Electrochemistry of some Ethyl α-Bromo(Dihalophenyl) Acetates and Electrochemical Synthesis of Diastereoisomeric Diethyl 2,3-Bis (dihalogenophenyl)Succinates[1]

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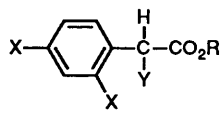
Ethyl α-bromo-2,4- or -3,4-dihalogenophenylacetates (ABr), where halogen = F or Cl, are prepared and electrolysed on reticulated vitreous carbon (RVC) in dimethylformamide containing Et_4NClO_4 (0.1 mol dm^{-3}). Potentiostatic reduction at $E = -1.6$ to -1.8 V *versus* SCE furnishes the corresponding racemic and *meso* succinates (AA) (**13**)–(**16**). Monoesters AH (**5**)–(**8**) are also isolated. An excess of racemic isomer is observed for (**14**), (**15**), and (**16**). Voltammetric experiments show practically no difference between the reduction potentials of the isomeric compounds. Diastereoisomers can be distinguished by NMR spectroscopy, allowing diastereoisomeric excess (de) to be evaluated before isolation of the single products. A mechanism involving radical intermediates A$^{\bullet}$ cannot be excluded. On this basis, the des can be explained by assuming different geometries for A$^{\bullet}$ when the phenyl group bears different substituents.

We recently described studies which led to the syntheses of a number of 1,2-bis(aryl)succinates from the electrochemical reduction of the corresponding ethyl α-bromo arylacetates,[2] equations (1) and (2).

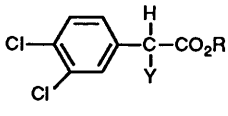
$$ArC(Br)(R)CO_2Et + 2\,e^- \longrightarrow ArC(R)CO_2Et^- + Br^- \quad (1)$$

$$ArC(Br)(R)CO_2Et + ArC(R)CO_2Et^- \longrightarrow (ArC[R]CO_2Et)_2 + Br^- \quad (2)$$
$$meso + DL$$

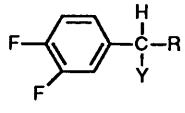
Most of the compounds we obtained in this manner were prepared for the first time.[2b–e] In addition, when Ar = *p*-X-phenyl, (X = F, Cl, Br), we noted[2e] an albeit small but regular diastereoisomeric excess (de) in the formation of the succinates, F > Cl > Br, in favour of the DL derivative. It is known[3] that substitution of fluorine for hydrogen in a molecule will not alter the steric bulk of the molecule significantly, whereas the other properties change dramatically. As a consequence, important biological effects, only partly explained,[3] arise. For this reason, and also for other reasons to be reported below, we decided to prepare compounds (**9**)–(**12**), *i.e.* the α-bromo-2,4- and 3,4-dihalophenylacetates, halogen = F or Cl. Electrochemical reduction of compounds (**9**)–(**12**) (ABr) should give the corresponding succinates (**13**)–(**16**) (AA), and also esters (**5**)–(**8**) (AH). It was anticipated that both monomeric AH and dimeric AA dichloro substituted esters were electrochemically active, albeit at potentials much more negative with respect to the corresponding α-bromo compounds ABr. Clearly, controlled-potential preparative electrolysis allows that the C–Br bond only will be involved in the reduction, when retaining the halo substituent in the phenyl group. In fact, this was the case; in addition, we have found that the difluoro-derivatives AH (**6**), (**8**), and the corresponding AA (**14a,b**), (**16a,b**) were also electrochemically active. Thus, the importance that the experiments should be performed at constant potential, not constant current, is evident, particularly for the chloro- and fluoro-derivatives ABr. We report herein the results of the electrochemical reduction of α-bromoesters (**9**)–(**12**) obtained



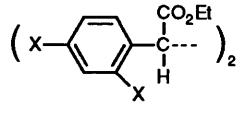
(**1**) X = Cl; Y = R = H (**5**) X = Cl; Y = H; R = Et (**9**) X = Cl; Y = Br; R = Et
(**2**) X = F; Y = R = H (**6**) X = F; Y = H; R = Et (**10**) X = F; Y = Br; R = Et



