a-*dihydrocyclobut*[a]*acenaphthylen*-7(6bH)-*one* (**5**).—To a stirred solution of acenaphthylene (**4**) (76 g, 0.500 mol) in dry hexane (500 ml) were added a solution of triethylamine (54.54 g, 0.54 mol) in dry hexane (400 ml) and a solution of dichloroacetyl chloride (73.50 g, 0.500 mol) in dry hexane (500 ml) during 9 h at room temperature. Approximately equimolar amounts of the two reagents were always maintained in the reaction mixture. After the mixture had been stirred for a further 17 h the resulting triethylamine salts were removed by filtration and the filtrate was washed in turn with water, 5% aqueous sodium carbonate, and water and dried ($MgSO_4$). The salts were dissolved in water and on extraction with ether gave black products. These were extracted with hot hexane. After removal of the hexane from both parts by rotary-evaporation, the residues were combined and chromatographed in hexane on a silica gel (500 g) column to give recovered acenaphthylene (**4**) (66.1 g, including some polymeric and halogenated acenaphthylene compounds). Subsequent elution with hexane–benzene mixtures, with the benzene concentration increasing from zero to 50%, afforded the *dichlorocyclobutanone* (**5**) (11.08 g, 9.69%) as cubes, m.p. 115—116 °C (from benzene–hexane) (Found: C, 63.95; H, 2.9. $C_{14}H_8Cl_2O$ requires C, 63.98; H, 3.07%); $\lambda_{max.}$(MeOH) 287 nm (log ε 4.18); $\nu_{max.}$ 1 796 cm^{-1}; δ 5.46 (1 H, d, *J* 7.0 Hz, 6b-H), 4.93 (1 H, d, *J* 7.0 Hz, 8a-H), and 6.67—8.33 (6 H, m, ArH).

8-*Chloro*-9-*hydroxycyclohepta*[de]*naphthalen*-10(7H)-*one* (**6**), *Cyclohepta*[de]*naphthalene*-7,8-*dione* (**2**), *and* 7-exo-*Chloro*-6b,9a-*dihydroacenaphtho*[1,2-c]*furan*-9(7H)-*one* (**8**).—(*a*) A sample of the finely powdered dichlorocyclobutanone (**5**) (1.000 g, 3.80 mmol) was treated with a well stirred mixture of triethylamine (10 g), glacial acetic acid (10 g), and water (2 ml) for 1 h at room temperature. The reaction mixture was poured into water (200 ml) and extracted with methylene dichloride (3 × 100 ml), and the extract was washed with water and dried ($MgSO_4$). After removal of the solvent, the residue was chromatographed on a silica gel (60 g) column with methylene dichloride as eluant to afford compound (**5**) (28 mg, 2.8% recovery) as pale brown needles, m.p. 104—111 °C; the γ-*lactone* (**8**) (10 mg, 1.1%) as pale yellow, subliming needles, m.p. 193.5—195.0 °C (from benzene); *m/z* (75 eV) 246 (M^+ + 2, 3.5%), 244 (M^+, 10), 165 (100), and 152 (32) (Found: C, 68.6; H, 3.75. $C_{14}H_9ClO_2$ requires C, 68.72; H, 3.71%); $\nu_{max.}$ 1 770 cm^{-1}; δ 4.87 (1 H, oct, *J* 10.5, 6.0, and 1.0 Hz, 6b-H), 5.33 (1 H, d, *J* 10.5 Hz, 9a-H), 6.43 (1 H, d, *J* 6.0 Hz, 7-H), and 7.5—8.2 (6 H, m, ArH); the *hydroxyketone* (**6**) (83 mg, 9.3%) as easily sublimed needles, m.p. 153.0—154.0 °C (from benzene–hexane) (Found: C, 68.6; H, 3.9. $C_{14}H_9ClO_2$ requires C, 68.72; H, 3.71%); $\lambda_{max.}$ 285—315 (log ε 3.83), 323 (3.84), 340 (3.85), and 360 nm (3.83); $\nu_{max.}$($CHCl_3$) 3 475 (OH), 1 659 (C=O), and 1 579 cm^{-1} (C=C); δ (100 MHz) 3.26 (1 H, d, *J* 13.1 Hz, 7-H), 3.30 (1 H, d, *J* 13.1 Hz, 7-H), 4.41 (1 H, s, OH, exchangeable with deuterium), and 7.1—8.5 (6 H, m, ArH); and the dione (**2**) (381 mg, 48.2%) as yellow, subliming needles, m.p. 115.0—116.0 °C (from benzene–hexane); *m/z* (75 eV) 208 (M^+, 3%), 180 (M^+ − CO, 75), 152 (M^+ − 2CO, 100), and 126 (M^+ − 2CO − C_2H_2, 10); *m/z* (15 eV) 210 (M^+ + 2, 1%), 209 (M^+ + 1, 2), 180 (M^+, 100), and 152 (M^+ − 2CO, 11) (Found: C, 80.8; H, 3.9. Calc. for $C_{14}H_8O_2$: C, 80.76; H, 3.87%); $\nu_{max.}$($CHCl_3$) 1 661 and 1 562 cm^{-1}; δ_C ($CDCl_3$) 124.3, 126.2, 126.8, 130.8 (q), 132.5 (q), 133.7 (q), 134.9, 135.5, 136.8, and 139.1 (q), 146.4, 191.6 (C=O), and 192.6 p.p.m. (C=O) (the signal for one tertiary carbon is hidden).

