Electrochemical Synthesis of 5,6,11,12-Tetrahydro-5,6,11,12-tetrakis(ethoxycarbonyl)dibenzo[*a,e*]cyclo-octene

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Electrochemical reduction of diethyl αα′-dibromobenzene-1,2-diacetate (1) in dimethylformamide solution at a vitreous carbon electrode results in the formation of diethylbenzene-1,2-diacetate (3) (15% of isolated products), *trans,trans*-tetrakis(ethoxycarbonyl)dibenzo[*a,e*]cyclo-octene (6) (16%), dimer (7) (16%), and a polymer (20%) as major products. Formation of benzocyclobutene (5) (7,8-bisethoxycarbonylbicyclo[4.2.0]octa-1,3,5-triene) takes place only to a very small extent (*ca.* 7% of isolated products). The intermediate formation of αα′-bis(ethoxycarbonyl)-*o*-quinodimethane, whose behaviour resembles that of a biradical, through the 2e electrochemical reductive elimination of the Br^- ions from (1), is proposed as the key step leading to the products.

In voltammetric measurements and preparative electrochemical processes with certain organic substrates, it has become useful to perform electrolyses at vitreous carbon electrodes (v.c.e.), thus overcoming some disadvantages of the more popular mercury electrode. Compounds which are expected to be reduced at relatively positive potentials, for example phenyl-α-bromoesters, can be studied [1] by taking advantage from the larger overpotential generally accompanying reduction of halogeno-compounds at a v.c.e. with respect to mercury electrodes.[2] In this study we have selected diethyl αα′-dibromobenzene-1,2-diacetate (1) as starting material, in the hope that benzocyclobutenes (4) and (5) could be obtained through electrochemical reduction of (1) in dimethylformamide. In fact, benzocyclobutenes are valuable intermediates in organic synthesis [3] and they have been prepared by a variety of methods; earlier efforts to obtain the dimethyl esters analogous to (4) and (5) by chemical means were unsuccessful.[4] As we will see below, our original goal was partly accomplished; moreover, the interesting compound 5,6,11,12-tetrahydro-5,6,11,12-tetrakis(ethoxycarbonyl)dibenzo[*a,e*]-cyclo-octene (6) was obtained, as well as dimer (7) and trimer (8).

Another reason for studying the electrochemistry of (1) is to discover whether the electrochemical reductive elimination of the two Br^- ions from (1) is a concerted or stepwise process (Scheme). The situation is in some respect analogous to the controversy concerning the electrochemical reduction of vicinal αα′-dihalogeno-compounds, and is characterized by conflicting views about the results in the literature.[5,6] The present study is an effort to achieve clarification in this direction.

Experimental

Materials.—*NN*-Dimethylformamide (DMF) and polarographic grade Et_4NClO_4 were as described previously.[1] Diethyl benzene-1,2-diacetate [7] (3) was prepared (a) from benzene-1,2-diacetic acid (Aldrich) or (b) from *o*-phenylenediacetonitrile $C_6H_4(CH_2CN)_2$ (Fluka). (a) Acid (15.5 g, *ca.* 0.08 mol) was mixed with EtOH (26 ml), benzene (74 ml), and concentrated H_2SO_4 (0.5 ml) for 6 h. The azeotrope was distilled. The mixture was evaporated under reduced pressure, washed, and neutralized, giving (3) (*ca.* 13 g). (b) Dinitrile (26 g, *ca.* 0.13 mol) was refluxed with absolute EtOH (80 ml), H_2O (8 ml), and concentrated H_2SO_4 (36 ml) for 6.5 h. After cooling and adding H_2O (200 ml), the organic layer was extracted with H_2O and $NaHCO_3$ and the product washed with water and distilled, b.p. 144—146 °C at 4 mmHg, δ_H (CCl_4) 7.1 (4 H, s, ArH), 4.05 (4 H, q, *J* 7 Hz, 2 × OCH_2), 3.56 (4 H, s, 2 × CH_2), and 1.2 (6 H, t, *J* 7 Hz, 2 × CH_3).

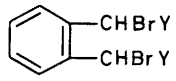
Diethyl αα′-Dibromobenzene-1,2-diacetate (1).—Diethyl benzene-1,2-diacetate (3) (17.5 g, *ca.* 0.07 mol) and *N*-bromosuccinimide (NBS) (25 g, *ca.* 0.14 mol) were added to CCl_4 (160 ml). The solution was continuously irradiated with an Osram 300 W sunlamp and stirred for 15 h at ambient temperature. The solution was filtered and the product dried and purified by column chromatography (SiO_2, hexane–diethyl ether, with ether up to 30%). The product (*ca.* 60%) (*meso*- and DL-mixture 1 : 1 by n.m.r.) had δ_H (CCl_4) 7.7—7.0 (4 H, m, ArH), 5.66 (2 H, s, 2 × CH), 4.1 (4 H, q, *J* 7.2 Hz, 2 × OCH_2), 1.20 and 1.18 (6 H, 2t, *J* 7.2 Hz, 2 × OCH_3), *i.e.* each isomer (1) gives a separate CH_3 signal of the CO_2Et group at δ 1.20 and 1.18, respectively, of equal intensity in the mixture obtained.