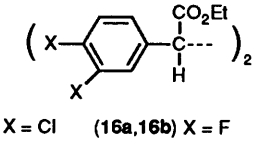
(**3**) Y = R = H (**7**) Y = H; R = Et (**11**) Y = Br; R = Et



(**4**) Y = H; R = CN (**8**) Y = H; R = CO_2Et (**12**) Y = Br; R = CO_2Et



(**13a,13b**) X = Cl (**14a,14b**) X = F **a** = *meso*; **b** = DL



(**15a,15b**) X = Cl (**16a,16b**) X = F **a** = *meso*; **b** = DL

using voltammetric experiments and preparative electrolyses. Some comments regarding the question of diastereoisomeric selectivity as applied to the present case are also presented.

Experimental

Apparatus and Procedures.—^{1}H NMR spectra were recorded at 60 MHz with a Varian EM 360 spectrometer in $CDCl_3$ solutions using $SiMe_4$ as an internal reference. Chemical shifts are expressed in δ(ppm). Mass spectra were recorded with a Balzers QMG 511 spectrometer using the direct inlet system. HPLC experiments were performed with apparatus previously described.[2] Column chromatographic experiments and thin-layer chromatographic separations were of conventional type. Occasionally, flash-chromatography was used, with a Buchi arrangement 681 (pump)–17982 (column) and the appropriate silica gel 60, 70–230 Mesh (Merck). Voltammetric measurements were carried out at ambient temperature with a three-electrode arrangement and using a 473 AMEL apparatus. The working electrode was a vitreous carbon electrode (GC) assembled by AMEL in a form of a flat disc, internal diameter *ca.* 3 mm. This electrode was polished before use by usual methods. The counter electrode was a platinum wire; the reference electrode was an SCE with multiple junctions;[2] its potential was *ca.* −35 mV *vs.* an aqueous SCE. The apparatus used in the preparative electrolyses included a potentiostat AMEL 552, an integrator AMEL 731 and a recorder Perkin-Elmer 561. The cathode compartment of the three electrode cell was separated by the anodic one by a porous glass plug in contact with a gelled solution of Et_4NClO_4 (0.1 mol dm^{-3}) in DMF. The working electrode was a piece of reticulated vitreous carbon (RVC, from ERG, Oakland). The reference electrode was the same as that used in the voltammetric experiments and the counter electrode was a platinum gauze cylinder. Melting points were determined on a Kofler or Büchi apparatus and are uncorrected.

Chemicals.—Solvent dimethylformamide, DMF, purchased from Riedel-de Haen, was purified by treatment with Al_2O_3 followed by distillation under vacuum with retention of the middle fraction only. Tetraethylammonium perchlorate, Et_4NClO_4, was recrystallized from water and dried at 50–60 °C under vacuum for several days. The solutions used in the electrochemical experiments were carefully deoxygenated with UPP-grade nitrogen. The following chemicals were supplied by Aldrich: 2,4-dichloro- and 2,4-difluoro-phenyl acetic acid, 3,4-dichlorophenyl acetic acid, and 3,4-difluorophenyl acetonitrile. Other chemicals and solvents were of the highest purity. Esters (**5**)–(**8**) were prepared from the corresponding acids or nitrile by standard methods. The α-bromoesters ABr (**9**)–(**12**) used as starting compounds in the preparative electrolyses were obtained by treatment of the ethyl esters (**5**)–(**8**) with NBS. The following are representative:

Ethyl 2,4-*dichlorophenylacetate* (**5**). 2,4-Dichlorophenyl acetic acid (**1**) $\xrightarrow[H_2SO_4]{ETOH,\ C_6H_6}$ (**5**) (95%) NMR $\delta_H(CDCl_3)$ 1.1 (3 H, t, *J* 7 Hz, CH_3), 3.6 (2 H, s, CH_2), 4.1 (2 H, q, *J* 7 Hz, OCH_2), and 7.1–7.3 (3 H, m, ArH).

