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Structural Dependence in a One-electron Transfer Process: Naphthalene *peri* Ketones[1)]

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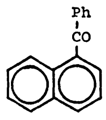
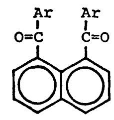
Synopsis. The cyclic voltammetry of several naphthalene *peri* ketones was carried out in anhydrous DMF containing TBAP. The cathodic peak potential for carbonyl reduction was found to be shifted toward a more anodic potential when carbonyl, oxygen, and sulfur groups were present in the *peri* position. The controlled potential electrolysis of *peri* diketones gave an intramolecular coupling product *via* a bis-anion radical.

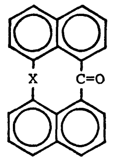
We have been exploring the relation between the oxidation-reduction potentials and the molecular geometry.[1,2)] It is particularly interesting to know how proximity effects influence an electron-transfer process. Since the *peri* positions in a naphthalene nucleus are only 2.4—2.5 Å apart,[3)] a series of those compounds with peri substituents will serve as good model substances for such studies. We examined the cyclic voltammetry (CV) of several naphthalene *peri* ketones in an aprotic solvent in order to elucidate the effect of the *peri* substituents on the carbonyl reduction.



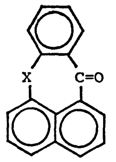
1



2, Ar=Ph
3, Ar=α-naphthyl



4, X=CO
5, X=O
6, X=S



7, X=CH_2
8, X=CO

The *peri* ketones used in the present study are **1**—**8**. The CV measurements were carried out in anhydrous DMF, containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte. The results are summarised in Table 1. For those compounds that gave a reversible voltammogram, such as **1** and **8**, the CV measurements were carried out at various scanning speeds. The results are shown in Table 2, together with several electrochemical parameters.

1-Benzoylnaphthalene (**1**) exhibited a quasi-reversible wave at $E°=-1.71$ V *vs.* SCE. The peak-to-peak potential difference, $E_{pc}-E_{pa}$, was 220 mV at the scanning rate of 500 mV/s, but it became much smaller for lower scanning rates, which improve the reaction reversibility (Table 2). The current ratio, i_{pc}/i_{pa}, was nearly equal to unity. An interpretation that the reversible couple may correspond to a one-electron transfer process was derived by calculating *n* by using Randles-Cevcik equation[4)] (Table 2). When the scanning range was further extended to the cathodic side, another cathodic peak appeared at −2.5 V. For this second peak, however, no corresponding anodic peak was observed by reversed scanning. The addition of methanol caused E_{pc} to shift to the anodic side (Table 1). These results are considered to be specific for an aromatic ketone which has undergone succesive electron-transfer steps to give an anion radical and a dianion.[5)]

Compared with the monobenzoyl compound **1**, the *peri* diketones **2**, **3**, and especially **4** showed E_{pc}'s at an appreciably anodic potential. For example, the E_{pc} for **4** was −1.52 V compared with that of −1.8 V for **1**. These compounds also showed less reversible waves, as was assumed from the high i_{pc}/i_{pa} ratio of

TABLE 1. CYCLIC VOLTAMMETRY DATA FOR COMPOUNDS **1**—**8**[a)]

Compound	E_{pc}/V	E_{pa}/V	$E°$/V	$(E_{pc}-E_{pa})$/mV	i_{pc}/i_{pa}	Additive
1[b)]	−1.82	−1.60	−1.71	220	1.1	
1[c)]	−1.78	−1.61	−1.70	170	1.8	
	−2.50	—	−2.42[f)]			
1[c)]	−1.80	−1.60	−1.70	200	1.7	MeOH
	—	—				
2	−1.67	−1.50[e)]	−1.59	170	2.5	
3	−1.60	−1.52[e)]	−1.56	80	3.2	
4	−1.52	−1.44	−1.48	80	2.3	
5	−1.40	−1.32	−1.36	80	2.0	
6[d)]	−1.46	−1.34	−1.40	120	1.5	
7	−1.54	−1.42	−1.48	120	1.2	
8	−1.30	−1.08	−1.19	220	1.1	
	−1.86	−1.62	−1.74	240	1.1	
8	−1.31	−1.10	−1.21	210	1.4	MeOH
	−1.86	−1.54	−1.70	320	1.5	

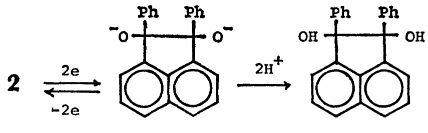
a) Determined in DMF-TBAP (0.1 M) at the scan rate of 500 mV/s using the method described in Ref. 2. Scanning potential range; 0—−2.0 V *vs.* SCE. $E°=E_{pc}+(E_{pc}-E_{pa})/2$. b) Potential range; 0—−2.2 V. c) Potential range; −0.5—−2.7 V. d) Determined in DMSO-TBAP (0.1 mol dm^{-3}). e) Shoulder. f) The potential at which $i=0.85\ i_{pc}$.

