Cathodic Reduction of Ethyl α-Bromonaphthalene-1- and -2-acetate: Electrochemical Synthesis and Voltammetric Behaviour of *meso-* and DL-Diethyl 2,3-Di-1- and -2-naphthylsuccinate

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Diethyl 2,3-dinaphthylsuccinates **(5)**—**(8)** can be prepared through electrochemical reduction of ethyl α-bromonaphthalene-1- and -2-acetate **(3)** or **(4)** (ABr) in DMF–0.1M-Et$_4$NClO$_4$ at a vitreous carbon electrode. These dinaphthylsuccinates **(5)**—**(8)** (A-A) are good model systems for the study of electron transfer to molecules containing two identical redox centres. Cyclic voltammetry shows that dimeric species A-A are reduced at more positive potentials than the corresponding AH compound; *meso*-diethyl 2,3-di-2-naphthylsuccinate **(7)** is reduced at a slightly more positive potential than the corresponding DL-succinate **(8)**. The 1-naphthyl derivatives are more easily reduced than the corresponding 2-naphthyl compounds, the difference being larger between bromoesters **(3)** and **(4)**.
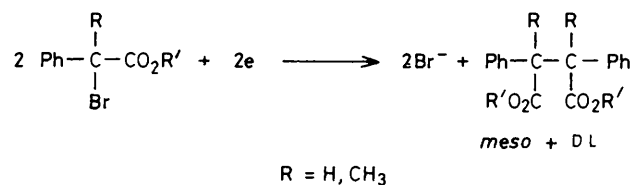
Previous studies[1–3] of the electroreduction of α-bromo-α-phenylalkanoic esters have led to the corresponding diesters. This contribution seeks to establish the ways in which changing from phenyl to 1- and 2-naphthyl will affect the electrochemistry of aryl α-bromoesters, giving, at the same time, a method for preparing the apparently unknown diethyl 2,3-dinaphthylsuccinates. These last compounds, as well as the non-brominated esters (1) and (2), were expected to be reduced in the potential range available. The following questions were appropriate. (i) What is the effect of changing the position from 1 to 2 upon the electroreduction of ethyl naphthaleneacetate [compounds (1) and (2)]? (ii) What is the corresponding difference between compounds (3) and (4)? (iii) What is the difference, in terms of electrochemical behaviour, between the monomeric compounds (1) or (2) and the corresponding dimers (5) and (6) or (7) and (8), respectively? (iv) What is the difference, if any, between the reduction potentials of the *meso-* and the corresponding DL compounds, *i.e.* between (5) and (6) or (7) and (8)?

Experimental

Materials.—Ethyl naphthalene-1-acetate (1)[4a–d] was prepared through hydrolysis and esterification of naphthalene-1-acetonitrile (Fluka) (50 g, ca. 0.2 mol) by refluxing with concentrated sulphuric acid (45 ml) and 95% ethyl alcohol (140 ml) for ca. 7 h, obtaining ester (1) (42 g, ca. 84%) as an oil. Its purity was checked by reversed-phase h.p.l.c. with CH$_3$CN–H$_2$O (83:17) as solvent, flow rate 35 ml min^{-1}, using u.v. detection at 253.7 nm. The retention time t_R was 3 min 24 s, δ$_H$(neat) 0.8 (3 H, t, J 7.5 Hz, CH$_3$), 3.8 (2 H, s, CH$_2$), 3.9 (2 H, q, J 7.5 Hz, CH$_2$), and 6.9—8.0 (7 H, m, ArH).

Ethyl naphthalene-2-acetate (2)[4d,5a,b] was obtained through esterification of naphthalene-2-acetic acid (Fluka, 11.2 g, ca. 0.06 mol) with ethyl alcohol (12 ml), concentrated H$_2$SO$_4$ (0.3 ml), and benzene (40 ml). By standard procedures, ester (2) (13.5 g, 100%) was obtained, m.p. 30 °C (lit.,[5] 30 °C), δ$_H$(CCl$_4$) 1.0 (3 H, t, J 7 Hz, CH$_3$), 3.5 (2 H s, CH$_2$), 3.9 (2 H, q, J 7 Hz, OCH$_2$), and 7.1—7.9 (7 H, m, ArH).