Ethyl α-*bromo*-2,4-*dichlorophenylacetate* (**9**). Compound (**5**) (10.59 g, 5 × 10^{-2} mol), and NBS (10 g, 6 × 10^{-2} mol) in CCl_4 (150 cm^3) as solvent were irradiated with a 300 W Osram solar lamp with stirring for 5 h. The succinimide formed was removed by filtration. Evaporation of the solvent gave 98.7% of a yellow liquid (TLC, HPLC, NMR), almost pure (**9**) $\delta_H(CDCl_3)$ 1.2 (3 H, t, *J* 7 Hz, CH_3), 4.2 (2 H, q, *J* 7 Hz, OCH_2), 5.8 (1 H, s, CHBr), and 7.2–7.9 (3 H, m, ArH).

Ethyl 2,4-*difluorophenylacetate* (**6**). $\delta_H(CDCl_3)$ 1.2 (3 H, t, *J* 7 Hz, CH_3), 3.6 (2 H, s, CH_2), 4.2 (2 H, q, *J* 7 Hz, OCH_2), and 6.7–7.5 (3 H, m, ArH).

Ethyl α-*bromo*-2,4-*difluorophenylacetate* (**10**). $\delta_H(CDCl_3)$ 1.3 (3 H, t, *J* 7 Hz, CH_3), 4.3 (2 H, q, *J* 7 Hz, OCH_2), 5.7 (1 H, s, CHBr), and 7.6–8.0 (3 H, m, ArH).

Ethyl 3,4-*dichlorophenylacetate* (**7**). $\delta_H(CDCl_3)$ 1.2 (3 H, t, *J* 7 Hz, CH_3), 3.5 (2 H, s, CH_2), 4.1 (2 H, q, *J* 7 Hz, OCH_2), and 7.0–7.4 (3 H, m, ArH).

Ethyl α-*bromo*-3,4-*dichlorophenylacetate* (**11**). $\delta_H(CDCl_3)$ 1.3 (3 H, t, *J* 7 Hz, CH_3), 4.2 (2 H, q, *J* 7 Hz, OCH_2), 5.3 (1 H, s, CHBr), and 7.5–7.7 (3 H, m, ArH).

Ethyl 3,4-*difluorophenylacetate* (**8**). $\delta_H(CDCl_3)$ 1.2 (3 H, t, *J* 7 Hz, CH_3), 3.5 (2 H, s, CH_2), 4.1 (2 H, q, *J* 7 Hz, OCH_2), and 6.9–7.4 (3 H, m, ArH).

Ethyl α-*bromo*-3,4-*difluorophenylacetate* (**12**). $\delta_H(CDCl_3)$ 1.3 (3 H, t, *J* 7 Hz, CH_3), 4.2 (2 H, q, *J* 7 Hz, OCH_2), 5.3 (1 H, s, CHBr), and 7.0–7.6 (3 H, m, ArH).

Constant-potential Electrolysis of Ethyl α-*Bromoesters* (**9**), (**10**), (**11**), *and* (**12**).—In the four-necked cell containing the RVC cathode, the SCE reference electrode, the platinum anode, magnetic stirrer, and gas-inlet tube, Et_4NClO_4–DMF (160 cm^3, 0.1 mol dm^{-3}) solution and α-bromo ester (4 cm^3, 0.4 mol dm^{-3}) solution were degassed with stirring for *ca.* 1 h. Electrolyses were then performed at the constant potential of −1.6 to −1.8 V *vs.* SCE for which the initial current was *ca.* 60 mA. Subsequent aliquots of bromoester were added when the current was *ca.* one hundredth of the initial value. Thus, the following quantities of bromoesters were electrolysed: (**9**), (2.5 g, 8 mmol); (**10**), (3 g, 10.8 mmol); (**11**), (2.5 g, 8 mmol); (**12**), (3 g, 10.8 mmol).

On completion of electrolysis pertaining to each bromoester ABr, the mixture obtained was distilled under vacuum to remove the solvent, the residue taken-up with benzene and then extracted with water–benzene to remove the water-soluble Et_4NClO_4. Each viscous mixture of products, after drying, was analyzed by TLC and ^{1}H NMR. The NMR spectra were used to evaluate relative yields of products before the subsequent work-up procedures of separation of the single substances.

