Synthesis and Properties of Acepleiadylene-5,6-dione and Acepleiadylene-5,8-dione†

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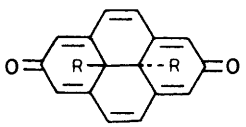
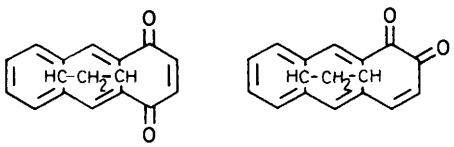
Acepleiadylene-5,8-dione (**1**) and acepleiadylene-5,6-dione (**2**) have been synthesized by the stepwise oxidation of 6,7-dihydrocyclohept[*fg*]acenaphthene-5,8-dione (**4**) and 7,8-dihydrocyclohept[*fg*]-acenaphthene-5,6-dione (**21**) derived from compound (**4**), respectively. The reduction potentials of compounds (**1**) and (**2**) were determined by cyclic voltammetry which showed that $E_1 = -0.50$ V and $E_2 = -0.84$ V for the former, and $E_1 = E_2 = -0.29$ V for the latter. Spectral and electrochemical data suggest that both diones (**1**) and (**2**) are [14]annulenediones with a vinyl cross-link. 5,8- and 5,6-Dihydroxyacepleiadylene, (**9'**) and (**22'**), exist in their keto-forms, 6,7-dihydrocyclohept[*fg*]-acenaphthylene-5,8-dione (**9**) and 7,8-dihydrocyclohept[*fg*]acenaphthylene-5,6-dione (**22**), respectively.

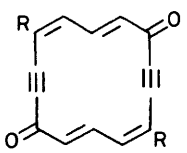
Although benzoquinone ([4*n* + 2]annulenedione, *n* = 1) has been intensively studied for many years, the nonbenzenoid quinones have only recently been investigated.[1] When *n* is large in the system of [4*n* + 2]- or [4*n*]-annulenedione, numerous interesting geometries for the compounds are conceivable. The physicochemical properties and chemical reactivity are very interesting especially in view of recent progress in the study of quinonoid compounds as electron receptors in the field of the material sciences[2] and as antitumour drugs in medicinal chemistry.[1b] The [14]annulenediones ([4*n* + 2], *n* = 3) have been synthesized by Boekelheide,[3] Vogel,[4] and Nakagawa,[5] but their properties have not been investigated in any detail.



R = Me, Et (ref;3 1967)



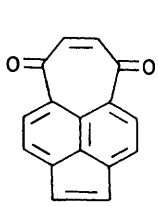
(ref. 4)



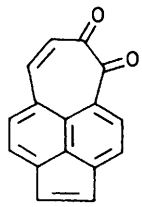
R = Bu^t, Ph (ref.5)

Previously we briefly reported the synthesis and electrochemistry of acepleiadylene-5,8-dione (**1**) and acepleiadylene-5,6-dione (**2**), which are [14]annulenediones with a notably high reduction potential.[6] In this paper we discuss the synthesis and physical properties of these compounds in more detail.

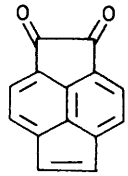
Acepleiadylene[7] is the parent hydrocarbon of compounds (**1**) and (**2**), and is known to have a *peri* 14π system with a vinyl cross-link in the centre of the molecule.[8] The diketone oxidation product has not been hitherto reported and is of interest in relation to the lower analogue, pyracyloquinone (**3**)[9] which belongs to a *peri* 12π annulene system.



(**1**)



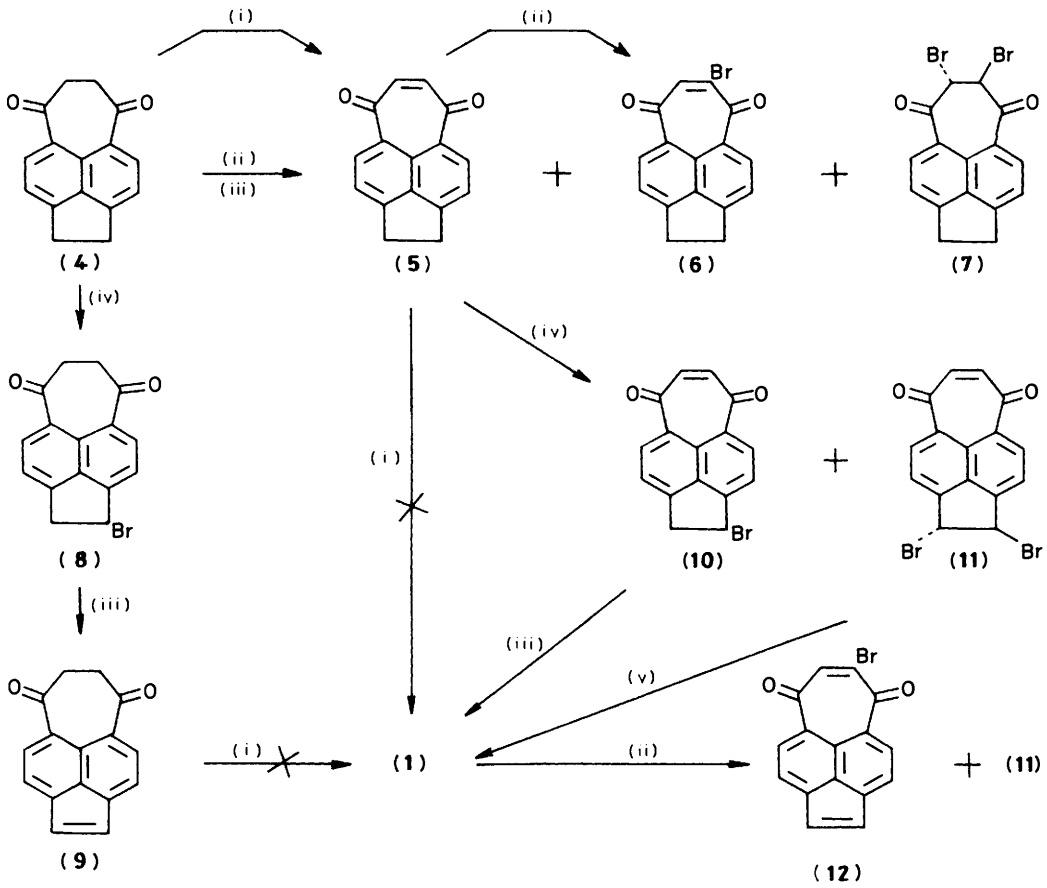
(**2**)



(**3**)

To synthesize acepleiadylene-5,8-dione (**1**), 6,7-dihydrocyclohept[*fg*]acenaphthene-5,8-dione (**4**)[10] was brominated with an equimolar amount of bromine in chloroform at −5 °C and subsequently treated *in situ* with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to yield cyclohept[*fg*]acenaphthene-5,8-dione (**5**) (41%) as yellow needles, and also 6-bromocyclohept[*fg*]-acenaphthene-5,8-dione (**6**) (3.2%), and 6,7-dibromo-6,7-dihydrocyclohept[*fg*]acenaphthene-5,8-dione (**7**) (0.8%). Compound (**5**) was also obtained by oxidation of the diketone (**4**) with 2.2 mol equiv. of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in refluxing dry benzene for 24 h, in 10% yield. Bromination of the diketone (**5**) in chloroform at −5 °C afforded the bromodiketone (**6**) in 56% yield. When the diketone (**4**) was refluxed with *N*-bromosuccinimide (NBS) and dibenzoyl peroxide (BPO) in tetrachloromethane for 30 min, the unstable monobromoketone (**8**) (73%) was obtained. This was treated with DBU in chloroform to give 6,7-dihydrocyclohept-[*fg*]acenaphthylene-5,8-dione (**9**) (54%) as orange needles. Oxidation of the diketone (**5**) or (**9**) with 1.5 mol equiv. of DDQ in refluxing dry benzene for 16 h did not produce the required diketone (**1**) and unchanged starting material was recovered. When the diketone (**5**) was refluxed with NBS and a catalytic amount of BPO in tetrachloromethane for 30 min, 1-bromocyclohept[*fg*]acenaphthene-5,8-dione (**10**) (71%) and *trans*-1,2-dibromocyclohept[*fg*]acenaphthene-5,8-dione (**11**) (12%) were obtained. Treatment of the bromodiketone (**10**) with DBU in chloroform solution for 15 min at room temperature and of dibromoketone (**11**) with potassium iodide in refluxing acetone for 4 h, afforded acepleiadylene-5,8-dione (**1**) as purple needles in yields of 43 and 60%. Bromination of this diketone (**1**) with bromine in chloroform solution afforded 6-bromoacepleiadyl-

† Acepleiadylene here refers to the 4-ring system cyclohept[*fg*]-acenaphthylene.



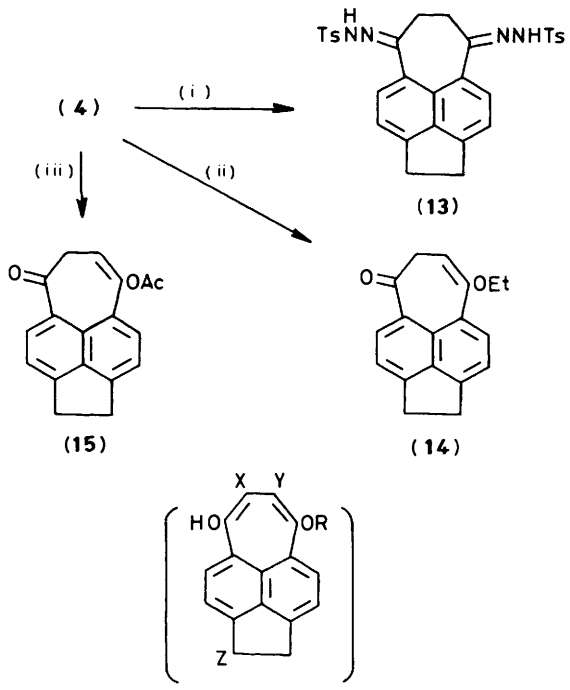
Scheme 1. *Reagents:* (i) DDQ; (ii) Br_2; (iii) DBU; (iv) NBS; (v) KI

ene-5,8-dione (**12**) (37%) and the dibromo compound (**11**) (18%) (Scheme 1).