Ethyl α-bromonaphthalene-1-acetate (3). Treatment of the ester (1) (40 g, ca. 0.14 mol) with N-bromosuccinimide (Fluka, 35 g, ca. 0.19 mol) in the usual way gave the bromoester (3)[6] (70%) as a viscous liquid, δ$_H$(CCl$_4$) 1.0 (3 H, t, J 7.5 Hz, CH$_3$), 4.06 (2 H, q, J 7.5 Hz, CH$_2$), 6.16 (1 H, s, CH), and 7.0—8.2 (7 H, m, ArH).

$$2\ Ph-\underset{\underset{Br}{|}}{\overset{\overset{R}{|}}{C}}-CO_2R' \ +\ 2e\ \longrightarrow\ 2Br^- \ +\ Ph-\underset{\underset{R'O_2C}{|}}{\overset{\overset{R}{|}}{C}}-\underset{\underset{CO_2R'}{|}}{\overset{\overset{R}{|}}{C}}-Ph$$

$$meso\ +\ DL$$

$$R = H, CH_3$$

Scheme. Solvent DMF, glassy carbon electrode
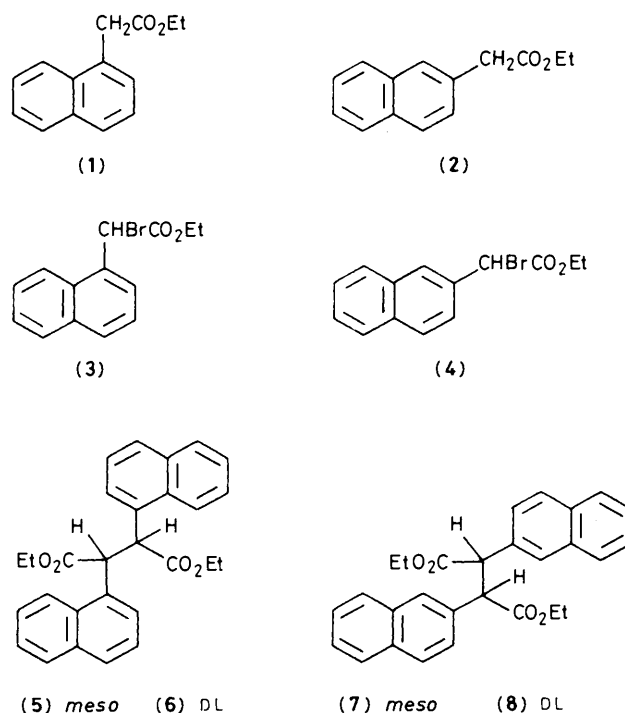
Ethyl α-bromonaphthalene-2-acetate (4). Bromination of the ester (2) (12 g, 0.056 mol) with NBS (9.5 g, 0.058 mol) in the usual way gave bromoester (4) (ca. 70%) as a solid, m.p. 79—80 °C (from CCl$_4$); δ$_H$ 1.2 (3 H, t, J 7.5 Hz, CH$_3$), 4.1 (2 H, q, J 7.5 Hz, CH$_2$), 5.3 (1 H, s, CH), and 7.2—7.9 (7 H, m, ArH).

Dimethylformamide was purified in the usual way[1–3] and

stored in the dark over molecular sieves 4A. All other materials were Fluka or Aldrich and of the best purity; solvents used in the h.p.l.c. experiments were of h.p.l.c. grade (Fluka or Merck).