(*b*) The dichlorocyclobutanone (**5**) (3.437 g, 13.06 mmol) was hydrolysed with a mixture of sodium hydroxide (12 g), acetic acid (75 ml), and water (75 ml) at 85 °C for 2 h. The reaction mixture was treated as described above to yield compound (**5**) (105 mg, 3.1% recovery), the hydroxyketone (**6**) (293 mg, 9.1%), and the dione (**2**) (1.411 g, 51.5%).

(*c*) A mixture of the dichlorocyclobutanone (**5**) (263 mg, 1 mmol), silver acetate (368 mg, 2.2 mmol), and acetic acid (10 ml) was refluxed for 6 h at 130 °C in the dark. The usual work-up gave compound (**5**) (69 mg, 26.2% recovery) and the dione (**2**) (78 mg, 37.4%) but no hydroxyketone (**6**).

9-*Acetoxy*-8-*chlorocyclohepta*[de]*naphthalen*-10(7H)-*one* (**7**).—A mixture of the hydroxyketone (**6**) (250 mg, 1.02 mmol) and acetic anhydride (3 ml) was refluxed for 6 h to give the *acetate* (**7**) (179 mg, 61.2%) as pale brown, subliming plates, m.p. 191.0—192.0 °C (from methanol) (Found: C, 66.8; H, 3.8. $C_{16}H_{11}ClO_3$ requires C, 67.01; H, 3.84%); $\nu_{max.}$ 1 773 and 1 658 cm^{-1}; δ 2.30 (3 H, s, $COCH_3$), 3.29 (1 H, d, *J* 9.9 Hz, 7-H), 3.37 (1 H, d, *J* 9.9 Hz, 7-H), and 7.28—8.51 (6 H, m, ArH).

* The data were taken from results obtained under similar conditions of measurement to ours: a more rigorous comparison will be reported elsewhere.

9-*Chlorocyclohepta*[de]*naphthalene*-7,8-*dione* (**9**).—A mixture of the hydroxyketone (**6**) (90 mg, 0.368 mmol), DDQ (174 mg, 0.766 mmol), and dry benzene (15 ml) was refluxed for 24 h. The reaction mixture was chromatographed on a silica gel column with methylene dichloride as eluant to give the *chloroquinone* (**9**) (35 mg, 39.2%) as yellow needles, m.p. 164.0 °C (from benzene–hexane) (Found: C, 69.1; H, 2.7. $C_{14}H_7ClO_2$ requires C, 69.29; H, 2.86%); $\lambda_{max.}$ 300 (log ε 3.49), 315 (3.46), 360 sh (3.71), and 405 nm (4.00); $\nu_{max.}$ 1 662 (α-chloro C=O), 1 652 (C=O), and 1 560 cm^{-1}; δ 8.10 (1 H, s, 10-H) and 7.55—8.59 (6 H, m, ArH).