Table 2. Slow cyclic voltammetry data and electrochemical parameters for compounds **1** and **8**[a)]

Compound	Scan rate / mV/s	$(E_{pc}-E_{pa})$/mV		i_{pc}/i_{pa}		$i_{pc}/v^{1/2}$		n	
1	10	100		1.0		24		0.93	
	25	130		0.9		19		0.79	
	50	160		1.0		19		0.81	
	100	190		1.2		22		0.87	
	250	250		1.2		19		0.81	
8	25	120	140	1.3	1.3	24	24	0.90	0.90
	50	140	150	1.3	1.2	24	21	0.91	0.91
	100	180	190	1.2	1.3	23	22	0.88	0.84
	250	220	250	1.2	1.3	22	19	0.84	0.77

a) Determined in DMF-TBAP (0.1 mol dm^{-3}) at 25 °C. For the calculation of the n value, the Randles-Cevcik equation was used assuming $D=7.9\times10^{-7}$ cm^{-2}/s (benzophenone); see Ref. 3.

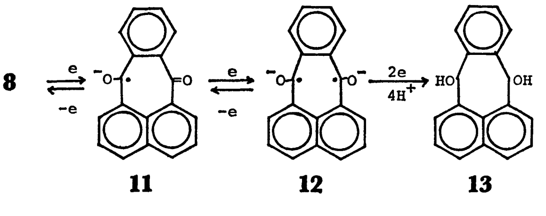
2.3—3.2. The results can be well interpreted to indicate a two-electron reduction, giving the pinacolate dianion **9**, since the intramolecular radical coupling of the bis-anion radical is geometrically favored. In fact, an intramolecular coupling product, **10**, was obtained by the controlled potential electrolysis of **1** at −2.0 V in ethanol containing potassium hydroxide, using a lead cathode. Similar results using a mercury cathode in aq ethanol have been reported.[6)] The unique geometry of **4** is assumed to be responsible for the anodic shift of the E_{pc}. It is considered that the steric strain in **4** caused by the steric interaction between the two parallel carbonyl groups is relieved by its being reduced to a dianion analogous to **9**.



9 **10**

The presence of hetero atoms, such as oxygen or sulfur, at the peri position was found to cause a further anodic shift of the cathodic waves. Both **5** and **6** showed $E°$ at −1.4 V, the $\Delta E°$ from **1** being 0.3 V, reflecting the intramolecular stabilization effect of the hetero atom toward the one-electron reduction of a nearby carbonyl group.

Unlike **2**, **3**, and **4**, 7,12-pleiadenedione (**8**) showed two reversible redox couples at −1.2 and −1.7 V, each corresponding to a one-electron transfer (Table 2). The controlled potential electrolysis of **8** gave a diol, **13**. In **8**, the intramolecular coupling of the bis-anion radical is sterically disfavored and results in a two-step reduction. It became evident that pleiadenone, **7**, was more readily reduced than benzoylnaphthalene, **1**.



11 **12** **13**

Experimental

CV Measurements. The cyclic voltammetry was carried out in anhydrous DMF containing TBAP (0.1 mol dm^{-3}) using a two-compartment cell equipped with a nitrogen bubbler and SCE. A platinum inlay electrode (Beckman 32273) and a platinum wire were used as the working and counter electrodes respectively. The surface area of the working electrode was 0.204 cm^2. The electrochemical equipment used was the same as that described before.[2)]

Materials. The preparation of the *peri* ketones **1**—**8** has been reported elsewhere.[7)]

Controlled Potential Electrolysis of 2 and 8. A solution of 476 mg (0.96 mmol) of **2** in 200 ml of 2 mol dm^{-3} ethanolic potassium hydroxide was electrolyzed at −2.0 V using a lead cathode. The electrolysis was continued until 9 F/mol of electricity had been consumed. Compound **10** was then obtained in a 27.3% yield by chromatography on alumina eluted with hexane–benzene.

When compound **8** was similarly electrolyzed at −2.0 V, a 17% yield of the diol, **13**, was obtained; this was identical with the authentic sample (mp 197—200 °C), prepared by the sodium borohydride reduction of **8**.[8)] The electricity required was 4 F/mol.

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