Apparatus and General Procedures.—They were the same as those described previously.[1-3] H.p.l.c., used mainly to separate the mixtures of *meso* and DL dimers, was performed with a Perkin-Elmer LC 2/2 instrument, equipped with a Perkin-Elmer LC 75 u.v. detector and a Perkin-Elmer 7105 sample injector. The columns used were (a) reversed-phase Perkin-Elmer $C_8/10$, 25 × 0.46 cm, 10μ or (b) SiO_2 Hibar, Merck Si 60, 250 × 10 mm, 7μ for analytical and preparative experiments respectively. M.p.s were determined with a Kofler apparatus and are uncorrected. All potentials are quoted *versus* a saturated calomel electrode.

Constant-potential Electrolysis of Ethyl α-Bromo-1-naphthyl-acetate (3).—The experiment was repeated three times, with 1.44 (5 × 10⁻³), 3.19 (1 × 10⁻²), and 0.98 g (3.3 × 10⁻³ mol) bromoester (3). In each run, compound (3) was dissolved in DMF (100 ml) containing $0.1M-Et_4NClO_4$ and electrolysed on a reticulated vitreous carbon (r.v.c.) electrode at a constant potential of − 1.8 V, until the current dropped to *ca.* 2 mA. The solvent was evaporated under vacuum and the products extracted continuously with water and benzene. The organic fraction, after removing the solvent and drying (Na_2SO_4), gave 850 mg (80), 1.9 g (90%), and 530 mg (75%) of a mixture of products in the first, second, and third runs respectively. Monoester (1) and the isomeric diesters (5) and (6) were present in significant percentages in each mixture (n.m.r.). Minor products were detected only after column chromatography $(SiO_2, 180 × 50 cm,$ prepared in hexane, with $CHCl_2$-hexane as eluant) and in variable amount. Thus column chromatography was effective in separating monoester (1) from diesters (5) + (6), but even in the best situations each isomer was contaminated (n.m.r.) by the other. Analytically pure *meso*-diester (5) and DL-diester (6) were obtained by subjecting the various (5) + (6) mixtures to preparative h.p.l.c. The products obtained by column chromatography were as follows. Run 1: the first eluted product $(V_{CHCl_3}/V_{hexane} 10:80$—30:70) was monoester (1), followed by a small amount (*ca.* 10 mg) of a compound with $\delta_H(CCl_4)$ 1.2 (6 H, t, *J* 7 Hz, 2 × CH_3), 4.2 (4 H, q, *J* 7 Hz, 2 × OCH_2),6.8(2H,s,2 × CH),and7.2—9.2(12H,m,ArH);*m/e* 426 (M^+, 1%), 384, 213 (*M/2*, 5%), 185, 157, 156, 155 (100), 141, and 127. With V_{CHCl_3}/V_{hexane} 50:50 we obtained diester (5) with traces of (6) followed by (6) with traces of (5). Finally, several fractions containing unidentified products in small quantities were obtained. Run 2: the first eluted product had $\delta_H(CCl_4)$ 1.43 (3 H, t, *J* 7 Hz, CH_3) 4.4 (2 H, q, *J* 7 Hz, OCH_2), 7.2—8.2 (6 H, m, ArH), and 9.0 (1 H, m, ArH); *m/e* 200, 172, 155, and 127, consisting of ethyl naphthalene-1-carboxylate. Elution with pure $CHCl_3$ gave compound (5), followed by a mixture of (5) and (6) (1:2), which was separated by preparative h.p.l.c. It was surprising that no monoester (1) was found in this run. In the third run, no column chromatography was performed on the mixture of products; n.m.r. showed that it contained 35% (1), 25% (5), and 40% (6). This mixture was dissolved in benzene and crystallised from CCl_4, giving a crystalline mixture (1:1) of (5) and (6), m.p. 130—165 °C. This mixture was separated by h.p.l.c. (preparative t.l.c. was unsuccessful in this respect).