Column chromatography with SiO_2 60 Merck (0.063–0.200 mm) was then used; hexane–ethyl acetate as eluant gave, in the order of leaving: AH, AA (*meso*), AA (DL), except for products from (**9**), where the order was AA (*meso*) before AH. In one case, dimer (**16a**) was obtained contaminated with AH (**8**); in this event, the products were further separated by HPLC (column Merck LiChrosorb Si60–7 μm). In a further electrolysis of (**12**), from ABr (1.95 g, 7 mmol), only (**16a**) and (**16b**), *i.e.* no detectable AH was obtained, and they were separated directly in the column chromatographic experiments. Other products different from AH and AA were also obtained; no attempt was made to identify them.

Meso-*Diethyl* 2,3-*bis*(2,4-*difluorophenyl*)*succinate* (**14a**).—Obtained as a pale yellow solid, m.p. 94–96 °C; $\delta_H(CDCl_3)$ 1.0 (6 H, t, *J* 7 Hz, 2 × CH_3), 3.9 (4 H, q, *J* 7 Hz, 2 × OCH_2), 4.7 (2 H, s, 2 × CH), and 6.6–7.8 (6 H, m, ArH); *m/z* 398 (M^+), 352 (M − EtOH), 324 (M − EtOH − CO), 252 (M − EtOH − CO − Et + H − CO_2), 232 (252 − HF), 199 (M/2), 171, 127, 95, and 75.

DL-*Diethyl* 2,3-*bis*(2,4-*difluorophenyl*)*succinate* (**14b**).—Obtained as a pale-yellow viscous liquid; $\delta_H(CDCl_3)$ 1.2 (6 H, t, *J* 7 Hz, 2 × CH_3), 4.1 (4 H, q, *J* 7 Hz, 2 × OCH_2), 4.6 (2 H, s, 2 × CH), and 6.4–7.5 (6 H, m, ArH); *m/z* 398 (M^+), 352, 324, 252, 232, 199, 171, 127, 95, and 75.

Meso-*Diethyl* 2,3-*bis*(3,4-*dichlorophenyl*)*succinate* (**15a**).—White solid, m.p. 126–128 °C; $\delta_H(CDCl_3)$ 1.0 (6 H, t, *J* 7 Hz,

Table 1. Results of electrochemical reduction of α-bromo dihalogenophenylesters (**9–12**) (ABr). Cathode: RVC; solvent system: DMF–Et_4NClO_4 (0.1 mol dm^{-3}).

ABr	Product	Yield (%)[a]	Product ratio DL:*meso*	de (%)[b]	n_{app}[c]
(**9**)	(**5**)	10.6			1.3
	(**13a**)	9.8	1.0:1	—	
	(**13b**)	19.6			
(**10**)	(**6**)	4.4			1.4
	(**14a**)	8	6.5:1	79.6	
	(**14b**)	32.8			
(**11**)	(**15a**)	13.5	3.0:1	50.0	1.6
	(**15b**)	38			
(**12**)	(**8**)	— (12)			
	(**16a**)	5.4 (7)	3.4:1	54.5	1.3
	(**16b**)	15.1 (40)			

[a] Based on ABr, % of isolated products; second run in parentheses. [b] Before work-up (NMR); de = diastereoisomeric excess. [c] Number of Faradays per mol of ABr consumed in the electrolysis; room temperature; $E = -1.6$ V for (**9**) and (**10**); $E = -1.7$ V for (**11**) and -1.8 V for (**12**).

Table 2. Voltammetric data for α-bromoesters ABr (**9–12**), for esters AH (**5–8**) and for diesters AA (**13–16**) in DMF–Et_4NClO_4 (0.1 mol dm^{-3}) solutions. Concentration of esters: 1×10^{-3} mol dm^{-3}. Potential sweep-rate V 0.2 V s^{-1}; glassy-carbon electrode; E/V *vs.* SCE.

