Electroreduction of Methyl 2-Bromo-2-phenylpropanoate on a Vitreous Carbon Electrode: *meso*- and DL-Dimethyl 2,3-Dimethyl-2,3-diphenylsuccinate

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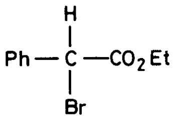
The electrochemical reduction of ethyl α-bromophenylacetate (1) and methyl 2-bromo-2-phenylpropanoate (5) in dry dimethylformamide on a vitreous carbon electrode has been studied. Dimeric products are formed as a consequence of controlled potential electrolysis of (1) and (5) on a reticulated vitreous carbon electrode. By this route, *meso*- and DL-diethyl 2,3-diphenylsuccinate and -dimethyl 2,3-dimethyl-2,3-diphenylsuccinate are obtained from ester (1) and (5), respectively. A triester is also obtained among the products. The spectral data (n.m.r., mass spectra) show the structure of this triester to be almost certainly $\mathrm{MeO_2C{\cdot}CMePh{\cdot}C_6H_4{\cdot}CMeCO_2Me{\cdot}CMePh{\cdot}CO_2Me}$ (9). To explain the results, a mechanism is proposed, involving the formation of dimer (10) as an intermediate.

WE have previously reported[1] that electrochemical reduction of ethyl α-bromophenylacetate (1) in dimethylformamide on a mercury electrode leads to *meso*- and DL-diethyl 2,3-diphenylsuccinate. There seems to be no report about the electrochemical behaviour of alkyl 2-bromo-2-phenylpropanoates. In this paper we describe the results obtained for the electrochemical reduction of methyl 2-bromo-2-phenylpropanoate (5) in DMF–$\mathrm{Et_4NClO_4}$ using a vitreous carbon electrode. The methyl ester was selected for study, among the alkyl esters, as the easiest to prepare. Further, the use of vitreous carbon was expected to avoid complications arising from the use of mercury as electrode (see ref. 1. and references therein).

Besides the intrinsic interest in the electrochemical reduction of a carbon–halogen bond,[2] there is a possible additional value in the study of 2-phenylpropanoic acid derivatives. In fact, the therapeutically useful 'ibuprofen' and related compounds[3] are all derivatives in which the $\mathrm{CPhMeCO_2R'}$ arrangement is preserved, substituents of various kind being present in the *para*- or, less frequently, the *meta*-position of the phenyl group. Whilst the same intermediates are not necessarily involved in the pharmacological activity as in the electrochemistry of the corresponding bromo-compounds, we feel that among the several reactions of such bromo-compounds so far studied, those taking place under mild conditions, such as electrode reactions, may be instructive.

Additional data on the electroreduction of (1) on vitreous carbon are also reported.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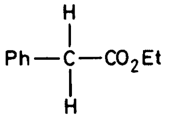
(1)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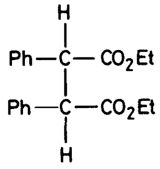
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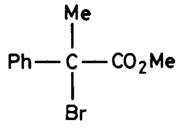
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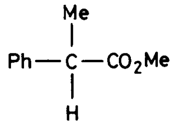
(5)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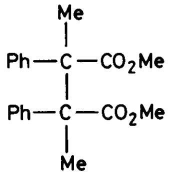
(6)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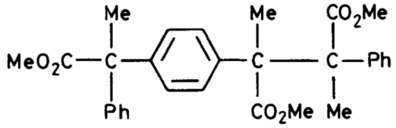
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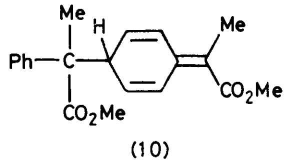
(10)