meso-Diethyl 2,3-di-1-naphthylsuccinate (5). This was obtained as a white solid, m.p. 177—180 °C; $\delta_H(CCl_4)$ 0.6 (6 H, t, *J* 7.5 Hz,2 × CH_3), 3.53 (4 H, q, *J* 7.5 Hz, 2 × OCH_2), 5.45 (2 H, s, 2 × CH), and 7—8.6 (14 H, m, ArH). The signals at δ 3.53 and 0.6 are to be attributed to the αα′-(ethoxycarbonyl) CH_2 and CH_3 respectively and are characteristic* of the *meso*- structure;[1-3] *m/e* 426 (M^+, 1%), 258 (19), 228 (5), 214 (13), 185 (23), 157 (64), and 155 (100) and appropriate peaks at lower *m/e*
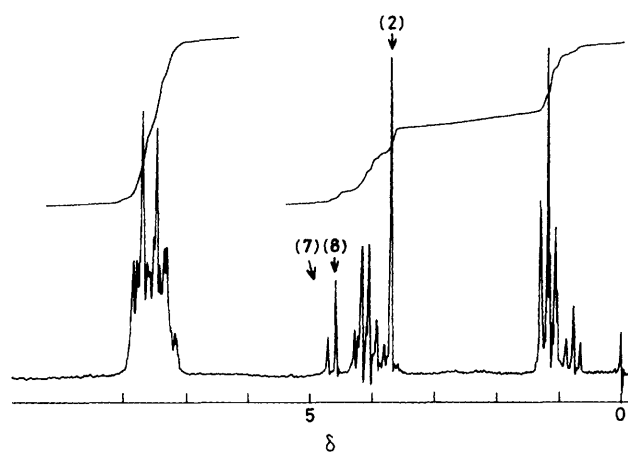

Figure 1. 60 MHz ^1H N.m.r. spectrum (in $CDCl_3$) of (2) + (7) + (8) obtained from controlled-potential electrolysis of bromoester (4) in DMF containing $0.1M-Et_4NClO_4$ as supporting electrolyte. *E* − 1.8 V. Reticulated vitreous carbon electrode. δ *versus* internal Me_4Si

Table 1. Relative yields of dimers A-A and naphthylacetic ester AH obtained in the electrochemical reduction of bromoesters (3) and (4) in DMF containing $0.1M-Et_4NClO_4$. Reticulated vitreous carbon electrode, *E* − 1.8 V

Starting ester	Run	AH (%)	A-A (*meso* + DL) (%)
(3)	1	45	55
	2		100
	3	35	65
(4)	1	50	50

(Found: *m/e* 426.1832 ± 0.002. $C_{28}H_{26}O_4$ requires *M*, 426.1830).

DL-*Diethyl 2,3-di-1-naphthylsuccinate* (6). This is a white solid, m.p. 149—150 °C; $\delta_H(CCl_4)$ 1.05 (6 H, t, *J* 7.5 Hz, 2 × CH_3), 4.00 (4 H, q, *J* 7.5 Hz, 2 × OCH_2), 5.25 (2 H, s, 2 × CH), and 7—8.2 (14 H, m, ArH); *m/e* 426 (M^+, 4%), 352, 308, 237 (4), 235 (4), 230 (26), 213 (*M/2*, 14), 185 (7), 157 (100), and 155 (12) (Found: *m/e* 426.1842 ± 0.002. $C_{28}H_{26}O_4$ requires *M*, 426.1830).

Constant-potential Electrolysis of Ethyl α-Bromo-2-naphthyl-acetate (4).—Compound (4) (3.22 g, 0.001 mol) dissolved in DMF (100 ml) containing $0.1M-Et_4NClO_4$ was electrolysed at − 1.8 V as in the case of (3), obtaining, after work-up, 75% of a mixture of (2), (7), and (8) (Figure 1) in the ratio *ca.* 50% (2) and *ca.* 50% (7) + (8), with DL-(8) prevailing over *meso*-(7): (8):(7) = 2:1. Crystallization of this mixture of monoester (2) and diesters from CCl_4 furnished (7) + (8) (n.m.r.). Column chromatography of the mother liquor (SiO_2, 500 × 18 mm prepared in $CHCl_3$-hexane 2:8) separated monoester (2) from another crop of (7) + (8) and minor products. The mixtures of (7) + (8) can be separated by preparative h.p.l.c. (SiO_2 column Hibar Merck Si 60, flow rate 20 ml min⁻¹, $CHCl_3$-hexane 82:18, λ 275 nm) giving pure (7) and (8).