ABr	E'_p[a]	AH	E'_p	E''_p	AA	E'_p	E''_p
(**9**)	−0.94	(**5**)	−2.45	−2.64	(**13a**)	−2.37	
					(**13b**)	−2.39	
(**10**)	−1.27	(**6**)	2.74	—	(**14a**)	−2.71	
					(**14b**)	−2.72	
(**11**)	−1.09	(**7**)	2.47	—	(**15a**)	−2.39	−2.72
					(**15b**)	−2.39	−2.72
(**12**)	−1.19	(**8**)	(−2.09)[b]	−2.66	(**16a**)	−2.69	
					(**16b**)	−2.69	

[a] For ABr, the first reduction peak, E'_p only, is tabulated. [b] Small peak.

2 × CH_3), 3.9 (4 H, q, *J* 7 Hz, 2 × OCH_2), 4.2 (2 H, s, 2 × CH), and 7.4–7.6 (6 H, m, ArH); *m/z* 461, 426, 415, 246, 231, 203, 159, 111, and 75.

DL-*Diethyl* 2,3-*bis*(3,4-*dichlorophenylsuccinate*) (**15b**).—Pale-yellow solid, m.p. 124–126 °C; $\delta_H(CDCl_3)$ 1.2 (6 H, t, *J* 7 Hz, 2 × CH_3), 4.1 (4 H, q, *J* 7 Hz, 2 × OCH_2), 4.2 (2 H, s, 2 × CH), and 6.8–7.4 (6 H, m, ArH); *m/z* 461, 426, 415, 246, 231, 203, 159, 111, and 75.

Meso-*Diethyl* 2,3-*bis*(3,4-*difluorophenyl*)*succinate* (**16a**).—White solid, m.p. 98–100 °C; $\delta_H(CDCl_3)$ 1.00 (6 H, t, *J* 7 Hz, 2 × CH_3), 3.9 (4 H, q, *J* 7 Jz, 2 × OCH_2), 4.2 (2 H, s, 2 × CH), and 6.7–7.4 (6 H, m, ArH); *m/z* 398 (M^+), 352, 324, 252, 232, 199, 171, 127, 195, and 75.

DL-*Diethyl* 2,3-*bis*(3,4-*difluorophenyl*)*succinate* (**16b**).—White solid, m.p. 78–80 °C; $\delta_H(CDCl_3)$ 1.2 (6 H, t, *J* 7 Hz, 2 × CH_3), 4.1 (4 H, q, *J* 7 Hz, 2 × OCH_2), 4.1 (2 H, s, CH), and 6.8–7.3 (6 H, m, ArH); *m/z* 398 (M^+), 352, 324, 252, 232, 199, 171, 127, 95, and 75.

Results and Discussion

Electrochemical Behaviour of Dihalogenophenyl Esters (**5**)–(**16**).—Once diesters (**13**)–(**16**) are obtained, see Experimental and Table 1, it is useful to compare the location of the peak potential for reduction of the various compounds (Table 2). All