EXPERIMENTAL

Materials.—*NN*-Dimethylformamide (DMF) (Riedel de Haan spectroanalytical) and polarographic grade $\mathrm{Et_4NClO_4}$ (Carlo Erba) were treated as described previously.[1] Commercially available ethyl α-bromophenylacetate (1) (K and K) was employed as received when used in the preparative electrolyses. For coulometric and voltammetric measurements, it was purified as follows. Distillation in a short apparatus at 13—15 mmHg gave three fractions boiling at 115, 120, and 130 °C, respectively. After examination of each fraction by t.l.c. on silica gel (Merck 60 $\mathrm{F_{254}}$) with hexane–ether 4 : 1 (v/v) as eluant, the middle fraction was subjected to preparative t.l.c. with hexane–ether 3 : 1 (v/v), giving practically pure (1) (t.l.c.). Ethyl phenylacetate (2) was Aldrich. Methyl 2-phenylpropanoate (6) was obtained from 2-phenylpropanonic acid (Aldrich) by treatment with diazomethane, δ_H (CCl_4) 7.2 (5 H, apparently s, ArH), 3.7 (1 H, q, *J* 7 Hz, CH), 3.56 (3 H, s, OCH_3), and 1.46 (3 H, d, *J* 7 Hz, CH_3), as in ref. 4; *m/e* 164 (M^+), 163, 149, and 105, as in ref. 4; $\nu_{max.}$ ($CHCl_3$) 1 730 (s), 1 170 (s), and 700 cm^{-1}.

2-Bromo-2-phenylpropanoic acid [5] was prepared by treatment of 2-hydroxy-2-phenylpropanoic acid (Fluka or Aldrich) in aqueous solution with hydrogen bromide gas at −2 °C,[5a] m.p. 93 °C (lit.,[5] 93.6 °C); δ_H (CCl_4) 11.3 (1 H, s, exchangeable with D_2O, CO_2H), 7.6—7.0 (5 H, m, ArH), and 2.2 (3 H, s, CH_3).

Methyl 2-*bromo*-2-*phenylpropanoate* (5). 2-Bromo-2-phenylpropanoic acid was converted into its methyl ester by the action of diazomethane. The reaction product (*ca.* 100%) had δ_H (neat) 7.6—7.0 (5 H, m, ArH), 3.5 (3 H, s, OCH_3), and 2.2 (3 H, s, CCH_3), δ_H (CCl_4) 7.6—7.0 (5 H, m, ArH), 3.7 (3 H, s, OCH_3), and 2.2 (3 H, s, CCH_3); b.p. 185 °C at 760 mmHg (decomp.).

All other chemicals were commercially available and of the best purity.

Apparatus and Procedures.—The instrumentation and procedures were identical to those used previously [1,6] except for the cell arrangement in the controlled potential electrolyses (c.p.e.) on reticulated vitreous carbon (r.v.c.). A piece of r.v.c. (Fluorocarbon, 2 × 5–100 S) was cut in the shape of a cylinder of *ca.* 7 mm diameter and *ca.* 90 mm height; electrical contact was made with a platinum wire which was gently inserted into the top of the cylinder. The r.v.c. cylinder was washed with acetone, stored in acetone for several days, rewashed, and dried before measurements. The r.v.c. electrode was placed vertically in the cell containing the solution without submerging the platinum contact. The counter electrode and the reference electrode were the same as previously reported.[1,6] Care was taken in deoxygenating the solution before electrolysis. As compared to the c.p.e. of the same quantities of material on the mercury electrode, longer times were needed to take the various electrolyses to completion. Stirring was provided by a magnetic Teflon bar and N_2 was bubbled slowly through the solution during c.p.e. Undoubtedly the r.v.c. electrode configuration and the relative cathode–anode positions used, together with conventional stirring, gives a very complicated dynamic situation and probably a non-uniform distribution of electrode potentials. The arrangement was chosen for the sake of simplicity, since we were interested mainly in the products formed.

M.p.s were determined on a Büchi apparatus and are uncorrected. ^1H N.m.r. spectra were obtained using a Varian A 60 or a Varian 80 FT instrument with tetramethylsilane as internal standard. ^{13}C N.m.r. spectra were recorded in the Fourier transform mode with a Varian 80 FT instrument using $CDCl_3$ as internal standard. Mass spectra were determined using an A.E.I. MS-12 instrument at 70 eV. I.r. spectra were recorded on a Perkin-Elmer model 177 grating spectrophotometer.