The study of the keto–enol tautomerism of these intermediate diketones provided interesting information about the stability of the hitherto unknown hydroxyacepleiadiene systems. The diketone (**4**) has been reported to give a dioxime,[10] to dissolve in alcoholic alkaline solution,[10] and to evolve a gas on consumption of methylmagnesium iodide at 100 °C.[10,11] It does not yield an enol acetate with boiling acetic anhydride and sodium acetate.[10] This suggests that the carbonyl groups can enolize, depending on the conditions, in spite of the strong electron-flow from the naphthalene ring, demonstrated by the unusually low i.r. absorption band of 1 650 cm^{-1}. On treatment with toluene-*p*-sulphonohydrazide the diketone (**4**) gave the bis(tosylhydrazone) (**13**). With absolute ethanol in the presence of acid it gave an enol ether (**14**), and with acetic anhydride in the presence of sulphuric acid it gave an enol acetate (**15**). Thus it is evident that the diketone (**4**) can enolize to a β,γ-enol ketone but preferentially assumes the diketo-form rather than the acepleiadienediol form (**4′**). Similarly, in chloroform solution compounds (**7**), (**8**), (**14**), and (**15**) favour the diketo-forms in preference to the forms (**7′**), (**8′**), (**14′**), and (**15**) respectively on the basis of ^1H n.m.r. and i.r. spectral data. This suggests that in the diol (**4′**) the resonance energy acquired by assuming the conjugated acepleiadiene structure is smaller than the strain energy caused by the seven-membered skeleton and the interactive energy between the C–OH groups and the 4- and 9-hydrogen (Scheme 2).

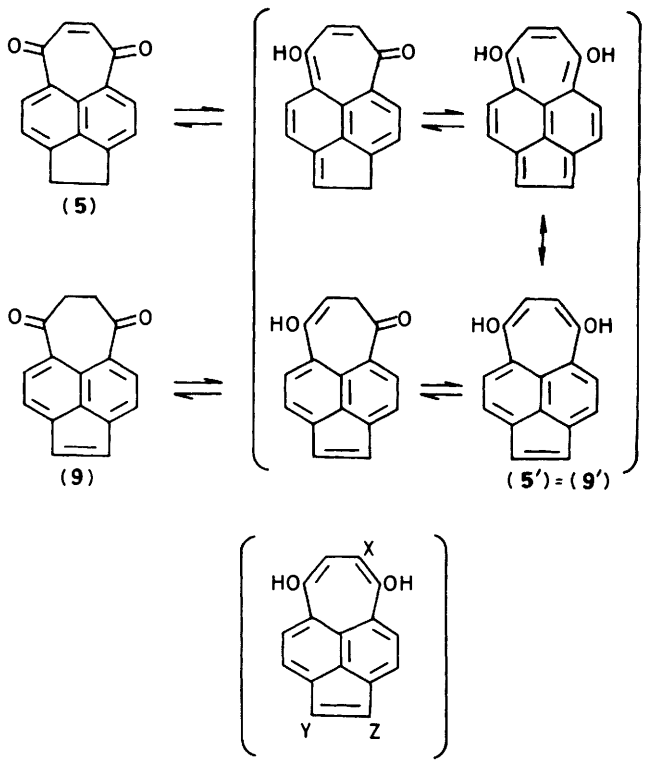
As shown in Scheme 3, the diketones (**5**), (**6**), (**9**), (**10**), and (**11**) have the possibility to aquire acepleiadylene-5,8-diol forms (**5′**), (**6′**), (**9′**), (**10′**), and (**11′**), but on the basis of ^1H n.m.r. and i.r. spectra they are carbonyl tautomers. To change into the diol tautomer, the carbonyl tautomers (**5**), (**6**), (**10**), and (**11**) must pass through a high-energy intermediate structure of a naphthoquinone dimethide-type and the resonance energy in the assumed acepleiadylene-5,8-diol must be larger than the strain energy in the fully conjugated or aromatized system. The isomerization between diketones (**5**) and (**9**) is an interesting problem but during recrystallization of each dione in ordinary organic solvents it is not observed.

To synthesize acepleiadylene-5,6-dione (**2**) the diketone (**4**) was refluxed with ethylene glycol and toluene-*p*-sulphonic acid in dry benzene for five days to give the monoacetal (**16**) (75.5%) but no diacetal. The carbonyl group of this compound (**16**) was reduced by the Wolff–Kishner reaction to the acetal (**17**) (75%), which was subsequently converted into the monoketone (**18**) (82%) by 6M hydrochloric acid. The monoketone (**18**) was allowed to react with 2.2 mol equiv. of methyl 2-nitrophenyl disulphide[12] and sodium hydride in THF for 13 h under nitrogen to afford the thioacetal (**19**) (84.3%). This was transformed into the dimethylacetal (**20**) (74.9%) by treatment with thallium(III) nitrate in anhydrous methanol for 1.5 h at room temperature.[12] The acetal (**20**) was hydrolysed with 4M hydrochloric acid in tetrahydrofuran (THF) for 3 h at room temperature to give 7,8-dihydrocyclohept[*fg*]acenaphthene-5,6-dione (**21**) (81.5%). This was also obtained from the thioacetal (**19**) by hydrolysis with 2 mol equiv. of mercury(II) perchlorate in THF for 5 min (43.6%). The *o*-diketone (**21**) was also synthesized by oxidation of the ketone (**18**) with selenium(IV) oxide in refluxing absolute ethanol for 5.5 h (23.5%). The diketone (**21**) has i.r. absorption bands at 1 710 and 1 670 cm^{-1} for the two *ortho* carbonyl groups. This structure



(4'); R = X = Y = Z = H
(7'); R = Z = H, X = Y = Br
(8'); R = X = Y = H, Z = Br
(14'); R = Et, X = Y = Z = H
(15'); R = Ac, X = Y = Z = H

Scheme 2. *Reagents:* (i) $TsNHNH_2$; (ii) abs. EtOH; (iii) Ac_2O



(5') = (9'); X = Y = Z = H
(6'); X = Br, Y = Z = H
(10'); X = Y = H, Z = Br
(11'); X = H, Y = Z = Br

Scheme 3.

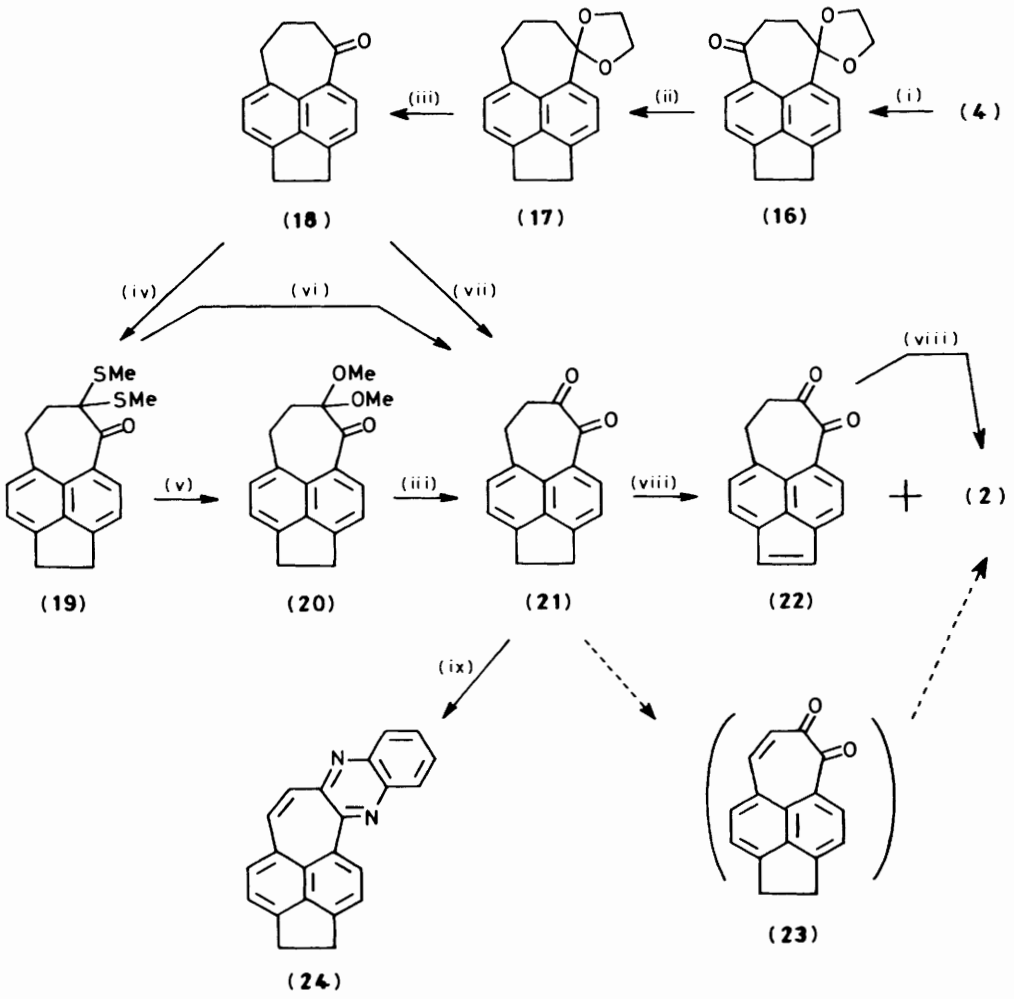
was confirmed by the formation of a quinoxaline derivative (**24**) on reaction with *o*-phenylenediamine. Bromination of the diketone (**21**) with a large excess of bromine in chloroform solution at room or refluxing temperature, or in the presence of acetic acid, caused a dark brown colouration of the solution and curiously gave a quantitative recovery of the starting material. With NBS in refluxing tetrachloromethane in the presence of a catalytic amount of BPO it afforded a mixture of unstable substances, presumably a mixture of bromo-derivatives. These were treated with pyridine in chloroform or lithium carbonate in *NN*-dimethylformamide (DMF) to yield only small amounts of several unidentified products. The α-diketone (**21**) was oxidized with DDQ in refluxing dry benzene for 12 h to afford 7,8-dihydrocyclohept[*fg*]acenaphthylene-5,6-dione (**22**) (12.8%) and acepleiadylene-5,6-dione (**2**) (23.7%). Since the former diketone (**22**) was oxidized with DDQ in refluxing dry benzene for 6 h to give the dione (**2**) (26.9%), the former is the precursor to the latter compound (**2**) but the possibility of the rapid intermediate formation of cyclohept[*fg*]acenaphthene-5,6-dione (**23**) and its subsequent transformation into the dione (**2**) cannot be excluded (Scheme 4).