meso-Diethyl 2,3-di-2-naphthylsuccinate (7). This had m.p. 190—193 °C (from $CHCl_3$); $\delta_H(CDCl_3)$ 0.8 (6 H, t, *J* 7.5 Hz,

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* $\delta(CH_3)_{DL}$ > $\delta(CH_3)_{meso}$ for the ethoxycarbonyl group; for example in diethyl 2,3-diphenylsuccinate $\delta(CH_3)_{DL}$ 1.17, $\delta(CH_3)_{meso}$ 0.89 (see ref. 1 and references cited therein). Likewise, $\delta(CH)_{DL}$ < $\delta(CH)_{meso}$ for the methine CH: $\delta(CH)_{DL}$ 4.22, $\delta(CH)_{meso}$ 4.37 in the case of diethyl 2,3-diphenylsuccinate.

2 × CH₃), 3.8 (4 H, q, *J* 7.5 Hz, 2 × OCH₂), 4.7 (2 H, s, 2 × CH), and 7.2—8.1 (14 H, m, ArH); *m/e* 426 (M^+, 4%), 380 (*M* − EtOH, 4), 352 (*M* − EtOH − CO, 2), 300 (*M* − naphthyl + H, 8), 279 (*M* − 2 × CO₂Et − H, 7), 256 (*M* − 2 × CHCO₂Et + 2 H, 18), 229 (18), 213 (*M*/2, 36), 195, and 155 (100) (Found: *m/e* 426.1835 ± 0.002. C₂₈H₂₆O₄ requires 426.1830). As in the case of the 1-naphthyl derivative, the *meso*-structure was assigned to this compound on the basis of the signals of the ethoxycarbonyl group in the n.m.r. spectrum.

DL-*Diethyl 2,3-di-2-naphthylsuccinate* (**8**). This had m.p. 146—148 °C (from CHCl₃); δ$_H$(CDCl₃) 1.15 (6 H, t, *J* 7.5 Hz, 2 × CH₃), 4.1 (4 H, q, *J* 7.5 Hz, 2 × OCH₂), 4.5 (2 H, s, 2 × CH), and 7—7.7 (14 H, m, ArH); *m/e* 426 (M^+, 37%), 380 (24), 352 (6), 306 (*M* − 2 × EtOH − CO), 213 (*M*/2, 100), 185 (25), and 157 (12) (Found: *m/e* 426.1838 ± 0.002. C₂₈H₂₆O₄ requires *M*, 426.1830).

Results and Discussion

Cyclic voltammetry of solution of ethyl α-bromonaphthalene-acetates (**3**) and (**4**) on vitreous carbon gave *i*–*E* curves basically consisting of three reduction peaks, as typified in
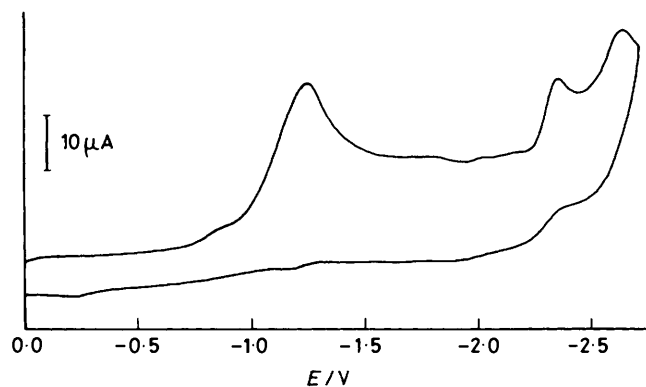