H.p.l.c. experiments were carried out 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 column used was a reversed-phase Perkin-Elmer C8/10, 25 × 0.46 cm i.d., 10μ. Conditions employed were: (a) flow rate 2 ml min^{-1}, linear gradient from 60 to 100 % methanol in water for 4 min and then held at 100% methanol, at room temperature, using u.v. detection at 254 nm. [The following retention times t_R were found: compound (6), t_R 5 min; adduct Y, 6 min 20 s; diester (8), 6 min 28 s; diester (7), 6 min 45 s; (b) linear gradient from 60 to 100% CH_3CN in water for 4 min and then held at 100% CH_3CN, other conditions being as in (a). In case (b), the following retention times were observed: ester (6), t_R 3 min 36 s; adduct Y, 4 min 48 s; diester (8), 5 min 6 s; diester (7), 5 min 42 s.

Constant Potential Electrolysis of Ethyl α-*Bromophenylacetate* (1).—In a typical experiment, ethyl α-bromophenylacetate (1) (1.73 g, 7.12 × 10^{-3} mol) in dimethylformamide (150 ml) containing Et_4NClO_4 (0.1M) was electrolysed on r.v.c. at a constant potential of −1.90 V. Conventional work-up yielded pure *meso*-diethyl 2,3-diphenylsuccinate (3) (240 mg) with m.p. and spectroscopic characteristics (n.m.r., i.r., mass spectra) identical with those previously reported,[1] and DL-diethyl 2,3-diphenylsuccinate (4) (100 mg),[1] containing *ca.* 10% of *meso*-dimer (3) (n.m.r.). In a second run, identical electrolysis conditions were employed, starting with bromo-ester (1) (1.94 g), other conditions being the same. To obtain pure (4), *ca.* 50 ml of the electrolysed solution [corresponding to 650 mg or 2.6 × 10^{-3} mol of (1)] were subjected to a slightly different work-up procedure. The solvent was evaporated gently under vacuum. T.l.c. (silica gel; Merck 60 F_{254}; spots detected under u.v. light) revealed no products other than DMF in the distillate. The product thus obtained contained (t.l.c.) ethyl phenylacetate (2), *meso*- and DL-dimers (3) and (4), and traces of other products with low R_F values. This mixture was poured into water (10 ml) and hexane (10 ml). Most of the products, (2)—(4) were in the hydrocarbon fraction. The aqueous fraction was re-extracted with hexane (15 ml). The hexane fractions were collected and washed with H_2O (10 ml). During the extraction, at the aqueous–organic interface, a solid was formed which was pure (3) (t.l.c.) The organic fractions were dried at reduced pressure, giving a mixture of solids [308 mg, mostly dimers (3) and (4)] and an oily [ester (2)] substance. This mixture was taken up with ether and acetone and subjected to preparative t.l.c. using plates of silica gel (20 × 20 cm; 2 mm in thickness; Merck 60 F_{254}) with hexane–ether 8 : 2 (v/v) as eluant. Five fractions were obtained (from ether–acetone), in the following order of decreasing R_F: (2) (90 mg), (3) (75 mg), (4) (85 mg), unknown products (36 mg), and a residue with R_F 0.

Constant Potential Electrolysis of Methyl 2-*Bromo*-2-*phenylpropanoate* (5).—The procedure for electrolysis of bromo-ester (5) on r.v.c. was analogous to that adopted for bromo-ester (1). The experiment was repeated several times, in order to ascertain if the same kinds of products were formed. Typical experiments were as follows. Methyl 2-bromo-2-phenylpropanoate (5) (2.2 g, 9.05 × 10^{-3} mol) dissolved in DMF (150 ml) containing Et_4NClO_4 (0.1M) was electrolysed at a constant potential of −2.0 V for 20 h. The initial current was 0.045 A. Electrolysis was interrupted when the current dropped to *ca.* 0.4 mA. The work-up was conventional. The solvent was evaporated under vacuum, the products extracted with water and hexane, most organic products being in the hydrocarbon fraction, and the aqueous fraction was re-extracted twice with hexane. The organic fraction, after drying (Na_2SO_4), was concentrated under reduced pressure to 3 ml of a viscous mixture of products which showed seven spots on t.l.c. (silica gel; hexane–ether 4 : 1 v/v). The mixture was subjected to column chromatography (SiO_2; 2.2 × 80 cm; prepared in hexane). Fractions (8 ml) were eluted as follows: fraction order (% ethyl acetate in hexane) 0—20 (0%), 20—120 (8%), 120—170 (10%), >170 (50%). The following products were obtained after drying: fractions 19–21 (55 mg), methyl 2-phenylpropanoate (6) (i.r., n.m.r. identical to those of an authentic sample); fractions 25—29 (8 mg), a scented, unidentified oily product; fractions 32—42 (400 mg), dimethyl 2,3-dimethyl-2,3-diphenylsuccinate (7), probably *meso*; fractions 30 + 31 + 43 + 46 (16 mg), diester (7); fractions 47—49 (4 mg), mixed (7) + (8); fractions 50—65 (450 mg), dimethyl 2,3-dimethyl-2,3-diphenylsuccinate (8), probably DL; fractions 66—95 (54 mg), a mixture Y (n.m.r.) for (6)—(8) in the molar ratio (6)/[(7) + (8)] = 2 : 1; fractions 96—120 (6 mg), unidentified mixture; fractions 121—143 (56 mg), triester (9); fractions 144—164 (5 mg), a product Z whose characteristics are described below; fractions 165—171 (3 mg) and 172*ff* (44 mg), probably (n.m.r.) isomers of Z.