Oxidation of the α-diketone (**21**) with 2.2 mol equiv. of tetrachloro-*o*-benzoquinone in dry refluxing benzene for 12 h did not afford the dione (**2**). By analogy to the 1,4-diketones, the diketones (**21**) and (**22**) cannot assume the tautomeric dienol forms (**21'**) and (**22'**) respectively, though an additional stabilizing contribution from intramolecular hydrogen bonding might be expected in this case. The diketone (**22**) does not transform into its isomer (**23**) in the common organic solvents during crystallization (Scheme 5).

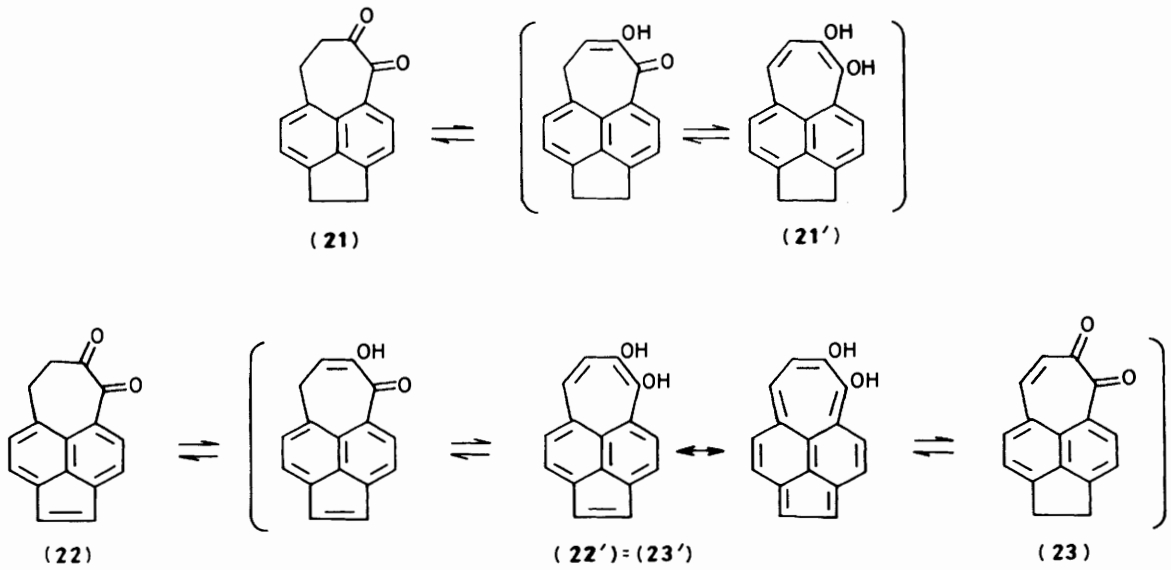
The mass spectra of the diones (**1**) and (**2**) showed weak ($M^{+\cdot}$ + 2) ion peaks, which are characteristic for quinones,[1a,13a] and $M^{+\cdot}$, $M^{+\cdot} - CO$, $M^{+\cdot} - 2CO$, and $M^{+\cdot} - 2CO - C_2H_2$ peaks, suggesting that they decompose successively through 5*H*-cyclopenta[*cd*]phenalen-5-one (**25**),[14] pyracylene (**26**),[15] and ancenaphthylene (**27**) radicals.

Compounds (**1**) and (**2**) are orange in solution but purple as solids, the latter dione (**2**) having a deeper colour. Compound (**1**) is stable for several years and compound (**2**) for a few days in the dark. Electronic spectra of the diones (**1**), (**5**), and (**9**) are shown in Figure 1 and those of the dione (**2**), (**22**), and cyclohepta-[*de*]naphthalene-7,8-dione (**29**)[1c,16] are shown in Figure 2. The i.r. absorption maxima of the carbonyl groups of the dione (**1**) at 1 630 cm^{-1} and of the dione (**2**) at 1 655 and 1 640 cm^{-1} are comparable with the values of 1 640 and 1 638 cm^{-1} for their isomers, 1,8- and 1,6-pyrenoquinone[17] respectively. However, the absorptions are at lower wavenumber than those at 1 661 or 1 660 cm^{-1} of cyclohepta[*de*]naphthalene-7,10-dione (**28**)[18] or -7,8-dione (**29**) which have a cross-conjugation system. This indicates that delocalized electrons flow from the naphthalene ring more readily into the carbonyl groups of the diketones (**1**) and (**2**) than into those of the diketones (**28**) and (**29**).

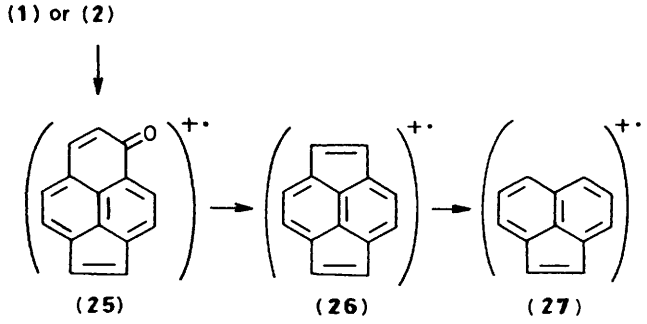
The ^1H n.m.r. spectrum of the diketone (**1**) showed four signals at δ 6.87 for 6-H and 7-H, δ 7.01 for 1-H and 2-H, δ 7.61 (d, *J* 7.5 Hz) for 3-H and 10-H, and δ 8.30 (d, *J* 7.5 Hz) for 4-H and 9-H, indicating a C_{2v} symmetry and supporting the proposed structure; this was confirmed by there being only nine signals in the ^{13}C n.m.r. spectrum. The ^1H n.m.r. spectrum of the diketone (**2**) showed signals at δ 6.35 (d, *J* 12.9 Hz) for 7-H and δ 7.29 (d, *J* 12.9 Hz) for 8-H, indicating a seven-membered ring. There were also signals at δ 6.90 for 1-H and 2-H, δ 7.48 for 9-H and 10-H, δ 7.58 (d, *J* 7.4 Hz) for 3-H, and δ 8.33 for 4-H (d, *J* 7.4



Scheme 4. *Reagents:* (i) HOC_2H_4OH, H^+; (ii) Wolff-Kishner reduction; (iii) H^+; (iv) *o*-$C_6H_4(NO_2)S_2Me$; (v) Tl^{3+}, MeOH; (vi) $Hg(ClO_4)_2$; (vii) SeO_2; (viii) DDQ; (ix) *o*-PDA



Scheme 5.



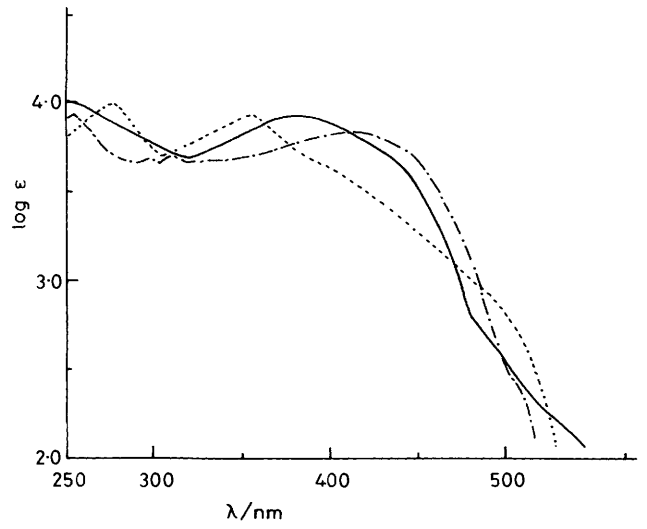


Figure 1. Electronic spectra of diones: —— (**1**); · · · · (**5**); — · — · — (**9**) (solution in chloroform)

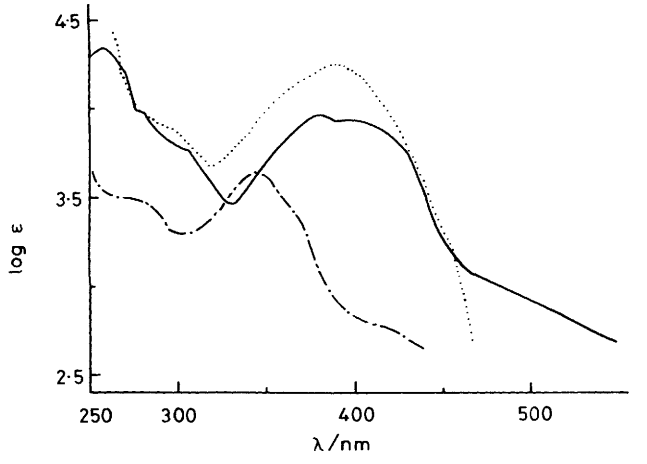


Figure 2. Electronic spectra of diones: —— (**2**); · · · · (**29**); — · — · — (**22**) (solution in chloroform)

Hz), which support the proposed structure. This was confirmed by the nonsymmetrical ^{13}C n.m.r. signals.