Hydrolysis of Compound (**6**) *to the Dione* (**2**).—(*a*) The hydroxyketone (**6**) (100 mg, 0.4 mmol) was hydrolysed with a mixture of triethylamine (3 g), glacial acetic acid (3 g), and water (0.3 g) for 1 h at room temperature to give the dione (**2**) (72 mg, 84.5%).

(*b*) Compound (**6**) (55 mg, 0.22 mmol) was hydrolysed with a mixture of acetic acid (5 ml), sodium hydroxide (0.8 g), and water (0.5 ml) at 85 °C for 40 min to give the dione (**2**) (41 mg, 88.6%).

Naphtho[1′,8′:3,4,5]*cyclohepta*[1,2-b]*quinoxaline* (**10**).—A mixture of the dione (**2**) (312 mg, 1.5 mmol), *o*-phenylenediamine (167 mg, 1.5 mmol), and methanol (20 ml) was refluxed for 2 h to give the *title compound* (**10**) (412 mg, 97.8%) as orange-yellow needles, m.p. 127.5—128.5 °C (from methanol) (Found: C, 86.0; H, 4.2; N, 9.9. $C_{20}H_{12}N_2$ requires C, 85.69; H, 4.32; N, 9.99%); $\nu_{max.}$ 1 653br (m), 1 602 (w), 1 559 (w), 1 513 (w), 1 483 (m), 1 398 (w), 1 373 (m), 1 059 (w), 1 044 (w), 843 (s), 768 (m), 750br (s), 615 (m), and 494 cm^{-1} (w); $\lambda_{max.}$(MeOH) 260 (log ε 4.69), 314 (4.41), and 428 nm (4.61); δ 6.65 (1 H, d, *J*, 12.7 Hz, 7-H), 6.82 (1 H, d, *J* 12.7 Hz, 8-H), 7.08—8.10 (9 H, m, ArH), and 8.55 (1 H, dd, *J* 7.4 and 1.7 Hz, 1-H).

8-*Chloronaphtho*[1′,8′:3,4,5]*cyclohepta*[1,2-b]*quinoxaline* (**11**).—A mixture of the 9-chlorodione (**9**) (200 mg, 0.825 mmol), *o*-phenylenediamine (76.3 mg, 0.825 mmol), and methanol (30 ml) was refluxed for 2 h to give the *title compound* (**11**) (117 mg, 45%) as long yellow needles, m.p. 147.0—148.0 °C (from methanol) (Found: C, 76.3; H, 3.4; N, 8.8. $C_{20}H_{11}ClN_2$ requires C, 76.31; H, 3.52; N, 8.90%); $\lambda_{max.}$(MeOH) 213 (log ε 4.69), 238 (4.74), 250 (4.69), 262 (4.70), 316 (4.10), 434—442 nm (4.30); $\nu_{max.}$ 1 616 (w), 1 582 (w), 1 555 (w), 1 343 (m), 1 203 (m), 1 143 (m), 1 071 (m), 915 (m), 903 (s), 885 (m), 877 (m), 818 (m), 801 (m), 773 (s), 761 (s), 603 (m), and 520 cm^{-1} (m); δ 7.25—8.33 (10 H, m) and 8.50 (1 H, dd, *J* 7.0 and 1.8 Hz, 1-H).