meso-*Dimethyl* 2,3-*Dimethyl*-2,3-*diphenylbutanedioate* (7).—This formed needles or leaflets from hexane, m.p. 127—128 °C; $\nu_{max.}$ ($CHCl_3$) 3 100—2 180, 1 725 (s), 1 240 (s), 1 090 (m), and 700 (m) cm^{-1}; δ_H (CCl_4) 7.3—6.6 (10 H, m, 2 × ArH), 3.66 (6 H, s, 2 × OCH_3), and 1.66 (6 H, s, 2 × CCH_3), with a characteristic splitting of the Ar signals forming a dip at δ 6.95; *m/e* 326 (M^+), 294 ($M - CH_3OH$), 263 ($M - H - 2 \times OCH_3$), 234 ($M - H - OCH_3 - CO_2CH_3 - H$), 208 ($M - 2 \times CO_2CH_3$), 193 ($M - 2 \times CO_2CH_3 - CH_3$), 178 ($M - 2 \times CO_2CH_3 - 2 \times CH_3$), 163 ($M/2$, base), 162, 134 ($M/2 - H - CO$), 120 ($M/2 - H - CH_2CO$), 105 ($M/2 + H - CO_2CH_3$), 104, 103, 91, and 77.

DL-*Dimethyl* 2,3-*Dimethyl*-2,3-*diphenylbutanedioate* (8).—This was a viscous, quasi-solid fluid which did not crystallize from the usual solvents, $\nu_{max.}$ ($CHCl_3$) 3 100—2 820, 1 725 (s), 1 240 (s), 1 130 (m), and 700 (m) cm^{-1}; δ_H (CCl_4) 7.22—6.68 (10 H, m, 2 × ArH), 3.66 (6 H, s, 2 × OCH_3), and 1.83 (6 H, s, 2 × CCH_3), with a characteristic multiplet for the Ar signals with the main signal at δ 6.99; *m/e* 326 (M^+), 295 ($M - OCH_3$), 267 ($M - CO_2CH_3$), 235 ($M - CH_3OH - CO_2CH_3$), 208, 193, 178, 164 ($M/2 + H$), 163 ($M/2$, base), 149 ($M/2 + H - CH_3$), 135, 131 ($M - Ph - 2 \times CO_2CH_3$), 121, 105, 103, 91, 78, and 77. Both diesters (7) and (8) show metastable peaks in the mass spectrum at *m/e* 81.5 (326→163), 110.5 (326→190), and 113.1.

