The Synthesis and Electrochemistry of Acepleiadylene-5,6-dione and Acepleiadylene-5,8-dione

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The acepleiadylenediones (**1**) and (**2**) have been synthesized and their reduction potentials determined by cyclic voltammetry show that they may be regarded as [14]annulenediones with an unexpectedly high quinone character.

Several [14]annulenediones have been prepared.[1] We now report the synthesis and electrochemical study of two new [14]annulenediones, acepleiadylene-5,6-dione (**1**) and -5,8-dione (**2**); these may be regarded as higher analogues of pyracycloquinone (**3**),[2a] and a comparison of the characteristics of (**1**) and (**2**) with those of the [12]annulenedione (**3**), which has been studied in detail,[2a] should be of interest.

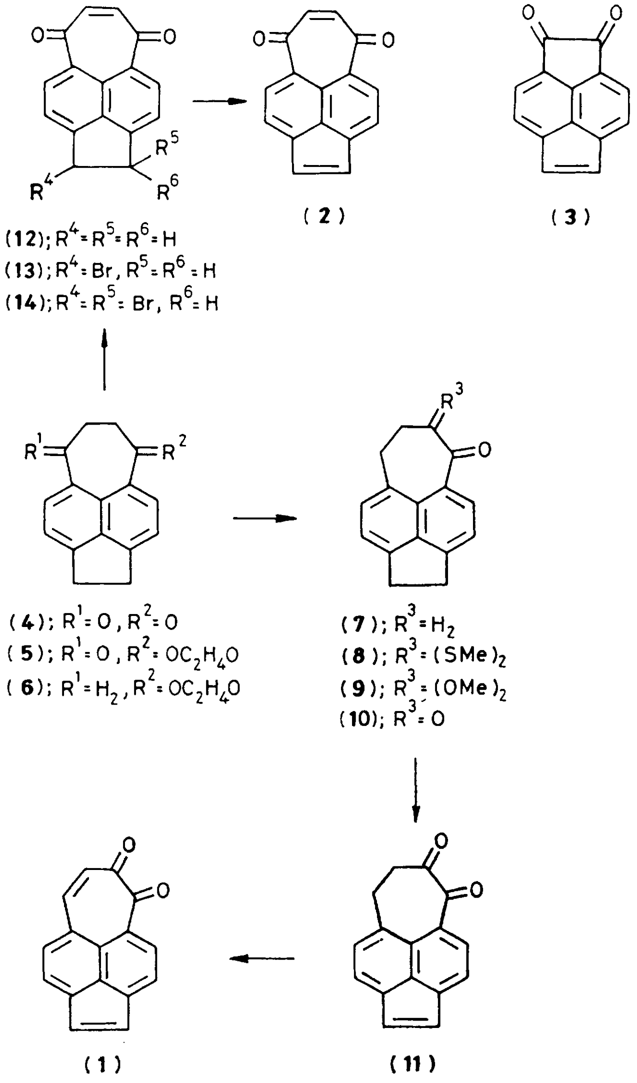
The diones (**1**) and (**2**) were synthesized by stepwise oxidation of the cyclohepta-acenaphthenedione (**4**)[3] (Scheme 1). Compound (**1**) was obtained as purple–red needles, m.p. 145 °C (decomp.) (from benzene–hexane),† and was stable for only a few days in the dark; (**2**) was also obtained as purple–red needles, m.p. 186 °C (decomp.) (from benzene–hexane), but was apparently stable in the dark. Compounds (**1**) and (**2**) showed weak ($M^+ + 2$) ions in their mass spectra,[4c] carbonyl absorptions at low wavenumbers [ν_{max} ($CHCl_3$) 1655 and 1620 cm^{-1} for (**1**) and 1633 cm^{-1} for (**2**)] in their i.r. spectra, and low-field carbonyl carbon resonances [δ (50 MHz, $CDCl_3$) 190.6 (C-5) and 192.3 p.p.m. (C-6) for (**1**) and δ 189.3 p.p.m. (C-5 and C-8) for (**2**)] in their ^{13}C n.m.r. spectra;[4c] these data are in complete accord with the structures shown and also suggested that they had considerable quinone character.