8-*Chloro*-8,8a-*dihydrocyclobut*[a]*acenaphthylen*-7(6bH)-*one* (**12**) *and* 8,8a-*Dihydrocyclobut*[a]*acenaphthylen*-7(6bH)-*one* (**13**).—(*a*) To a vigorously stirred solution of the dichloroketone (**5**) (7.00 g, 26.6 mmol) in glacial acetic acid (130 ml) at room temperature was added dropwise a suspension of zinc dust (10.436 g, 0.160 g-atom) in glacial acetic acid (35 ml) during 30 min. After the addition was complete, the temperature was raised to and maintained at 75 °C for 3.5 h. To the cooled reaction mixture was added ether (200 ml) and the zinc residues were filtered. The ethereal layer was washed with saturated aqueous sodium carbonate and dried ($MgSO_4$). The solvent was removed on a rotary evaporator and the title compounds (**12**) (3.734 g, 61.4%) and (**13**) (544 mg, 10.5%) were isolated by recrystallization: (**12**) *needles*, m.p. 154.0—155.0 °C (from hexane–benzene) (Found: C, 73.3; H, 4.1. $C_{14}H_9ClO$ requires C, 73.53; H, 3.97%); $\nu_{max.}$ 1 780 cm^{-1} (C=O); δ 4.61—4.88 (1 H, m, 8-H), 5.13—5.47 (2 H, m, 6b- and 8a-H), and 7.37—7.93 (6 H, m, ArH); (**13**), plates, m.p. 74.0—75.0 °C (from hexane) (lit.,[13] 79.0—80.0 °C) (Found: C, 86.7; H, 5.5. Calc. for $C_{14}H_{10}O$: C, 86.57; H, 5.19%); 1 777 cm^{-1} (C=O); δ 2.64—3.06 (1 H, m, *endo*-8-H), 3.42—3.93 (1 H, m, *exo*-8-H), 4.13—4.46 (1 H, m, 8a-H), 5.15—5.36 (1 H, m, 6b-H), and 7.38—7.83 (6 H, m, ArH). These n.m.r. assignments were based on those of dihydrocyclobut[*a*]acenaphthylene.[28]

(*b*) To a vigorously stirred suspension of zinc dust (4.96 g, 19 mg-atom) in glacial acetic acid (20 ml) at 118 °C was added dropwise a solution of the dichloroketone (**5**) (2.000 g, 7.6 mmol) in glacial acetic acid (140 ml) during 60 min and the mixture was stirred for a further 85 min. Work-up in similar manner as above afforded only the cyclobutanone (**13**) (1.014 g, 68.7%) as needles, m.p. 74.0—75.0 °C.

7,7-*Dichloro*-8-endo-*hydroxy*-6b,7,8,8a-*tetrahydrocyclobut*[a]*acenaphthylene* (**14**).—To a well stirred suspension of the dichloroketone (**5**) (263 mg, 1 mmol) in ethanol (15 ml) was added sodium borohydride (19 mg, 0.5 mmol). The reaction mixture was stirred for 1 h at room temperature, quenched by acetone, and extracted with methylene dichloride, and the extract was washed with water and dried ($MgSO_4$). After the solvent had been removed the yellowish residue was chromatographed on a silica gel column with methylene dichloride as eluant to give the *title compound* (**14**) (210 mg, 79.2%) as pale yellow needles, m.p. 92—94 °C (from benzene) (Found: C, 63.5; H, 3.9. $C_{14}H_{10}Cl_2O$ requires C, 63.42; H, 3.80%); $\nu_{max.}$ 3 650—3 200 (OH) and 1 125 cm^{-1} (C–O); δ 4.26—5.21 (4 H, m, one hydrogen is exchangeable with deuterium) and 6.95—7.35 (6 H, m, ArH).

8,8a-*Dihydrocyclobut*[a]*acenaphthylen*-7(6bH)-*one* p-*Tolylsulphonylhydrazone* (**15**).—To a solution of the cyclobutanone (**13**) (750 mg, 3.86 mmol) in methanol (6 ml) was added a solution of toluene-*p*-sulphonohydrazide (717 mg, 3.85 mmol) in methanol (6 ml) and conc. sulphuric acid (2 drops) and the mixture was left overnight. The almost pure *tosylhydrazone* (**15**) (1.260 g, 90.0%) was obtained as needles, m.p. 199.0—200.0 °C (decomp.) (from methanol) (Found: C, 69.5; H, 5.1; N, 7.5. $C_{21}H_{18}N_2O_2S$ requires C, 69.59; H, 5.01; N, 7.73%); $\nu_{max.}$ 3 400 (NH), 1 162 and 1 334 cm^{-1} (S=O); δ ([$^2H_5$]pyridine–D_2O) 2.13 (3 H, s, CH_3), 2.63 (1 H, m, *endo*-8-H), 3.26 (1 H, m, 8a-H), 3.91 (1 H, m, *exo*-8-H), 4.94 (1 H, m, 6b-H), and 7.00—8.21 (10 H, m, ArH).