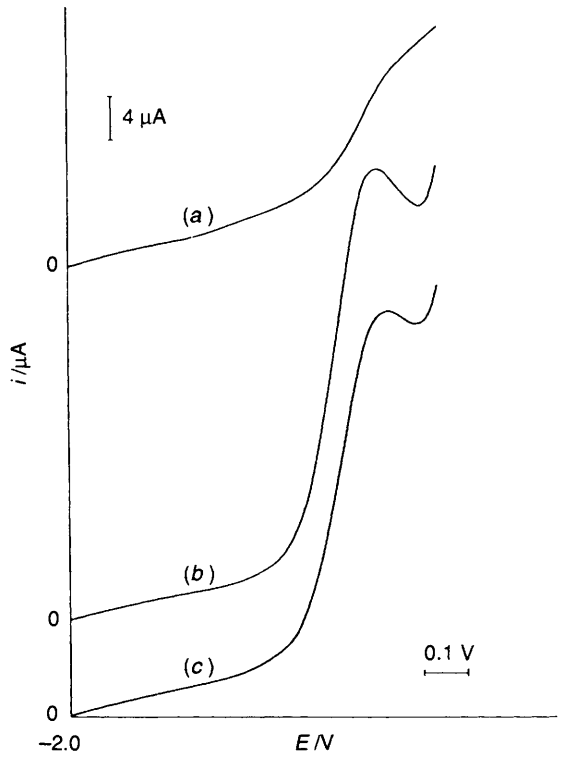


Figure. Cyclic voltammograms for (*a*) ester (**6**), (*b*) *meso*-diester (**14a**), and (*c*) DL-diester (**14b**), all 10^{-3} mol dm^{-3} in DMF–Et_4NClO_4 (0.1 mol dm^{-3}). Sweep rate 200 mV s^{-1}. Glassy-carbon electrode. E/V *vs.* SCE.

electron transfers are irreversible, see the Figure for an example. Every bromoester ABr shows, as expected, at least three reduction peaks, the first one pertaining to the breaking of the C–Br bond; the subsequent reduction peaks are those of the products. The order for reduction of C–Br bond seems to be E'_p(**9**) > (**11**) > (**12**) > (**10**), that is, the two Cl or F substituents in the phenyl group exert a definite influence on the free energy of activation of electron exchange on vitreous carbon electrode. The reduction potential of the 2,4-difluorophenyl α-bromoester (**10**) is very close to the potential of ethyl α-bromophenylacetate on the same electrode,[2a] whereas the 3,4-difluoroderivative is more easily reduced. The most positive potential is found for the 2,4-dichloroderivative (**9**). Steric crowding and proximity effects may contribute to the situation, as we observed in other α-bromoesters.[2] The last effects are not to be expected for reduction of (**5**) and (**7**) (AH) where the Ar–Cl bond is involved, resulting in approximately the same value of E_p in (**5**) and (**7**). The corresponding chloro-substituted diesters (**13**) and (**15**) show practically the same reduction potential, E_p(**13a,b**) = E_p(**15a,b**), which are *ca.* 80 mV more positive than the AHs. Similarly, E_p(**14a,b**) and E_p(**16a,b**) are practically the same. Thus, no significant difference is found between *meso*- and DL-diesters in this series, with respect to the reduction potential. As expected, the chlorine-substituted compounds are more easily reduced than the fluorine substituted, compare (**13**) with (**14**) or (**15**) with (**16**).

The Figure shows, as an example, the voltammogram of the 2,4-difluorophenyl ester (**6**) and of the corresponding succinates (**14a**) and (**14b**), the latter originate from the electrochemical synthesis. It is beyond the scope of the present work to examine the fate of (**13–16**) after reduction. One point can be noted: 2,3-bis(*p*-fluorophenyl)succinate is not reduced under the present conditions;[2e] the results show that an additional

fluorine in the phenyl group enables the diester to be reducible within the available potential range.

We now consider the question of product selectivity that emerges from the present and previous[2e] results, in terms of diastereoisomeric excess, de, for each couple of the halogenophenylsuccinates prepared through the electrochemical method.[4] Inspection of Table 1 reveals that the DL de is the highest in the case of (**14**), the 2,3-bis(2,4-difluorophenyl)-succinate; (**15**) and (**16**), the 3,4-dichloro or -difluoro derivatives show about the same value (50%) whereas in the case of the 2,4-dichloro derivative the de is practically zero. It is to be noted that such de are based on freshly-formed mixtures before isolation of the single isomers. Owing to the value of the potential applied in the electrolysis, it is highly improbable that a single diastereoisomer be preferentially consumed in a side reaction, see also electrochemical data of Table 2. In other words, the applied potential for breaking of the C–Br bond is far more positive than others pertaining to AH and AA. Since no chemicals different from ABr or solvent system are employed, it is difficult to imagine a route for destroying or missing any AA (*meso*) in favour of the AA (DL). Thus, the figures for the des in Table 1 can be considered with some confidence. The few data at our disposal seem to indicate a preference of the fluorine-substituted AAs for the DL *vs.* *meso*-structure. The α-bromoesters, obtained through NBS bromination of the corresponding AH, are inactive DL mixtures. The simplest way to account for the observed behaviour is as follows: the electrode reaction is followed by a chemical reaction involving chiral intermediates; the kinetics of coupling of intermediates favours homochiral coupling when de are observed, and this happens preferentially for fluorine-containing compounds.