Dimethyl 2,3-*Dimethyl*-2-*phenyl*-3-[p-(1-*methoxycarbonyl*-1-*phenylethyl*)*phenyl*]*butanedioate* (9).—This was obtained as an apparently amorphous solid or quasi-solid which failed to crystallize, δ_H ($CHCl_3$) 7.2—6.6 (14 H, m, 3 × ArH), 3.74 and 3.73 (9 H, each s, 3 × OCH_3), 1.92 (3 H, s, Ar_2-CCH_3), 1.68 (3 H, s, CCH_3), and 1.65 (3 H, s, CCH_3); δ_C (CH_2Cl_2) (high-field region): 128.7—126.7 (ArC), 57.1br (quaternary C), 52.4 (OCH_3), 52.3 (OCH_3), 52 (OCH_3), 26.9 (CCH_3), 26.7 (CCH_3), and 22.7 (CCH_3); *m/e* 488 (M^+), 458 ($M - 2 \times CH_3$), 439, 397 ($M - CH_3OH - CO_2CH_3$), 369 ($M - H - 2 \times CO_2CH_3$), 339 ($M - H - 2 \times CO_2CH_3 - 2 \times CH_3$), 325, 311 ($M - 3 \times CO_2CH_3$), 297, 291, 282, 266, 235, 231, 223, 164, 163, 135, 119, 118, 103, 82, and 77.

RESULTS AND DISCUSSION

Bromo-esters (1) and (5) give similar irreversible voltammetric curves on a glassy carbon electrode (Figure) with peak potential E_{pc} of −1.28 and −1.29 V, respectively, at a sweep rate of 200 mV s^{-1}. For each compound, the cathodic peak represents the only organobromine-related process, while the anodic peak may be attributed to Br^- oxidation processes.* In order to estimate the number of electrons involved in the cathodic process from the voltammetric measurements, the peak current i_{pc} values for (1) and (5) were compared to those of perylene (P) ($P + e \longrightarrow P^{\dot{-}}$) under the same conditions, suggesting a value of *n ca.* 1 for both compounds.†

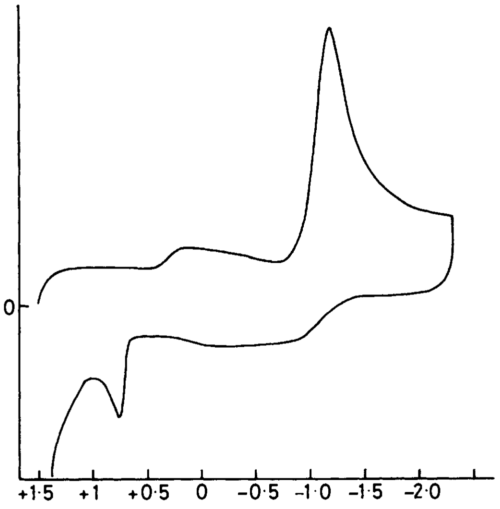

FIGURE Cyclic voltammogram for bromo-ester (1) (1.0 × 10^{-3}M) in dimethylformamide containing Et_4NClO_4 (0.1M) as supporting electrolyte. Sweep rate 200 mV s^{-1}, glassy carbon electrode, *E*/V *versus* s.c.e.

The results of coulometric measurements for the reduction of (1) and (5) on r.v.c. are collected in the Table.

Controlled potential electrolyses were carried out on r.v.c. at *E* −1.9 and −2.0 V in dry DMF-Et_4NClO_4 (0.1M) for compounds (1) and (5) respectively, as indicated in the Experimental section. Dimeric products were isolated and fully characterized (see Experimental section), as follows: (i) $PhCHBrCO_2Et$ (1) gave *meso*- and DL-diethyl 2,3-diphenylsuccinate (3) and (4), respectively; (ii) $PhCMeBrCO_2Me$ (5) gave *meso*- and DL-dimethyl 2,3-dimethyl-2,3-diphenylsuccinate (7) and (8), respectively.

No ambiguity exists in the attribution of the *meso*- and DL-structures for (3) and (4) (see ref. 1 and references cited therein). In the case of (7) and (8), the attribution of the *meso*-structure to (7) and of the DL-structure to (8) can be rationalized on the following grounds: $R_F(7) > R_F(8)$ for t.l.c. with a corresponding order of elution in

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* This was checked by recording voltammograms for DMF–Et_4NClO_4 (0.1M) solutions containing 10^{-3}M-Et_4NBr or -Bu_4NBr.