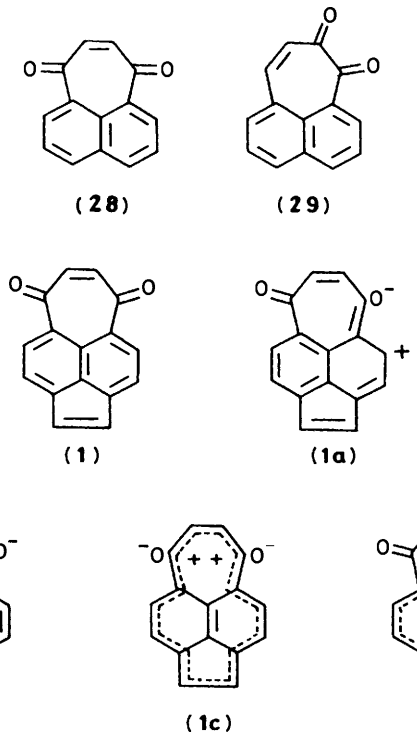
Comparison of the ^{1}H n.m.r. spectrum of the dione (**1**) in deuteriochloroform with that in trifluoroacetic acid showed slightly lower field chemical shifts of the signals under acidic conditions. This suggested a small contribution from a benzotropolonate structure such as (**1a**) or (**1b**) but none from a dication (**1c**) or homocation (**1d**) structure (Table 1).

Pyracyloquinone (**3**), and the diketones (**1**) and (**2**), could be

Table 1. ^{1}H N.m.r. spectra (δ values) of the dione (**1**) in neutral and acidic solvents[a]

Position	$CDCl_3$	CF_3CO_2H	$\delta(CDCl_3) - \delta(CF_3CO_2H)$
1, 2	7.01	7.07	−0.06
3, 10	7.61	7.59	+0.02
4, 9	8.30	8.49	−0.19
6, 7	6.87	7.00	−0.13

[a] Chemical shifts are in p.p.m. relative to tetramethylsilane as internal standard.



formed by union of acenaphthylene and α-diketone, ene-1,4-dione, and ene-1,2-dione moieties, respectively. Except for the positions strongly influenced by a carbonyl group, proton signals of the diketones (**1**) and (**2**) appear at higher field than those of pyracyloquinone (**3**)[8] (at the 4- and 7-position, δ 8.26, and at the 5- and 6-position, δ 7.69). This shows that the ene-dione groups have a larger perturbation effect on the electron attraction from the acenaphthylene group than does the α-dicarbonyl group. Interestingly, the chemical shift values of the diones (**1**) and (**2**) appear at higher field than those of the parent hydrocarbon, acepleiadylene (δ 7.77 for 1-H and 2-H, and δ 8.23 for 3-H and 10-H).[8,19] This indicates the existence of a diamagnetic ring current in acepleiadylene. Since such an effect cannot be expected between pleiadiene-7,8-dione (**29**) and pleiadiene, both of which have a cross-conjugated system, the proton resonance signals of the part of the naphthalene ring of the dione (**29**) appear at δ 7.30—8.70, while those of the latter are at δ 6.45—7.30.[20] This indicates the existence of the strong electron-attracting force of an ene-dione group. Similarly, pleiadiene-7,10-dione (**28**) shows[18] lower chemical shift values of δ 7.65—8.46 for the protons of the naphthalene ring than those of pleiadiene. Similarly acepleiadienedione (**5**) shows lower chemical shift values of δ 7.24 (3- and 10-position) than

Table 2. Electrochemical reduction potentials of diones (1) and (2) and reference compounds[a]

Compound	E_1	E_2	$E_1 - E_2$	$E_1 + E_2$
o-Chloranil	+0.21	−0.69	0.90	−0.48
Dione (2)	−0.29	−0.29	0.00	−0.58
p-Benzoquinone	−0.40	−1.17	0.77	−1.57
Dione (1)	−0.50	−0.84	0.34	−1.34
1,4-Naphthoquinone	−0.59	−1.40	0.81	−1.99
Dione (3) (on DMSO)[b]	−0.738	−1.305	0.567	−2.043

[a] At 22.5 ± 0.5 °C in dry dimethylformamide as described in the text. Potentials relative to a standard calomel electrode. [b] Ref. 9.

those of the parent acepleiadiene, δ 6.63 (3- and 10-position). ^{13}C N.m.r. chemical shift values for the carbonyl carbons of diketones (1), δ_C 189.3, and (2), δ_C 190.6 and 192.3 p.p.m., are between those of unsaturated ketones and those of quinones.[21]

Few redox potentials of nonbenzenoid quinones have been reported but those of [4*n* + 2]annulenediones would be expected to show interesting behaviour. These potentials should reflect the unsymmetrical character between the ground and excited energy-levels of nonbenzenoid aromatic systems. The electrochemical reduction of the diones (1) and (2), as well as that of a series of reference compounds, was examined by cyclic voltammetry and the formal potentials are listed in Table 2. All the compounds listed showed good electrochemical reversibility of both the first and second waves (Figure 3). A two-electron reduction of the dione (2) seemed to occur. Only one pair of oxidation–reduction waves was observed. The peak current for the reduction wave (*ca.* 160 μA) was larger than that for the dione (1) (*ca.* 120 μA) and the area for the reduction wave was equal to that of the sum of the two reduction waves for the dione (1). Since the value of E_1 reflects the energy change on conversion of the dione into the anion radical, it is interesting that E_1 for the dione (2) is higher than that for *p*-benzoquinone, and comparable with the value for *o*-benzoquinone.* Similarly E_1 for the dione (1) is higher than that for 1,4-naphthoquinone, and the E_1 values for both diones (2) and (1) seem to be considerably higher than those for the isomeric 1,6-, 1,8-, and 4,5-pyrenequinones.[13b,22] The potential difference $(E_1 - E_2)$, to a simple approximation, reflects the electrostatic repulsion of the two electrons which enter the same LUMO successively. The small value of $(E_1 - E_2)$ for the dione (2) is also surprising,[23] although the observed $(E_1 - E_2)$ values are often smaller for nonbenzenoid quinones of similar size.[5,24] This abnormality might be attributed to the existence of a pair of degenerate energy levels. Alternatively it could suggest that the structural and electronic change ascribed to the dipole–dipole repulsion between the two oxygens and the steric congestion of the two oxygens and a hydrogen at the 4-position might cause the anion radical to lower its LUMO and apparently cancel the energy for two-electron repulsion. A small $(E_1 - E_2)$ value was also observed for compound (1) and a similar explanation could apply in this case. Since the sum of the two potentials $(E_1 + E_2)$ reflects the total energy change on conversion of the quinone into the aromatized dianion, the $(E_1 + E_2)$ value for the dione (2) is also interesting; it is much more positive than the value for *p*-benzoquinone and approaches the value for *o*-chloranil, a strong oxidizing reagent. Similar comments apply to the $(E_1 + E_2)$ value for compound (1), but the effect is less marked. The values of E_1, E_2, and $(E_1 + E_2)$ for the diones (2) and (1) are more positive than those for pyracyloquinone (3), suggesting

* With a few exceptions, fusion of a benzene ring to a basic quinone unit tends to lower the E_1 value of the system.[13b,13c]

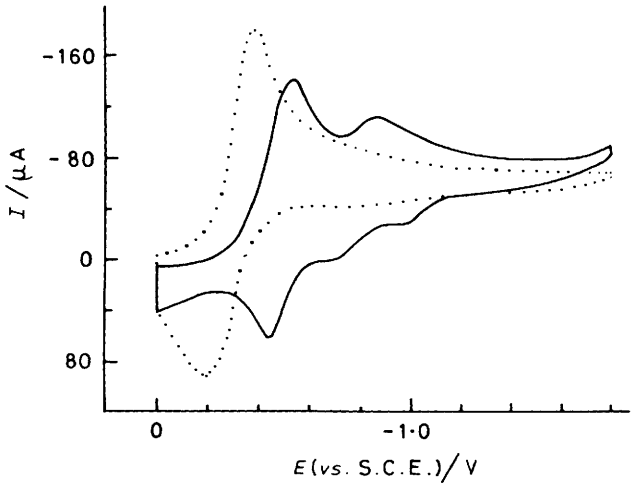


Figure 3. Cyclic voltammograms of diones: —— (1); · · · · (2)

that pyracylene is unstable since it is a [12]annulene,[9,15] whereas acepleiadylene is stable, since it is a [14]annulene.[8]

We therefore conclude from the electrochemical and spectral data that the diones (2) and (1) have a high quinone character and may be regarded as [14]annulenediones with a vinyl cross-link.

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. Unless otherwise stated the spectra were taken in the following solvents/media: u.v., $CHCl_3$; i.r., KBr; ^1H and ^{13}C n.m.r., $CDCl_3$. The cyclic voltammogram was recorded in the usual manner with a home-made voltammetric analyser with a three-electrode cell. 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 22.5 ± 0.5 °C in dry dimethylformamide with 0.1M tetrabutylammonium perchlorate as supporting electrolyte. Substrates were present at 0.5 mM, and the reduction potentials were determined under nitrogen atmosphere in a standard three-electrode cell equipped with a saturated calomel electrode as reference. The formal potentials were recorded at a scan rate of 100 mV s^{-1}.