Figure 2. Cyclic voltammogram for bromoester (**4**) (3 × 10⁻³M) in DMF–Et₄NClO₄ (0.1M). Sweep rate 200 mV s⁻¹. Glassy carbon electrode. *E*/V *versus* s.c.e.
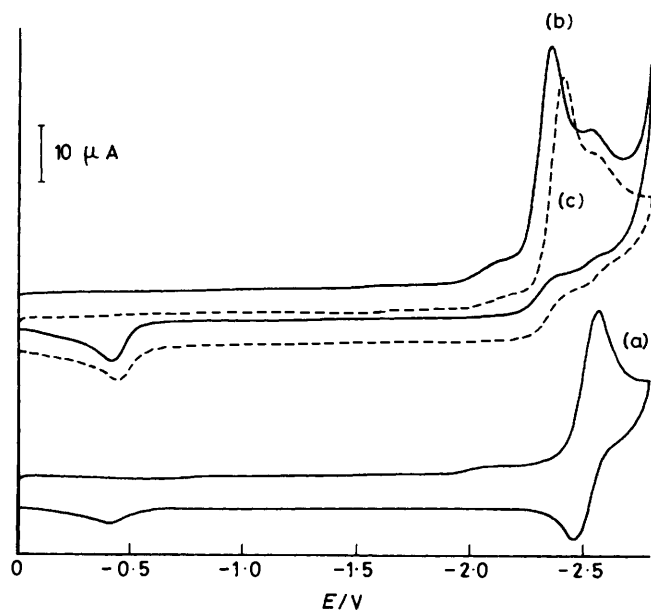
Figure 3. Cyclic voltammograms for (a) ester (**2**), (b) *meso*-diester (**7**), and (c) DL-diester (**8**), all 10⁻³M in DMF–Et₄NClO₄ (0.1M). Sweep rate 200 mV s⁻¹. Glassy carbon electrode. *E*/V *versus* s.c.e.

Figure 2 for the 2-naphthyl derivative. C.p.e. (controlled-potential electrolysis) at a potential selected between the first, more positive, and the second peak results in the near exclusive formation of monoester (**1**) [or (**2**)] and diesters (**5**) + (**6**) [or (**7**) + (**8**)] from (**3**) [or (**4**)], respectively, with n_{app} = 1. Thus, having prepared pure monoester (**1**) [or (**2**)] chemically or electrochemically, and diesters (**5**) and (**6**) [or (**7**) and (**8**)] electrochemically, the voltammetric behaviour of (**5**)—(**8**) can be studied (Figures 3 and 4). Data of interest are collected in Table 2. Thus, the three cathodic peaks (Figure 2) in the forward *i*–*E* curve of (**3**) and (**4**), are to be assigned to ABr reduction, A-A (*meso*-DL) reduction, and AH reduction, respectively, where ABr is the α-bromo-α-naphthyl ester, A-A the corresponding dimer, and AH the corresponding monoester (**1**) or (**2**). It is evident from Figures 3 and 4 and from the data in Table 2, as well as from the results of c.p.e. on the brominated esters, that reduction of ABr results in the formation of the corresponding A-A + AH. Since the peak potentials for reduction of the *meso*-diesters are very close to the peak potentials of the corresponding DL diesters (Table 2), the second peak in the voltammograms of the bromoesters results from the overlapping peaks of *meso* + DL diesters. The third peak in the voltammograms of ABr corresponds to the reduction of AH stemming both from A-A (see voltammetric behaviour of A-A), as well as directly from ABr (see results of c.p.e.). The voltammetric behaviour of A-A and A-Br is now discussed separately.
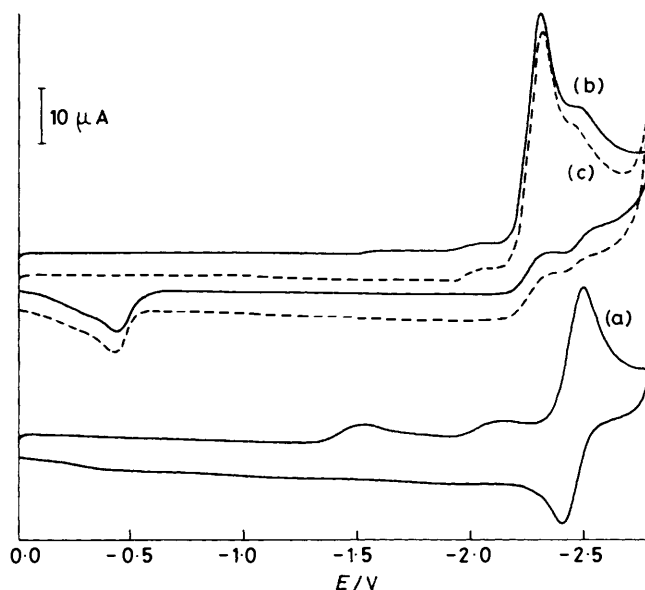