† Estimated by using the equation $i_P(E)/i_P(P) = 1.11n(E)(\alpha n_a)^{1/2}(D_E)^{1/2}/n(P)(D_P)^{1/2}$ (see R. N. Adams, ' Electrochemistry at Solid Electrodes,' Marcel Dekker, New York, 1969, pp. 135*ff*) where $i_P(E)$ and $i_P(P)$ are the peak currents observed at the same sweep rate *v* and concentration *C* for the bromo-ester and perylene, respectively. From $E_{P/2}$ *versus* log *v* or from $E_P - E_{P/2}$ values, at low sweep rates we obtained αn_a 0.3 for the bromo-ester. Our data were, for example, $i_P(P)$ 32 μA and $i_P(E) = i_P(1) = 24$ μA at *C* 10^{-3}M and *v* 0.25 V s^{-1}. Assuming $D_P = D_E$ (actually, D_P should be somewhat less than D_E) one obtains n_E 1.2.

column chromatography, albeit with different pairs of solvents, thus paralleling the order of increasing polarity, (7) < (8); the same order was found for (3) and (4). The two isomers (7) and (8) can be clearly distinguished by their ^{1}H n.m.r. spectra, particularly in the aromatic region, as well as the different location of the CCH_3 signals at δ 1.66 and 1.83. The chemical shift of the CCH_3 protons of the monoester (6) is at δ 1.46; thus, substitution of the CMePhCO$_2$Me group for H in (6) to obtain (7) or (8) causes a downfield shift of 0.2—0.4 p.p.m. The preferred conformation of *meso*-compounds of the type $(CRPhCO_2R')_2$ is almost certainly that having the phenyl groups *trans*, whereas two of the three preferred conformations for DL-compounds of the same type would have the phenyl groups *gauche*. This fact probably determines the variation of bond angles, with respect to the *meso*-structure, which leads ultimately to the CCH_3 hydrogens resonating at lower field in the n.m.r. spectrum.

Results of coulometric measurements for the electroreduction of bromoesters (1) and (5) on an r.v.c. electrode in DMF–Et$_4$NClO$_4$ (0.1M) solutions

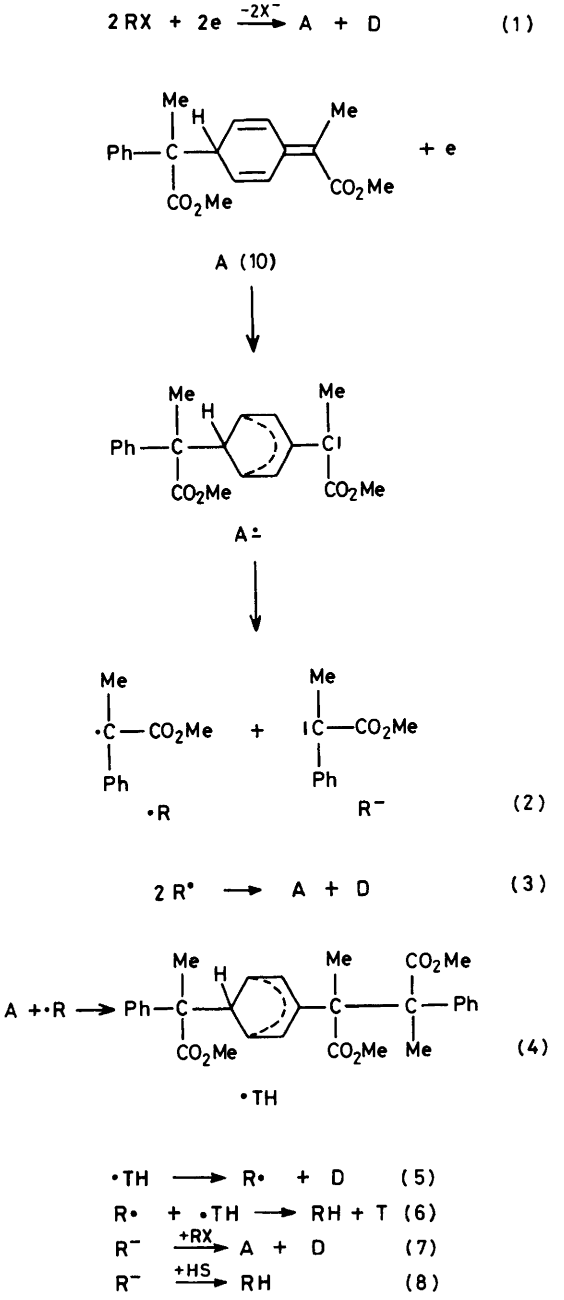
Compound	$-E$ [a]	10^3 C [b]	n_{app} [c]
(1)	1.15	2.0	1.02
(1)	1.90	2.0	1.11
(1)	1.90	1.0	1.38
(5)	2.0	10	1.01
(5)	2.0	5.12	1.23
(5)	2.0	2.56	1.35
(5)	2.0	1.28	1.49