Cyclohept[fg]*acenaphthene-5,8-dione* (5), *6-Bromocyclohept*-[fg]*acenaphthene-5,8-dione* (6), *and 6,7-Dibromo-6,7-dihydrocyclohept*[fg]*acenaphthene-5,8-dione* (7).—To a cooled (−10 to −5 °C) and rapidly stirred chloroform solution (100 ml) of 6,7-dihydrocyclohept[*fg*]acenaphthene-5,8-dione (4)[10] (3.46 g, 1.57 mmol) was added dropwise a solution of bromine (2.50 g, 1.57 mmol) in chloroform (5 ml) during 40 min. After being stirred for a further 100 min the reaction mixture was treated dropwise with a solution of DBU (4.87 g, 3.14 mmol) in chloroform (5 ml) during 30 min. After a further 120 min the organic phase was washed successively with 0.1M hydrochloric acid, water, 5% aqueous sodium hydrogencarbonate, and water, and dried ($MgSO_4$). After removal of chloroform under a slightly reduced

pressure below 50 °C, the residue was separated into three sections by chromatography on a silica-gel column with dichloromethane as eluant. The first fraction gave 6,7-*dibromo*-6,7-*dihydrocyclohept*[fg]*acenaphthene*-5,8-*dione* (**7**) (14 mg, 0.82%) as yellow needles, m.p. 192—193 °C (from ethyl acetate) (Found: C, 48.8; H, 3.0. $C_{16}H_{10}Br_2O_2$ requires C, 48.76; H, 2.55%); $\nu_{max.}$ 1 653 and 1 595 cm^{-1}; δ 3.44 (4 H, s, 1- and 2-H_2), 4.21 (2 H, s, 6- and 7-H), 7.43 (2 H, d, *J* 7.3 Hz, 3- and 10-H), and 8.01 (2 H, d, *J* 7.3 Hz, 4- and 9-H). The second fraction was 6-*bromocyclohept*[fg]*acenaphthene*-5,8-*dione* (**6**) (157 mg, 3.2%) as brown needles, m.p. 130 °C (decomp.) (from ethyl acetate) (Found: C, 61.7; H, 2.9. $C_{16}H_9BrO_2$ requires C, 61.43; H, 2.58%); $\nu_{max.}$ 1 642sh, 1 631br, and 1 612sh cm^{-1}; δ 3.44 (4 H, s, 1- and 2-H_2), 7.41 (2 H, d, *J* 7.6 Hz, 3- and 10-H), 7.60 (1 H, s, 6-H), and 8.41 (2 H, d, *J* 7.6 Hz, 4- and 9-H). The third fraction was *cyclohept*[fg]*acenaphthene*-5,8-*dione* (**5**) (1.514 g, 41%) as yellow needles, m.p. 168—170 °C (from methanol); *m/z* (75 eV) 234 ($M^{+\bullet}$, 100%), 206 ($M^{+\bullet}$ − CO, 58), 178 ($M^{+\bullet}$ − 2CO, 44), and 152 ($M^{+\bullet}$ − 2CO − C_2H_2, 38) (Found: C, 81.8; H, 4.3. $C_{16}H_{10}O_2$ requires C, 82.04; H, 4.30%), $\nu_{max.}$ 1 629, 1 619, 1 591, and 1 565 cm^{-1}; $\nu_{max.}$($CHCl_3$) 1 625 and 1 595 cm^{-1}; δ 3.30 (4 H, s, 1- and 2-H_2), 6.79 (2 H, s, 6- and 7-H), 7.24 (2 H, d, *J* 7.6 Hz, 3- and 10-H), and 8.33 (2 H, d, *J* 7.6 Hz, 4- and 9-H); $\lambda_{max.}$ 252 (log ε 3.92), 297.5 (3.68), and 409 nm (3.82).

Oxidation of Compound (**4**) *to the Dione* (**5**).—(*a*) A mixture of the diketone (**4**) (300 mg, 1.27 mmol), DDQ (98% purity; 636 mg, 2.79 mmol), and dry benzene (50 ml) was refluxed for 24 h. After removal of a residue insoluble in benzene and dichloromethane, the reaction mixture was chromatographed on a silica-gel column with dichloromethane as eluant. The first eluate gave the dione (**5**) (38 mg, 10%) as yellow needles, m.p. 165—168 °C, and the second fraction gave the diketone (**4**) (154 mg recovery).

(*b*) A mixture of compound (**4**) (300 mg, 1.27 mmol), DDQ (294 mg, 1.27 mmol), and dry benzene (35 ml) was refluxed for 6 h to give only recovery of the starting compound (256 mg).

Bromination of Compound (**5**) *to the Bromodiketone* (**6**).—To a cold (−5 to −10 °C) and rapidly stirred chloroform solution (4 ml) of compound (**5**) (100 mg, 4.27 mmol) was added dropwise bromine (69 mg, 4.32 mmol) during 3 min. After a further 30 min, the reaction mixture was chromatographed on a silica-gel column with dichloromethane as eluant to give the bromodiketone (**6**) (75 mg, 56.2%) and recovery of the diketone (**5**) (43 mg).

1-*Bromo*-6,7-*dihydrocyclohept*[fg]*acenaphthene*-5,8-*dione* (**8**).—A mixture of the diketone (**4**) (1.200 g, 5.08 mmol), NBS (1.000 g, 5.59 mmol), BPO (30 mg, 0.123 mmol), and dry tetrachloromethane (40 ml) was refluxed for 30 min. The reaction mixture was cooled with ice, insoluble materials were filtered off, and from the filtrate yellow crystals of the *title compound* (**8**) (505 mg) were obtained, m.p. 115—120 °C (with blackening). The mother liquor was chromatographed on a silica-gel column with dichloromethane as eluant to afford the *title compound* (**8**) (651 mg, total 72.5%) as fine yellow needles, m.p. 105—125 °C (decomp.). The compound is unstable and at room temperature decomposes completely in a week; $\nu_{max.}$ 1 656 and 1 603 cm^{-1}; δ 3.09 (4 H, s, 6- and 7-H_2), 3.99 (2 H, m, 2-H_2), 5.81 (1 H, m, 1-H), 7.39 (1 H, d, *J* 7.6 Hz, 9-H), 7.59 (1 H, d, *J* 7.6 Hz, 4-H), and 8.47 (2 H, d, *J* 7.6 Hz, 3-and 10-H).

6,7-*Dihydrocyclohept*[fg]*acenaphthylene*-5,8-*dione* (**9**).—To a rapidly stirred and cooled (−5 to −10 °C) chloroform (20 ml) solution of the monobromoketone (**8**) (458 mg, 1.45 mmol) was added dropwise DBU (442 mg, 2.91 mmol) during 2 min. After 90 min at room temperature the reaction mixture was washed successively with 0.2M hydrochloric acid, 5% aqueous sodium hydrogencarbonate, and water, and dried ($MgSO_4$). After removal of the solvent the residue was chromatographed on a silica-gel column with dichloromethane as eluant to give the *title compound* (**9**) (185 mg, 54.3%) as orange needles, m.p. 151—152 °C (from benzene–hexane) (Found: C, 82.35; H, 4.4. $C_{16}H_{10}O_2$ requires C, 82.04; H, 4.30%); $\lambda_{max.}$ 275 (log ε 3.99), 337.5sh (3.86), 354 (3.94), and 374.5sh nm (3.78); $\nu_{max.}$($CHCl_3$) 1 670 and 1 588 cm^{-1}; $\nu_{max.}$ 1 656 and 1 585 cm^{-1}; δ 3.15 (4 H, s, 6- and 7-H_2), 7.11 (2 H, s, 1- and 2-H), 7.71 (2 H, d, *J* 7.3 Hz, 3- and 10-H), and 8.47 (2 H, d, *J* 7.3 Hz, 4- and 9-H).

1-*Bromocyclohept*[fg]*acenaphthene*-5,8-*dione* (**10**) *and trans*-1,2-*Dibromocyclohept*[fg]*acenaphthene*-5,8-*dione* (**11**).—(*a*) A mixture of the diketone (**5**) (200 mg, 0.853 mmol), NBS (167 mg, 0.939 mmol), BPO (20 mg, 0.08 mmol) and tetrachloromethane (30 ml) was refluxed for 30 min. After the insoluble substances were filtered off, the hot filtrate was eluted on a silica-gel column with dichloromethane to give, as the first eluate, the *dibromo-ketone* (**11**) (40 mg, 11.9%) as yellowish brown needles, m.p. 145 °C (decomp.) (from ethyl acetate) (Found: C, 49.2; H, 2.2. $C_{16}H_8Br_2O_2$ requires C, 49.01; H, 2.05%); $\nu_{max.}$ 1 630 and 1 600 cm^{-1}; δ 5.99 (2 H, s, 1- and 2-H), 7.06 (2 H, s, 6- and 7-H), 7.82 (2 H, d, *J* 7.9 Hz, 3- and 10-H), and 8.77 (2 H, d, *J* 7.9 Hz, 4- and 9-H). The second eluate gave the *monobromoketone* (**10**) (213 mg, 71%) as yellow needles, m.p. 130 °C (decomp.) (from ethyl acetate) (Found: C, 61.6; H, 2.9. $C_{16}H_9BrO_2$ requires C, 61.31; H, 2.58%); $\nu_{max.}$ 1 623, 1 651, and 1 601 cm^{-1}; δ 4.06 (2 H, m, 2-H_2), 5.09 (1 H, m, 1-H), 7.01 (2 H, s, 6- and 7-H), 7.56 (1 H, d, *J* 7.8 Hz, 3-H), 7.77 (1 H, d, *J* 7.8 Hz, 10-H), 8.67 (1 H, d, *J* 7.8 Hz, 4-H), and 8.69 (1 H, d, *J* 7.8 Hz, 9-H). The last eluate gave recovery of diketone (**5**) (14 mg, 7%).