7,8,10-*Triacetoxycyclohepta*[de]*naphthalene* (**16**) *and* 7,8-*Diacetoxycyclohepta*[de]*naphthalene* (**17**).—(*a*) To a well stirred solution of the dione (**2**) (300 mg, 1.44 mmol) in acetic anhydride (10 ml) was added conc. sulphuric acid (0.1 ml) dropwise and the mixture was stirred for 3 h at room temperature, then poured into ice–water, and extracted with methylene dichloride, and the extract was dried ($MgSO_4$). The solvent was removed and the residue chromatographed on a silica gel column with methylene dichloride as eluant to give the *triacetate* (**16**) (51 mg, 9.8%) as straw-yellow needles, m.p. 210.5—211.5 °C (from methanol) (Found: C, 65.2; H, 4.2. $C_{20}H_{16}O_6 \cdot \frac{1}{2}H_2O$ requires C, 65.03; H, 4.63%); $\lambda_{max.}$(MeOH) 250 (log ε 4.36), 256.5 (4.33), 322.5 (3.75), 370 (4.11), and 395 nm (4.10); $\nu_{max.}$ 1 780br ($OCOCH_3$), 1 646, 1 235, and 1 183 cm^{-1}; δ 2.13 (6 H, s, 2 CH_3), 2.49 (3 H, s, CH_3), 8.46 (1 H, s, 9-H), and 7.58—8.80 (6 H, m, ArH).

(*b*) When acetic anhydride from an old bottle was used, the dione (**2**) (400 mg, 1.92 mmol) afforded the triacetate (**16**) (16 mg, 2.3%) and the *diacetate* (**17**) (218 mg, 38.5%) as plates, m.p. 170.0—170.5 °C (from methanol) (Found: C, 69.5; H, 4.6. $C_{18}H_{14}O_4 \cdot H_2O$ requires C, 69.22; H, 5.16%); $\lambda_{max.}$(MeOH) 229.5 (log ε 4.28), 247.5 (4.09), and 336 nm (3.74); $\nu_{max.}$ 1 757 ($OCOCH_3$), 1 698, 1 235, and 1 228 cm^{-1}; δ 1.81 (6 H, s, 2 CH_3), 6.47 (1 H, d, *J* 11.6 Hz), 7.04 (1 H, d, *J* 11.6 Hz), and 7.34—8.27 (6 H, m, ArH).

(*c*) An acetic anhydride–acetic acid (10 : 1)–conc. sulphuric acid system afforded only the triacetate (**16**) (13.3%).

1-Hydroxyphenalene-1-carboxylic Acid (**19**).—To a well stirred solution of the dione (**2**) (200 mg, 0.962 mmol) in dioxane (3 ml) was added 1M aqueous sodium hydroxide (3 ml) dropwise during 30 min and the mixture was acidified with 10% sulphuric acid. The precipitates were extracted with ether (300 ml) and the extract was dried ($MgSO_4$). After removal of the solvent the residue was recrystallized from methanol to give the *acid* (**19**) (158 mg, 23%) as brownish yellow fine needles, m.p. 280 °C (decomp.) (from dioxane) (Found: C, 74.3; H, 4.5. $C_{14}H_{10}O_3$ requires C, 74.41; H, 4.08%); $\nu_{max.}$ 3 470 (OH), 3 065—2 800 (CO_2H), 1 679 (C=O), 1 641 (C=C), and 1 268 cm^{-1} (C–O). The acid (**19**) was esterified with ethereal diazomethane to give the methyl ester as orange crystals, m.p. 193—197 °C; δ 3.88 (1 H, s, OH, exchangeable with deuterium), 3.89 (3 H, s, CO_2CH_3), 6.49 (1 H, d, *J* 9 Hz), 6.54 (1 H, d, *J* 9 Hz), and 7.34—9.06 (6 H, m, ArH).

D.C. Polarography.—The measurements were carried out at 22.0 ± 0.5 °C and the potentials were referred to the standard calomel electrode. The half-wave reduction potentials of quinone (**2**) were $E_1 = -0.23$ V (0.6 μA), $E_2 = -0.40$ V (0.6 μA), and $E_3 = -1.14$ V (2.4 μA); concentration = 1.05mM in 28% aqueous ethanol solution; pH 5.28, McIlvaine buffer solution (0.05M citric acid and 0.1M Na_2HPO_4); supporting electrolyte 0.1M KNO_3. These waves gave a diffusion-controlled current.

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