[a] E = applied potential, *versus* the s.c.e. described in the Experimental section. [b] C = concentration of the substrate (mol l^{-1}). [c] n_{app} = number of Faradays per mol of substrate at room temperature.

In addition to the reported dimeric products (7) and (8), trimer (9) was also found among the products of controlled potential electrolysis of (5). The isolated product was identified as (9) from its n.m.r. spectrum and fragmentation patterns in the mass spectra; since the compound gave a clean n.m.r. spectrum, it is probably a single isomer.

A puzzling feature of the results obtained was the fact that various chromatographic experiments designed to separate the compounds resulting from the controlled potential electrolysis of (5) gave fractions containing the same molar ratio, 2 : 1, of monoester (6) to dimers [(7) + (8)]. This mixture behaved as a single compound, showing a single spot on t.l.c. with different pairs of solvents, and apparently a single peak in h.p.l.c. One possible explanation is that a 2 : 1 complex Y between (6) and (7) or (8) is formed. This complex could persist even in polar solvents such as those used in reversed-phase h.p.l.c. We have not attempted to elucidate this behaviour further. An analogous situation occurs with fractions 144–164 from work-up of the products of controlled potential electrolysis of (5). A few milligrams (5—40 mg) of a solid compound were isolated, having the following n.m.r. spectrum; δ_H 7.1—6.5 (2 × 5 H, m, ArH), 3.63 (3 H, s, OCH$_3$), 3.6 (3 H, s, OCH$_3$), 1.76 (3 H, s, CCH$_3$), and 1.70 (3 H, s, CCH$_3$), with additional weak signals for (6). In this case, if a 1 : 2 complex Z between (6) and (7) or (8) is assumed {(6)/[(7) + (8)] = 1 : 2 from integrated CCH_3 signals}, the consequence seems to be a shift of the OCH$_3$ and CCH$_3$ signals of (7).

The nature of the products obtained from controlled potential electrolysis of bromo-ester (5) is consistent with a reaction sequence, initiated by electrochemical reductive dimerization of (5), yielding 'normal' dimers (7) and (8) and a further dimer (10), *e.g.* reaction (1) where



RX is (5), D (7) + (8), and A (10). The *para*-dimer (10), being an activated alkene, can be further reduced, at the applied potential, to its anion-radical, which subsequently decomposes to radical ·R and carbanion R^- [reaction (2)]. The fate of radical ·R is to give dimeric products again. Concurrent attack of ·R on the alkene A can also take place [reactions (3) and (4)] followed by decomposition of ·TH to ·R and D; hydrogen abstraction from ·TH by ·R leads to trimer T (9) and monoester RH (6) [reactions (5) and (6)]. The fate of carbanion R^- arising from reaction (2) is, as usual, to be protonated by traces of adventitious water or acidic substances in the solvent, and to interact with RX in the bulk of the solution [reactions (7) and (8)].

Thus, the formation of αα-dimers (7) and (8) can be traced to the fact that they are formed through reaction (1) as well as through reactions (5) and (7). A decomposition similar to that in reaction (5) and an addition analogous to reaction (4) have been demonstrated to occur[7] in the case of R = CH_2Ph and A = the corresponding α,*para*-dimer. It is not possible to decide in our case whether the main route to αα-dimers D is the direct one (1) or the sequence (1)—(7). The choice is related to steric, conjugative, and polarity factors concerning the relative thermodynamic and kinetic stability of αα (D) with respect to α,*para* (A) structures.[8] Electrochemical data alone are not very useful in this respect. In fact, if the sequence (1)—(7) is supposed to involve the α,*para*-dimer A (10) only, if follows that n_{app} (the number of Faradays per mol of substrate as determined in coulometric experiments) has a value of 1, as experimentally observed at the higher concentrations of substrate (5).

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