(*b*) A mixture of the diketone (**5**) (391 mg, 1.67 mmol), NBS (594 mg, 3.34 mmol), BPO (20 mg, 0.08 mmol), and tetrachloromethane (50 ml) was refluxed for 40 min. After the insoluble materials were filtered off the filtrate was chromatographed on a silica-gel column with dichloromethane as eluant to give the dibromoketone (**11**) (146 mg, 22.8%) and the monobromodiketone (**10**) (294 mg, 56.1%)

Cyclohept[fg]*acenaphthylene*-5,8-*dione* (*Acepleiadylene*-5,8-*dione*) (**1**).—(*a*) To a rapidly stirred chloroform solution (20 ml) of the bromodiketone (**10**) (208 mg, 0.665 mmol) was added dropwise a chloroform solution (2 ml) of DBU (208 mg, 1.37 mmol) during 2 min at room temperature. After 15 min the reaction mixture was washed successively with 0.2M hydrochloric acid, 5% aqueous sodium hydrogencarbonate, and water, and dried ($MgSO_4$). After removal of the chloroform by rotary-evaporation, the residue was chromatographed in dichloromethane on a silica-gel column to give the *title compound* (**1**) (67 mg, 43.3%) as purple needles, m.p. 186 °C (decomp.) (from benzene–hexane); *m/z* (50 eV) 234 ($M^{+\bullet}$ + 2, 4%), 233 ($M^{+\bullet}$ + 1, 18), 232 ($M^{+\bullet}$, 100), 204 ($M^{+\bullet}$ − CO, 73), 176 ($M^{+\bullet}$ − 2CO, 98), and 150 ($M^{+\bullet}$ − 2CO − C_2H_2, 49) (Found: C, 82.6; H, 3.6. $C_{16}H_8O_2$ requires C, 82.75; H, 3.47%); $\lambda_{max.}$ 377.5 nm (log ε 3.94); $\nu_{max.}$ 1 630 and 1 593 cm^{-1}; $\nu_{max.}$($CHCl_3$) 1 633 and 1 595 cm^{-1}; δ 6.87 (2 H, s, 6- and 7-H), 7.01 (2 H, s, 1- and 2-H), 7.61 (2 H, d, *J* 7.5 Hz, 3- and 10-H), and 8.30 (2 H, d, *J* 7.5 Hz, 4- and 9-H); δ_C 123.2 (q, C-10b), 124.4 (C-1 and -2), 129.0 (q, C-10c), 132.8 (C-3 and -10), 133.8 (q, C-2a and -10a), 136.4 (C-4 and -9), 138.3 (C-6 and -7), 145.9 (q, C-4a -8a), and 189.3 (q, C-5 and -8).

(*b*) A mixture of the dibromoketone (**11**) (37 mg, 0.094 mmol), potassium iodide (100 mg, 0.603 mmol), and acetone (10 ml) was refluxed for 4 h under nitrogen. The reaction mixture was poured into cold 5% aqueous sodium thiosulphate and extracted with chloroform. The chloroform layer was washed with water and dried ($MgSO_4$). After removal of the chloroform by rotary-evaporation, the residue was chromatographed on a

silica-gel column with dichloromethane as eluant to give the title compound (**1**) (13 mg, 59.6%) in pure form.

6-*Bromoacepleiadylene*-5,8-*dione* (**12**).—A chloroform solution (1 ml) of bromine (35 mg, 0.216 mmol) was added dropwise into a rapidly stirred and cooled (−5 to −10 °C) chloroform solution (5 ml) of the quinone (**1**) (50 mg, 0.216 mmol). After 30 min the reaction mixture was chromatographed on a silica-gel column with dichloromethane as eluant to give, as the first fraction, the *title compound* (**12**) (25 mg, 37%) as orange-red needles, m.p. 151—152 °C (from benzene–hexane) (Found: C, 61.7; H, 2.3. $C_{16}H_7BrO_2$ requires C, 61.76; H, 2.27%); $\nu_{max.}$($CHCl_3$) 1 660sh, 1 650sh, 1 604, and 1 593 cm^{-1}; δ 7.00 (2 H, s, 1- and 2-H), 7.60 (2 H, d, *J* 7.5 Hz, 3- and 10-H), 7.62 (1 H, s, 7-H), 8.33 (2 H, d, *J* 7.5 Hz, 4- and 9-H). The second fraction was the dibromodiketone (**11**) (16 mg, 18%) and the third was the recovered quinone (**1**) (20 mg, 40%).

6,7-*Dihydrocyclohept*[fg]*acenaphthene*-5,8-*dione Bis*(p-*toluylsulphonylhydrazone*) (**13**).—A mixture of the diketone (**4**) (501 mg, 2.12 mmol), toluene-*p*-sulphonohydrazide (396 mg, 2.13 mmol), one drop of 1M hydrochloric acid, and chloroform (30 ml) was refluxed for 24 h. The reaction mixture was cooled and the *title compound* (**13**) (249 mg, 20.5%) was deposited as a yellow powder, m.p. 220 °C (decomp.) (Found: C, 62.7; H, 4.75; N, 9.5. $C_{30}H_{28}N_4O_4S_2$ requires C, 62.92; H, 4.93; N, 9.78%); $\nu_{max.}$ 1 600, 1 310, 1 160, and 850 cm^{-1}; δ ([$^2H_6$]DMSO) 2.42 (6 H, s, CH_3), 2.96 (4 H, br s, 6- and 7-H_2), 3.38 (4 H, s, 1- and 2-H_2), 7.29—8.09 (12 H, m, ArH), and 10.80 (2 H, s, 2 NH). The mother liquor afforded recovered diketone (**4**) (114 mg).

8-*Ethoxycyclohept*[fg]*acenaphthen*-5(6H)-*one* (**14**).—A mixture of the diketone (**4**) (1.06 g, 4.48 mmol), toluene-*p*-sulphonic acid monohydrate (58 mg, 0.30 mmol), and absolute ethanol (50 ml) was refluxed for 24 h in a Soxhlet extractor, which also contained a mixture of anhydrous sodium sulphate and molecular sieve 4 Å in a filter paper thimble. To this reaction mixture was added cooled ether and the ether layer was washed with water and dried ($MgSO_4$). After removal of the ether, the residue was chromatographed on a silica-gel column with dichloromethane as eluant to give recovered diketone (**4**) (676 mg) and the *title compound* (**14**) (299 mg, 25.2%) as yellow granules, m.p. 130—133 °C (from hexane) (Found: C, 81.8; H, 5.9. $C_{18}H_{16}O_2$ requires C, 81.79; H, 6.10%); *m*/*z* 264 ($M^{+\bullet}$, 23%), 236 ($M^{+\bullet}$ − CO, 100), and 152 ($M^{+\bullet}$ − 2CO − C_2H_4, 32); $\nu_{max.}$ 1 670, 1 635, 1 600, 1 505, 1 445, 1 220, 1 045, and 855 cm^{-1}; δ 1.40 (3 H, t, *J* 6.9 Hz, CH_3), 3.25 (2 H, d, *J* 7.8 Hz, 6-H_2), 3.41 (4 H, s, 1- and 2-H_2), 3.92 (2 H, q, *J* 6.9 Hz, CH_2CH_3), 5.10 (1 H, t, *J* 7.8 Hz, 7-H), 7.33 (1 H, d, *J* 7.1 Hz, 10-H), 7.43 (1 H, d, *J* 7.1 Hz, 3-H), and 8.12 (2 H, d, *J* 7.1 Hz, 4- and 9-H). When the reaction time was extended to 4 days, the yield of the enol ether (**14**) was unchanged.

8-*Acetoxycyclohept*[fg]*acenaphthen*-5(6H)-*one* (**15**).—A mixture of the diketone (**4**) (400 mg, 1.69 mmol), acetic anhydride (10 ml), and a drop of conc. sulphuric acid was stirred overnight at room temperature. The reaction mixture was poured into ice–water (100 ml) and extracted with benzene (150 ml) and the organic layer was washed with water and dried ($MgSO_4$). After removal of the benzene the residue was recrystallized from methanol to give the *title compound* (**15**) (219 mg, 48%), m.p. 200—201 °C, as subliming yellow plates, $\nu_{max.}$ 1 733, 1 658, and 1 599 cm^{-1}; δ 2.22 (3 H, s, CH_3), 3.26 (2 H, d, *J* 8.5 Hz, 6-H_2), 3.38 (4 H, s, 1-and 2-H_2), 5.72 (1 H, t, *J* 8.5 Hz, 7-H), 7.27 (2 H, *J* 7.6 Hz, 3- and 10-H), 7.62 (1 H, d, *J* 7.6 Hz, 9-H), and 8.07 (1 H, d, *J* 7.6 Hz, 4-H).

Spiro{*cyclohept*[fg]*acenaphthene*-5-(6H),2′-[1,3]-*dioxolan*}-8(7H)-*one* (**16**).—Into a two-necked flask fitted with a Dean–Stark trap and condenser were placed the diketone (**4**) (9.09 g, 38.5 mmol), etheylene glycol (91 ml), toluene-*p*-sulphonic acid monohydrate (480 mg, 2.5 mmol), and dry benzene (500 ml). The contents were refluxed to separate water, and the apparatus was replaced by a Soxhlet extractor containing a mixture of anhydrous calcium sulphate and molecular sieve 4 Å in a filter paper thimble. After being refluxed for a further 5 days the contents were washed with water and dried ($MgSO_4$). After removal of the solvent the residue was recrystallized from benzene to give the *title compound* (**16**) (7.40 g, 68.5%), as yellow plates, m.p. 122—123 °C; *m*/*z* 280 ($M^{+\bullet}$, 100%), 252 ($M^{+\bullet}$ − CO, 13), 224 ($M^{+\bullet}$ − CO − C_2H_4, 84), and 152 ($M^{+\bullet}$ − CO − C_2H_4 − $C_3H_4O_2$, 65) (Found: C, 77.1; H, 5.8. $C_{18}H_{16}O_3$ requires C, 77.13; H, 5.75%); $\nu_{max.}$ 1 660, 1 600, 1 500, 1 440, 1 150, 1 145, 1 030, and 850 cm^{-1}; δ 2.44—3.04 (4 H, 4′- and 5′-H_2), 3.42 (4 H, s, 1- and 2-H_2), 3.68—4.11 (4 H, m, 6- and 7-H_2), 7.31 (2 H, d, *J* 7.3 Hz, 3- and 10-H), 7.80 (1 H, d, *J* 7.3 Hz, 4-H), and 7.88 (1 H, d, *J* 7.3 Hz, 9-H). From the mother liquor the diketone (**4**) (832 mg) was recovered.