Figure 4. Cyclic voltammograms for (a) ester (**1**), (b) *meso*-diester (**5**), and (c) DL-diester (**6**), all 10⁻³M, conditions as in Figure 3

Table 2. Voltammetric data for reduction of 1- and 2-naphthyl derivatives (**1**)—(**8**) on a vitreous carbon electrode in dimethylformamide containing 0.1M-Et₄NClO₄. Potential sweep rate *v* 0.2 V s⁻¹

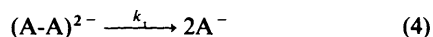| Compound	*C*/mM		E_{pc}/V	
(**1**)	1.0			−2.50
(**3**)	3.0	−1.14	−2.30	−2.49
(**5**)	1.0		−2.31	−2.50
(**6**)	1.0		−2.32	−2.48
(**2**)	1.0			−2.56
(**4**)	3.0	−1.25	−2.36	−2.62
(**7**)	1.0		−2.36	−2.54
(**8**)	1.0		−2.41	−2.53

Electrochemical Reduction of α,α'-*Di*-1- *or* -2-*naphthylsuccinates*.—It is evident from Figures 3 and 4 and from the data in Table 2 that reduction of diesters A-A results in the formation of the corresponding AH; a slow chemical step is interposed between the reduction process of A-A and the subsequent reduction of AH, as revealed by the i_p/v dependence of the AH peak in the voltammograms of A-A. In addition, an anodic peak at E −0.42 V is present, representing the oxidation of the residual anionic intermediate stemming from the reduction of A-A. Thus, electrochemical reduction of diesters (5)—(8) constitutes a pertinent example of what is known about electron-transfer to molecules containing identical multiple (two in this case) redox centres.[7,8] In fact, the voltammetric curves for reduction of the dimeric species (Figure 3b, c, Figure 4b, c) can be compared to the corresponding voltammetric curves (Figure 3a, Figure 4a) for compounds, having only a single reducible centre (the naphthalene nucleus).* The peak and half-peak potentials of (5)—(8) first reduction process are separated by *ca.* 60 mV (25 °C), as expected for a one-electron transfer; on the other hand, a single larger curve is obtained, as expected,[7] from molecules bearing two identical reducible groups. The peak currents obey equation (1)[7] where $i_{p(A-A)}$ is the

$$i_{p(A-A)} = i_{p(AH)}(D_{A-A}/D_{AH})^{1/2} \times 2 \qquad (1)$$

peak current observed with each diester, $i_{p(AH)}$ is the peak current for the corresponding monoester when the concentrations of diester and monoester are the same, the i_p values being determined on the pure compounds, and D_{A-A} and D_{A-H} are the diffusion coefficients for diesters and corresponding monoesters, respectively. The relative values of the diffusion coefficients can be approximately evaluated by equation (2)[7b]