Diethyl α-Bromobenzene-1,2-diacetate (2).[7]—This was obtained as for the preparation of (1), *i.e.* by treating (3) with NBS (1 : 1 mol/mol). Column chromatography as before separated (2) (63%) from (1) (10%) and (3) (19%). Compound (2) had δ_H (CCl_4) 7.8—7.0 (4 H, m, ArH), 5.7 (1 H, s, CH), 4.1 (2 H, q, *J* 7 Hz, OCH_2), 3.9 (2 H, q, *J* 7 Hz, OCH_2), 3.66 (2 H, s, CH_2), 1.23 (3 H, t, *J* 7 Hz, CH_3), and 1.20 (3 H, t, *J* 7 Hz, CH_3). All other chemicals used were commercially available.

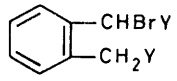
Apparatus and Procedures.—M.p.s, measured on a Kofler apparatus, are uncorrected. Electrochemical instrumentation and procedures for electrolysis on reticulated vitreous carbon (r.v.c.) have been described.[1] Spectral data were obtained with the same instruments used previously.[1] Routine 60 MHz n.m.r. spectra were obtained using a Varian A 60 instrument with tetramethylsilane as internal standard. Mass spectra were determined using an A.E.I. M.S. 12 or a LKB 2130 instrument at 70 eV.† Analytical t.l.c. (silica gel, Merck 60 F_{254}) was used, whenever necessary, with more than one solvent system.

Constant Potential Electrolysis of Diethyl αα′-Dibromobenzene-1,2-diacetate (1).—This experiment was performed in duplicate. In the first electrolysis, diethyl αα′-dibromo-

† The high-resolution mass spectra were recorded on a VG model ZAB-2F instrument in Padova.



(1)



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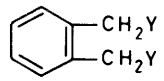

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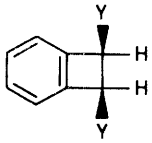

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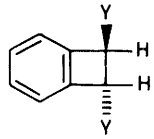

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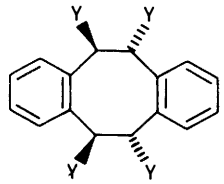

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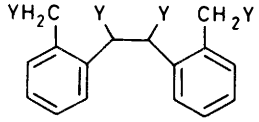
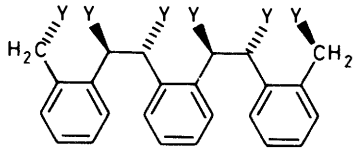
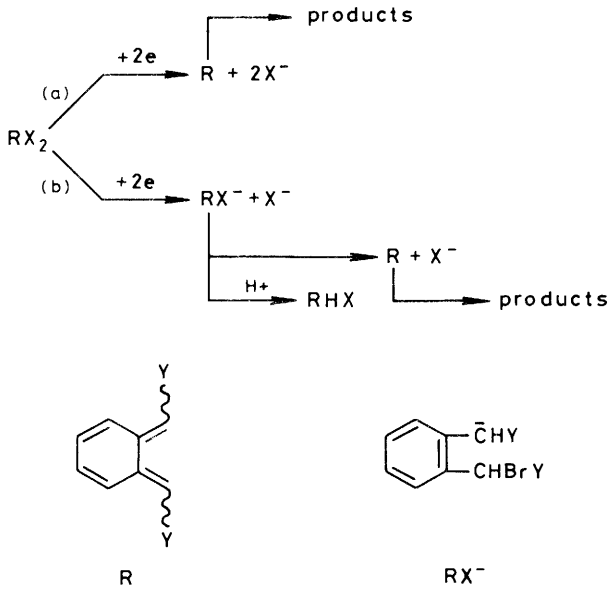


(7) a; *meso*
b; DL



(8)



Scheme. Y = CO_2Et

benzene-1,2-diacetate (1) (2.60 g, 6.4×10^{-3} mol) in DMF (125 ml) containing Et_4NClO_4 (0.1M) was electrolysed on r.v.c. at the potential of -1.5 V. By the end of the electrolysis, 617 C had passed, corresponding to n_{app} 1.97. The substance to be electrolysed was added in small portions, to reduce intermolecular coupling. The electrolysed solution was subjected to conventional work-up, giving a viscous mixture of products, which was analysed by t.l.c. and then subjected to column chromatography (SiO_2, 2.5×60 cm, prepared in hexane with 5% diethyl ether). Elution with hexane–ether gave in turn (3), and (6)—(8). Finally, polymeric material was obtained.