7,8-*Dihydrospiro*{*cyclohept*[fg]*acenaphthene*-5(6H),2′-[1,3]-*dioxolane*} (**17**).—A mixture of the ketone (**16**) (500 mg, 1.79 mmol), hydrazine monohydrate (0.3 ml, 5.25 mmol), 2-hydroxyethyl ether (3 ml), and potassium hydroxide (356 mg, 5.40 mmol) was warmed and the water was removed. After being refluxed for 2.5 h at 190 °C under nitrogen, the reaction mixture was extracted with ether and the organic layer was washed and dried ($MgSO_4$). After removal of the ether, the residue was chromatographed on a silica-gel column with a mixture of benzene–hexane (3:1) to give the *title compound* (**17**) (357 mg, 75.0%), as pale yellow scales, m.p. 95—97 °C (from hexane); *m*/*z* 266 ($M^{+\bullet}$, 100%), 194 ($M^{+\bullet}$ − C_3H_4O, 21), and 152 ($M^{+\bullet}$ − $C_3H_4O_2$ − C_3H_6, 18) (Found: C, 81.2; H, 6.9. $C_{18}H_{18}O_2$ requires C, 81.17; H, 6.81%); $\nu_{max.}$ 1 600, 1 500, 1 235, 1 035, and 845 cm^{-1}; δ 1.62—2.61 (4 H, m, 6- and 7-H_2), 3.35 (4 H, s, 1- and 2-H_2), 3.18—3.59 (2 H, m, 8-H_2), 3.63—4.25 (4 H, m, 4′- and 5′-H_2), 7.23 (2 H, s, 9- and 10-H), 7.23 (1 H, d, *J* 7.1 Hz, 3-H), and 7.75 (1 H, d, *J* 7.1 Hz, 4-H).

7,8-*Dihydrocyclohept*[fg]*acenaphthen*-5(6H)-*one* (**18**).—A mixture of the acetal (**17**) (401 mg, 1.51 mmol), 6M hydrochloric acid (20 ml), and ether was stirred for 4.5 h. The ether layer was washed and dried ($MgSO_4$). Removal of the ether gave the *title compound* (**18**) (274 mg, 82.65%), as yellow scales, m.p. 124—125 °C (from hexane); *m*/*z* 222 ($M^{+\bullet}$, 100%), 194 ($M^{+\bullet}$ − CO, 52), and 152 ($M^{+\bullet}$ − CO − C_3H_6, 13) (Found: C, 86.2; H, 6.4. $C_{16}H_{14}O$ requires C, 86.45; H, 6.35%); $\nu_{max.}$ 1 655, 1 600, 1 505, 1 445, 1 155, and 840 cm^{-1}; δ 1.97—2.45 (2 H, m, 7-H_2), 2.76—3.32 (4 H, m, 6- and 8-H_2), 3.41 (4 H, s, 1- and 2-H_2), 7.32 (2 H, s, 3- and 10-H), 7.34 (1 H, d, *J* 7.5 Hz, 9-H), and 7.94 (1 H, d, *J* 7.5 Hz, 4-H).

6,6-*Bis*(*methylthio*)-7,8-*dihydrocyclohept*[fg]*acenaphthen*-5(6H)-*one* (**19**).—A mixture of the ketone (**18**) (326 mg, 1.47 mmol), sodium hydride (139 mg, 3.47 mmol), and anhydrous THF (30 ml) was stirred for 45 min at room temperature under nitrogen. To this mixture was added dropwise a solution of methyl 2-nitrophenyl disulphide[12] (660 mg, 3.28 mmol) in anhydrous THF (3 ml). After being stirred for a further 12 h at room temperature, the reaction mixture was extracted with ether. The ethereal extract was washed and dried ($MgSO_4$). After removal of the ether the residue was chromatographed on a silica-gel column with a mixture of benzene–hexane (3:1) to give the *title compound* (**19**) (389 mg, 84.3%) as pale yellow scales, m.p. 147.5—148.5 °C (from hexane); *m*/*z* 314 ($M^{+\bullet}$, 21%), 267 ($M^{+\bullet}$ − SCH_3, 22), and 239 ($M^{+\bullet}$ − SCH_3 − CO, 100)

(Found: C, 68.6; H, 5.8. $C_{18}H_{18}OS_2$ requires C, 68.75; H, 5.77%); $\nu_{max.}$ 1 650, 1 600, 1 500, 1 080, and 850 cm^{-1}; δ 2.07 (6 H, s, 2 CH_3), 2.15—2.49 (2 H, m, 7-H_2), 3.40 (4 H, s, 1- and 2-H_2), 3.09—3.45 (2 H, m, 8-H_2), 7.25 (2 H, s, 3- and 10-H), 7.39 (1 H, d, *J* 7.4 Hz, 9-H), and 7.84 (1 H, d, *J* 7.4 Hz, 4-H).

6,6-*Dimethoxy*-7,8-*dihydrocyclohept*[fg]*acenaphthen*-5(6H)-*one* (**20**).—To a mixture of thallium(III) nitrate trihydrate (1.73 g, 3.90 mmol) and anhydrous methanol (10 ml) was added rapidly a solution of the bisthioacetal (**19**) (559 mg, 1.78 mmol) in a mixture of anhydrous methanol and THF (1:1; 20 ml) under nitrogen. After being stirred for a further 1.5 h the reaction mixture was extracted with ether and the ethereal extract was washed and dried ($MgSO_4$). After removal of the ether the residue was chromatographed on a silica-gel column with dichloromethane as eluant to give the *title compound* (**20**) (376 mg, 74.9%) as yellow granules, m.p. 133.5—134.5 °C (from hexane); *m/z* 282 ($M^{+\bullet}$, 22%), 251 ($M^{+\bullet} - OCH_3$, 6), and 223 ($M^{+\bullet} - OCH_3 - CO$, 100) (Found: C, 76.65; H, 6.7. $C_{18}H_{18}O_3$ requires C, 76.57; H, 6.43%); $\nu_{max.}$ 1 695, 1 600, 1 500, 1 120, 1 040, and 850 cm^{-1}; δ 2.25—2.64 (2 H, m, 7-H_2), 3.16 (6 H, s, 2 CH_3), 2.85—3.24 (2 H, m, 8-H_2), 3.35 (4 H, s, 1- and 2-H_2), 7.28 (2 H, s, 9- and 10-H), 7.34 (1 H, d, *J* 7.2 Hz, 3-H), and 7.84 (1 H, d, *J* 7.2 Hz, 4-H).

7,8-*Dihydrocyclohept*[fg]*acenaphthene*-5,6-*dione* (**21**).—(*a*) A mixture of the bismethoxyacetal (**20**) (376 mg, 1.33 mmol), 4M hydrochloric acid (20 ml), and THF (20 ml) was stirred for 4 h. The reaction mixture was extracted with dichloromethane and the extract was washed and dried ($MgSO_4$). After removal of the solvent the residue was chromatographed on a silica-gel column with dichloromethane as eluant to give the *title compound* (**21**) (255 mg, 81.1%) as yellow plates, m.p. 160 °C (decomp.) (from hexane–dichloromethane); *m/z* 236 ($M^{+\bullet}$, 64%), 208 ($M^{+\bullet} - CO$, 100), 180 ($M^{+\bullet} - 2CO$, 47), and 152 ($M^{+\bullet} - 2CO - C_2H_4$, 20) (Found: C, 80.9; H, 5.2. $C_{16}H_{12}O$ requires C, 81.34; H, 5.12%); $\lambda_{max.}$ 263 (log ε 4.09) and 367 nm (3.74); $\nu_{max.}$ 1 710, 1 670, 1 505, 1 445, and 850 cm^{-1}; $\nu_{max.}(CHCl_3)$ 1 710, 1 670, 1 600, 1 450, and 850 cm^{-1}; δ 2.85—3.52 (4 H, m, 7- and 8-H_2), 3.46 (4 H, s, 1- and 2-H_2), 7.37 (1 H, d, *J* 7.1 Hz, 10-H), 7.47 (1 H, d, *J* 7.4 Hz, 3-H), 7.50 (1 H, d, *J* 7.1 Hz, 9-H), and 8.03 (1 H, d, *J* 7.4 Hz, 4-H).

(*b*) To a vigorously stirred THF (15 ml) solution of the bisthioacetal (**19**) (192 mg, 0.61 mmol) was rapidly added a solution of mercury(II) perchlorate (584 mg, 1.22 mmol) in THF (15 ml). After one min the reaction was quenched by the addition of water and the reaction mixture was extracted with dichloromethane. The extract was washed with water and dried ($MgSO_4$). After removal of the dichloromethane the residue was chromatographed on a silica-gel column with dichloromethane as eluant to give the α-diketone (**21**) (63 mg, 43.6%), m.p. 150 °C (decomp.) as yellow plates (from hexane–dichloromethane).

(*c*) To a heated and stirred solution of the ketone (**18**) (200 mg, 0.90 mmol) in absolute ethanol (30 ml) was added dropwise a solution of selenium(IV) oxide (101 mg, 0.91 mmol) in absolute ethanol (5 ml) during 30 min. The mixture was gently refluxed for a further 5 h during which time selenium was deposited. The precipitate was filtered off and the ethanol was removed under reduced pressure. The residual red oil was chromatographed on a silica-gel column with dichloromethane as eluant to give the α-diketone (**21**) (50 mg, 23.5%), m.p. 150 °C (decomp.), and the ketone (**18**) (40 mg, recovery). Purification of the required ketone (**21**) prepared in this manner was difficult.