$$D_{A-A}/D_{AH} = (M_{AH}/M_{A-A})^{0.55} = (1/2)^{0.55} \qquad (2)$$

where M_{AH} and M_{A-A} are the masses of the monoester and diester respectively. That is, taking into account the approximate character of equation (2), a 2e process is indicated for each voltammetric peak of (5)—(8). Obviously, this is a direct consequence of the 1e process for each monoester (1) and (2), leading to the anion radical AH·⁻ (Figure 3a, Figure 4a). In other words, accurate calculations and discussions[7] arrive at the same conclusions as the naïve ones: every A-A behaves as two single AHs. Thus the overall electrode reaction, first peak of A-A, results in the 1e electron transfer to every naphthalene centre in the diester molecules, dianion (A-A)²⁻ being formed in this way. The last (A-A)²⁻ of every (5)—(8) seems to be unstable, decomposing into the two corresponding anions (A)⁻, which can abstract a proton from HS, and partly survive until the proper potential for oxidation is reached in the reverse scan [equation (3)—(5)]. In this context, the fact that the peak

$$A\text{-}A + 2e \longrightarrow (A\text{-}A)^{2-} \qquad (3)$$

$$(A\text{-}A)^{2-} \xrightarrow{k_1} 2A^- \qquad (4)$$

$$A^- + HS \xrightarrow{k_2} AH + S^- \qquad (5)$$

potential of A-A is more positive than the corresponding peak potential of the corresponding AH could be the consequence either of some sort of co-operative interaction[7] between

groups in A-A, or of the presence of reaction (4), subsequent to the intrinsically reversible electron transfer (3), or both. That diesters (5)—(8) exhibit such behaviour is entirely consistent with other studies. In fact, cleavages of carbon–carbon single bonds, as a consequence of electrochemical[9] or chemical[10] reduction, have been described. It is not the aim of the present work to discuss alternative pathways, different from those described by equations (3)—(5), which can lead to the same results.

Collecting the most important features of the voltammetric behaviour of diesters (5)—(8), we can observe that (i) dimeric species A-A are reduced at more positive potentials than the corresponding monoesters, the difference being *ca.* 200 mV; (ii) the *meso*-compound (7), *i.e.* the 2-naphthyl substituted diester, is reduced at slightly more positive potential than the corresponding DL compound (8) (Figure 3), whereas in the case of (5) and (6) such difference is hardly detectable (Figure 4); (iii) diesters with 1-naphthyl substituents are reduced at potentials slightly more positive than the corresponding diesters with 2-naphthyl substituents. This difference is also detectable between monoesters (1) and (2), with the same trend.

Electrochemical Behaviour of Ethyl α-*Bromonaphthalene*-1- *and* -2-*acetate*.—(i) The 1-naphthyl α-bromoester is more easily reduced than the 2-naphthyl α-bromoester, the difference being *ca.* 0.1 V at v 0.2 V s⁻¹; it should be remembered that we are dealing with irreversible reductions, with potentials affected by high values of overpotentials on a glassy carbon electrode (*cf.* ref. 1 and references therein). (ii) The reduction potential of the 2-naphthyl α-bromoester is near the potential for reduction of ethyl α-bromophenylacetate on the same electrode:[1,2] $E_p(3) > E_p(4) \approx E_p(\text{PhCHBrCO}_2\text{Et})$. It is possible that relief of steric crowding in going from the 1-naphthyl derivative ABr to the corresponding non-brominated products plays some role in this respect. (iii) Distribution of products obtained by c.p.e. of ABr is highly dependent on experimental conditions, especially if A = 1-naphthylCHCO₂Et. We obtained, at the best, 50% of A-A as isolated products, based on ABr.

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* The small anodic peak at *ca.* −0.4 V in Figure 3a is probably due to traces of A⁻ formed through interaction of AH with electrogenerated base. The very small cathodic peaks at −1.5 and −2.1 V in Figure 4a are tentatively attributed to adsorption phenomena.