Thus, the question is split in two: what are the chiral intermediates involved in the rate-determining step, and what is the reason underlying the 'stereochemical recognition?' It is now generally accepted that the overall electrode reaction leading to AA from ABr:

$$ABr + e \longrightarrow \tfrac{1}{2}AA + Br^- \quad (3)$$

actually results from the electron exchange

$$ABr + 2e \longrightarrow A^- + Br^- \quad (4)$$

followed by the chemical reaction, in solution,[2b–e]

$$A^- + ABr \longrightarrow 2A\cdot \longrightarrow AA \quad (5)$$

Obviously, the involvement of radical intermediates would lead to a loss of chiral identity with zero de as a consequence.[5] This happens for planar A·; if A· is pyramidal, and with a high energy of inversion, the chiral identity is preserved. At this point, it is not contrary to expectation that the kinetics will be different. Thus, one would be tempted to infer that, if (**5**) is valid, some of the A· are pyramidal. It is known that electronegative substituents at the radical centre favour deviation from planarity,[6] whereas steric bulkiness encourages a planar configuration.[7] The conclusion will be that the fluorine-containing A· are more prone to be pyramidal; the 2,4-dichlorophenyl A· would be planar. Since no direct information is available concerning this point, we cannot test the above-mentioned conclusion.

NMR Spectroscopy and Assignment of the Diastereoisomeric Structures.—In previous studies we found that the *meso* and the DL structures, for each couple of diethylsuccinates, can be assigned on the following grounds: $\delta(CH_3)(meso) < (CH_3)(DL)$ of the CO_2Et group; if present, ArCH(*meso*) > ArCH(DL), and, finally we found[2e] that the Ar patterns (AB in that case) are very different, being more well developed (higher values for J(AB) and of $\Delta\delta$(AB)) for the DL compounds. We also observed the same trends in the present case, so that a useful correlation can be made. It is to be noted that it was important to detect the signal of the phenyl group pertaining to hydrogen with no other adjacent H, as in (**5–8**). Persistence of such a signal in (**13–16**) indicates that both Cl or F are still present, thus granting that equation (3) is obeyed.

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References

1 Presented at the 7th EUCHEM Conference on Electrochemistry, Assisi, 1989.
2 (*a*) L. Rampazzo and A. Inesi, *J. Electrochem. Soc.*, 1980, **127**, 2388; (*b*) C. De Luca, A. Inesi, and L. Rampazzo, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1403; (*c*) *ibid.*, 1983, 1821; (*d*) *ibid.*, 1985, 209; (*e*) *ibid.*, 1987, 847.
3 See for example J. Mann, *Chem. Soc. Rev.*, 1987, **16**, 381 and references cited therein.
4 Other examples of de, involving electrochemically driven dimerization, were found in other systems, leading to vicinal diols: P. C. Cheng and T. Nonaka, *J. Electroanal. Chem.*, 1989, **269**, 223; A. Bewick and D. J. Brown, *J. Chem. Soc., Perkin Trans. 2*, 1977, 99; D. F. Tomkins and J. H. Wagenknecht, *J. Electrochem. Soc.*, 1978, **125**, 372, and references cited therein.
5 Ch. Tamm, 'Stereochemistry,' Elsevier, Amsterdam, 1982.
6 M. Kira, M. Akiyama, M. Ichinose, and H. Sakurai, *J. Am. Chem. Soc.*, 1989, **111**, 8256; R. C. Bingham and M. J. S. Dewar, *ibid.*, 1973, **95**, 7180 and 7182.
7 K. U. Ingold, D. C. Nonhebel, and J. C. Walton, *J. Phys. Chem.*, 1986, **90**, 2859; W. J. Le Noble, 'Highlights of Organic Chemistry,' M. Dekker, New York, 1974, p. 636.

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