The electrochemical reduction of the diones (**1**) and (**2**) and various reference compounds, was examined by cyclic voltammetry; the potentials found are in Table 1. In all cases good reversible behaviour was observed. 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 (**1**)‡ is higher than that for *p*-benzoquinone, and comparable with the value for *o*-benzoquinone.[4a] Similarly E_1 for (**2**) is higher§ than that

Table 1. Electrochemical reduction potentials.[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 (**1**)	−0.29	−0.29	0.00	−0.58
p-Benzoquinone	−0.40	−1.17	0.77	−1.57
Dione (**2**)	−0.50	−0.84	0.34	−1.34
1,4-Naphthoquinone	−0.59	−1.40	0.81	−1.99
Dione (**3**) (in Me_2SO)[2b]	−0.738	−1.305	0.567	−2.043

[a] Potentials (in V) were determined by cyclic voltammetry in a standard three-electrode cell equipped with a standard calomel electrode as reference; 22.5 ± 0.5 °C in dry dimethylformamide with 0.1 M-$Bu^n_4NClO_4$ under nitrogen; scan rate, 100 mV/s.



Scheme 1. (**4**)→(**5**); $HOCH_2CH_2OH$, *p*-$MeC_6H_4SO_3H$ in benzene, reflux, 4 days, 76%; (**5**) → (**6**); 80% NH_2NH_2, KOH in diethylene glycol, 190 °C, 2.5 h, 75%; (**6**) → (**7**); 6M-HCl in ether, room temp., 4.5 h, 82%; (**7**) → (**8**); methyl 2-nitrophenyl disulphide, NaH in tetrahydrofuran (THF),[9] room temp., 14 h, 84%; (**8**) → (**9**); $Tl(NO)_3 \cdot 3H_2O$ in MeOH,[9] room temp., 1.5 h, 75%; (**9**) → (**10**); 4M-HCl in THF, room temp., 3 h, 81%; (**8**) → (**10**); $Hg(ClO_4)_2 \cdot 3H_2O$ in THF, room temp., 5 min, 44%; (**10**) → (**11** + **1**); dichlorodicyanobenzoquinone (DDQ) in benzene, reflux, 12 h; 13% of (**11**) and 24% of (**1**); (**11**) → (**1**); DDQ in benzene, reflux, 12 h, 27%; (**4**) → (**12**); Br_2 in $CHCl_3$, −10 °C, 140 min, then 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 150 min, 41%; (**12**) → (**13**) + (**14**); *N*-bromosuccinimide in CCl_4, reflux, 30 min, 71% of (**13**) and 12% of (**14**); (**13**) → (**2**); DBU in $CHCl_3$, room temp., 17 min, 43%; (**14**) → (**2**); KI in acetone, reflux, 4 h, 60%.

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† All new compounds gave satisfactory microanalytical and spectral data in agreement with the assigned structures.

‡ Two-electron reduction of (**1**) seemed to occur. Only one pair of oxidation–reduction waves was observed. The peak current for the reduction wave (*ca.* 150 μA) was larger than that for (**2**) (*ca.* 120 μA) and the area for the reduction wave was equal to that of the sum of the two reduction waves for (**2**).

§ With a few exceptions, fusion of a benzene ring to a basic quinone unit tends to lower the E_1 value of the system.[4a,4b]

for 1,4-naphthoquinone, and the E_1 values for both (**1**) and (**2**) seem to be considerably higher than those for the isomeric pyrenequinones.[4b,5] The potential difference ($E_1 - E_2$), on a simple approximation, reflects the electrostatic repulsion of the two electrons which enter the same LUMO successively and the fact that ($E_1 - E_2$) for (**1**) is zero is also surprising, although the observed ($E_1 - E_2$) values are often smaller for nonbenzenoid quinones than for benzenoid quinones of similar size.[6,1b] A small ($E_1 - E_2$) value was also obtained for (**2**). Since the sum of 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 (**1**) is striking; it is much more positive than the value for *p*-benzoquinone and even approaches the value for *o*-chloranil, a strong oxidizing reagent. Similar comments apply to the ($E_1 + E_2$) value for (**2**), but the effect is less marked.

The values of E_1, E_2, and ($E_1 + E_2$) for (**1**) and (**2**) are more positive than those for (**3**), which suggests that the pyracyclene (**3**) is unstable as a [12]annulene,[2,7] whereas the acepleiadylenes (**1**) and (**2**) are stable as [14]annulenes.[8] We therefore conclude from the electrochemical and spectral data that (**1**) and (**2**) have a high quinone character and may be regarded as [14]annulenediones with a vinyl cross-link.¶

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¶ These compounds could be considered to be quinones related to the corresponding [14]annulenes in the same way that benzoquinone is related to benzene.