1,2,5,6-*Tetrahydroacenaphtho*[5′,6′:3,4,5]*cyclohepta*[1,2-b]-*quinoxaline* (**24**).—A mixture of the α-diketone (**21**) (53 mg, 0.23 mmol), *o*-phenylenediamine (29 mg, 0.27 mmol), ethanol (8 ml), THF (2 ml), and one drop of pyridine was refluxed for 1 h. The reaction mixture was extracted with dichloromethane and the extract was washed with water and dried ($MgSO_4$). After the solvent was removed the residue was chromatographed on a silica-gel column with dichloromethane as eluant to give the *title compound* (**24**) (56 mg, 81%) as yellow needles, m.p. 203.5—204.5 °C (from hexane–dichloromethane) (Found: C, 85.6; H, 5.5; N, 8.8. $C_{22}H_{16}N_2$ requires C, 85.69; H, 5.23; N, 9.08%); $\nu_{max.}$ 1 605, 1 480, 850, and 760 cm^{-1}; δ 3.51 (4 H, s), 3.17—3.78 (4 H, m), and 7.17—8.73 (8 H, m, ArH).

7,8-*Dihydrocyclohept*[fg]*acenaphthylene*-5,6-*dione* (**22**) *and Cyclohept*[fg]*acenaphthylene*-5,6-*dione* (*Acepleiadylene*-5,6-*dione*) (**2**).—A mixture of the α-diketone (**21**) (192 mg, 0.81 mmol), DDQ (517 mg, 2.05 mmol), and dry benzene (5 ml) was refluxed for 12 h. The insoluble hydroquinone was filtered off and the filtrate was chromatographed on a silica-gel column with dichloromethane as eluant to give the *title dihydro compound* (**22**) (24 mg, 12.8%) as orange-red needles, m.p. 150 °C (decomp.); *m/z* 234 ($M^{+\bullet}$, 19%), 206 ($M^{+\bullet} - CO$, 50), 178 ($M^{+\bullet} - 2CO$, 100), and 150 ($M^{+\bullet} - 2CO - C_2H_4$, 27); $\lambda_{max.}$ 274sh (log ε 3.50) and 345 nm (3.65); $\nu_{max.}$ 1 705, 1 670, 1 600, 1 480, 1 440, and 850 cm^{-1}; $\nu_{max.}(CHCl_3)$ 1 710, 1 675, 1 605, 1 485, 1 445, and 855 cm^{-1}; δ 2.88—3.66 (4 H, m, 7- and 8-H_2), 7.00 (1 H, d, *J* 5.5 Hz, 2-H), 7.16 (1 H, d, *J* 5.5 Hz, 1-H), 7.42 (1 H, d, *J* 7.3 Hz, 10-H), 7.58 (1 H, d, *J* 7.3 Hz, 9-H), 7.75 (1 H, d, *J* 7.3 Hz, 3-H), and 8.04 (1 H, d, *J* 7.3 Hz, 4-H); and *acepleiadylene*-5,6-*dione* (**2**) (45 mg, 23.7%) as purple needles, m.p. 145 °C (decomp.) [purified by l.p.l.c. on a Lobar column (Lichroprep Si 60, Merck) with dichloromethane as eluant], *m/z* (75.eV) 234 ($M^{+\bullet} + 2$, 0.4%), 233 ($M^{+\bullet} + 1$, 0.9), 232 ($M^{+\bullet}$, 2), 204 ($M^{+\bullet} - CO$, 89), 176 ($M^{+\bullet} - 2CO$, 100), and 150 ($M^{+\bullet} - 2CO - C_2H_2$, 16); $\lambda_{max.}$ 258 (log ε 4.26), 281sh (3.96), 306sh (3.75), 379 (3.96), and 402sh nm (3.92); $\nu_{max.}$ 1 655, 1 635, 1 615, 1 590, 1 480, 1 450, 850, and 745 cm^{-1}; $\nu_{max.}(CHCl_3)$ 1 655, 1 620, 1 595, 1 485, and 865 cm^{-1}; δ 6.35 (1 H, d, *J* 12.9 Hz, 7-H), 6.90 (2 H, s, 1-and 2-H), 7.29 (1 H, d, *J* 12.9 Hz, 8-H), 7.48 (2 H, s, 9- and 10-H), 7.58 (1 H, d, *J* 7.4 Hz, 3-H), and 8.33 (1 H, d, *J* 7.4 Hz, 4-H); δ_C 123.3 (q, C-10b), 124.7 (C-2), 124.8 (C-1), 125.0 (C-7), 129.8 (q, C-10c), 132.0 (q, C-10a), 132.1 (C-10), 132.1 (q, C-2a), 133.0 (C-3), 137.1 (C-9), 138.8 (C-4), 144.5 (q, C-8a), 144.6 (C-8), 147.1 (q, C-4a), 190.6 (q, C-5), and 192.3 (q, C-6) [tentative assignments by analogy with compound (**1**)].

Oxidation of the Dihydroketone (**22**) *with DDQ*.—A mixture of compound (**22**) (21 mg, 0.09 mmol), DDQ (56 mg, 0.22 mmol), and dry benzene (8 ml) was refluxed for 6 h. After removal of the hydroquinone the residue was chromatographed on a silica-gel column to give compound (**2**) (5.5 mg, 26.9%).

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References

1 For leading references, see (*a*) T. A. Turney, in 'The Chemistry of the Quinonoid Compounds,' ed. S. Patai, Wiley, London, 1974, part 2, p. 857; (*b*) L. T. Scott, M. D. Roseboom, K. N. Houk, T. Fukunaga, H. J. Lindner, and K. N. Hafner, *J. Am. Chem. Soc.*, 1980, **102**, 5169; (*c*) J. Tsunetsugu, M. Kanda, M. Takahashi, K. Yoshida, H. Koyama, K. Shiraishi, Y. Takano, M. Sato, and S. Ebine, *J. Chem. Soc., Perkin Trans. 1*, 1984, 1465.

2 N. Acton, D. Hou, J. Schwarz, and T. J. Katz, *J. Org. Chem.*, 1982, **47**, 1011, and references cited therein.

3 V. Boekelheide and J. B. Phillip, *J. Am. Chem. Soc.*, 1963, **85**, 1545; 1967, **89**, 1695: V. Boekelheide and T. Miyasaka, *ibid.*, p. 1709.

4 E. Vogel, A. Alsher, and K. Wilms, *Angew. Chem.*, 1974, **86**, 407.

5 M. Nakagawa, M. Iyoda, and Y. Ohnishi, 41st National Meeting of the Chemical Society of Japan, Higashiosaka, March 1980, Abstr. No. 2K42; 13th Symposium on Nonbenzenoid Aromatic Compounds, Nagoya, October 1980, Abstr. No. C1-12.
6 J. Tsunetsugu, T. Ikeda, N. Suzuki, M. Yaguchi, M. Sato, S. Ebine, and K. Morinaga, *J. Chem. Soc., Chem. Commun.*, 1983, 28.
7 V. Boekelheide and G. K. Vick, *J. Am. Chem. Soc.*, 1956, **78**, 653.
8 A. J. Jones, P. D. Gardner, D. M. Grant, W. M. Litchman, and V. Boekelheide, *J. Am. Chem. Soc.*, 1970, **92**, 2395; 'Nonbenzenoid Aromatics,' ed. J. P. Schneider, Academic Press, New York, 1971, vol. II.
9 B. M. Trost, *J. Am. Chem. Soc.*, 1966, **88**, 853; 1969, **91**, 918; B. M. Trost, in 'Topics in Nonbenzenoid Aromatic Chemistry,' eds. T. Nozoe, R. Breslow, K. Hafner, S. Itô, and I. Murata, Hirokawa Publishing Co., Tokyo, 1973, vol. 1, p. 243.
10 L. F. Fieser and M. A. Peters, *J. Am. Chem. Soc.*, 1932, **54**, 4347.
11 V. Boekelheide, W. E. Langeland, and Chu-Tsin Liu, *J. Am. Chem. Soc.*, 1951, **73**, 2432.
12 Y. Nagao, K. Kaneko, K. Kawabata, and E. Fujita, *Tetrahedron Lett.*, 1978, 5021.
13 (*a*) S. Berger and A. Rieker, in 'The Chemistry of the Quinonoid Compounds,' ed. S. Patai, Wiley, London, 1974, part 2, p. 737; (*b*) G. J. Gleicher, *ibid.*, part 1, p. 18; (*c*) J. Q. Chambers, *ibid.*, part 2, p. 737.
14 I. Murata, K. Yamamoto, H. Hirotsu, and M. Morioka, *Tetrahedron Lett.*, 1972, 331.
15 B. M. Trost, G. M. Bright, C. Frihart, and D. Britteri, *J. Am. Chem. Soc.*, 1971, **93**, 737.
16 J. Tsunetsugu, M. Sato, M. Kanda, M. Takahashi, and S. Ebine, *Chemistry Lett.*, 1977, 885.
17 M. L. Josién and N. Fuson, *Bull. Soc. Chim. Fr.*, 1952, **19**, 389; *C. R. Hebd. Séances, Acad. Sci.*, 1952, **234**, 1680; M. L. Josién, N. Fuson, J. M. Lebas, and T. M. Gregory, *J. Chem. Phys.*, 1953, **21**, 331.
18 G. Ashworth, D. Berry, and D. C. C. Smith, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2995.
19 W. G. Schneider, H. J. Bernstein, and J. A. Pople, *Can. J. Chem.*, 1963, **41**, 966.
20 I. Murata and K. Nakasuji, *Tetrahedron Lett.*, 1973, 47.
21 G. C. Levy, R. L. Lichter, and G. L. Nelson, 'Carbon-13 Nuclear Magnetic Resonance Spectroscopy,' 2nd edn, Interscience, Chichester, 1980; J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, New York and London, 1972.
22 E. J. Moriconi, B. Racoczy, and W. F. O'Conner, *J. Org. Chem.*, 1962, **27**, 2772.
23 Recently, two-electron reduction within a single voltammetric wave for a polyquinone have been also reported; D. E. Wellman and R. West, *J. Am. Chem. Soc.*, 1984, **106**, 355.
24 R. Breslow, D. Maruyama, R. Drury, and F. Sondheimer, *J. Am. Chem. Soc.*, 1974, **96**, 249.

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