In the second electrolysis, dibromo-ester (1) (3.26 g, 8×10^{-3} mol) in DMF–0.1M-Et_4NClO_4 (145 ml) was electrolysed on r.v.c. at E -1.5 V as before, until the current was 0.003 A and 711 C were consumed (n_{app} 1.94). Work-up of the solution yielded a viscous mixture which was subjected to column chromatography (SiO_2; 2×60 cm). Early fractions gave an oil (20 mg, 3%) which showed δ_H (CCl_4) 7.95—7.1 (4 H, m, ArH), 4.57 (2 H, s, $2 \times$ CH), 4.4 (4 H, q, J 7 Hz, $2 \times OCH_2$), 1.3 (6 H, t, J 7 Hz, $2 \times CH_3$), consistent with structure (4). On standing in CCl_4 solution, a crystalline compound, m.p. 114—116 °C, separated, with n.m.r. spectrum quite different from that previously obtained, δ_H (CCl_4) 8.9—7.3 (8 H, m, ArH), 4.5—3.9 (8 H, 2q, J 7 Hz, $4 \times OCH_2$), 2.8 and 3.1 (inner lines of an AB system, J 16 Hz) and 2.9 (s) (total 4 H, $2 \times CH_2$), 1.43, 1.35, 1.23, and 1.21 (12 H, 4 overlapping t, J 7 Hz, $4 \times CH_3$); *m/e* 272 (34%), 244, 227 (49), 218, 199 (26), 190 (22), 162 (100), 133, and 105. Both n.m.r. and mass spectra are consistent with a mixture of ($CPhCO_2Et{\cdot}CH_2CO_2Et)_2$ isomers. Next a viscous compound (55 mg, 7%) was obtained whose n.m.r. and mass spectra are consistent with (5) (Found: *m/e* 248.104 $\pm$ 0.002. $C_{14}H_{16}O_4$ requires M, 248.104), δ_H (CCl_4) 7.1 (4 H, s, ArH), 4.43 (2 H, s, $2 \times$ CH), 4.1 (4 H, q, J 7 Hz, $2 \times OCH_2$), and 1.26 (6 H, t, J 7 Hz, $2 \times CH_3$); *m/e* 248 (18.2%, M^+), 202 (35.4, M – EtOH), 175 (39.1, M – CO_2Et), 174 (100, M – HCO_2Et), 147 (27.7), 119 (27.9), 102 (54.4, $M - 2 \times CO_2Et$), 91 (45.1), and 29 (36.7). The next compound eluted was diethyl benzene-1,2-diacetate (3) (110 mg, 15%) with the spectroscopic properties identical with those of an authentic sample. Next was obtained *trans,trans*-5,6,11,12-tetrahydro-5,6,11,12-tetrakis-(ethoxycarbonyl)dibenzo[*a,e*]cyclo-octene (6) (120 mg, 16%). There followed a mixture of products. On standing, a crystalline crop (80 mg) of *meso*-(7a) separated (see below.) The oily residue was recrystallized from EtOH to give another crop of (7a) (total 120 mg, 16%). The penultimate product was the quasi-solid DL-(7b) (20 mg, 3%), δ_H (CCl_4) 7.8—6.9 (m, ArH), 4.4 (s, $2 \times$ CH), 4.15 and 4.1 (2q, J 7.5 Hz, $2 \times OCH_2$), 3.6 (d, J 16 Hz, CH_2), 3.5 (d, J 16 Hz, CH_2), 1.26 (t, J 7.5 Hz, $2 \times CH_3$), and 1.16 (t, J 7.5 Hz, $2 \times CH_3$); *m/e* 498 (M^+), 452 (M – EtOH), 406 (M – EtOH – EtOH), 360 ($M - 2 \times$ EtOH – EtOH), 333 ($M - 2 \times$ EtOH – CO_2Et), and 249 ($M/2$), with the correct metastable peaks for the transitions 498 ⟶ 452 (410.2), 452 ⟶ 406 (364.7) and 406 ⟶ 360 (319.2). The final product obtained was (8) (80 mg, 11%). The remaining fractions were shown by n.m.r. to be polymeric material.

trans,trans-5,6,11,12-*Tetrahydro*-5,6,11,12-*tetrakis*(*ethoxycarbonyl*)*dibenzo*[a,e]*cyclo-octene* (6).—This had m.p. 171—172 °C (sublimed), δ_H (CCl_4) 7.7—6.7 (8 H, m, ArH), 4.8 (2 H, d, J 8 Hz, $2 \times$ CH), 4.4 (2 H, d, J 8 Hz, $2 \times$ CH),

4.4—3.8 (8 H, 2q, *J* 7 Hz, 4 × OCH_2), and 1.2 and 1.12 (12 H, 2t, *J* 7 Hz, 4 × CH_3); δ_H ($CDCl_3$) 7.3—6.7 (8 H, m, ArH), 5.1 (2 H, d, *J* 8 Hz, 2 × CH), 4.7 (2 H, d, *J* 8 Hz, 2 × CH), 4.36 (4 H, q, *J* 7 Hz, 2 × OCH_2), 4.03 (4 H, q, *J* 7 Hz, 2 × OCH_2), 1.36 (6 H, t, *J* 7 Hz, 2 × CH_3), and 1.23 (6 H, t, *J* 7 Hz, 2 × CH_3) (Found: *m/e* 496.210 ± 0.005. $C_{28}H_{32}O_8$ requires *M*, 496.209); *m/e* 496 (12.85%, M^+), 450 (*M* − EtOH), 423 (*M* − CO_2Et); 404 (71.70, *M* − 2 × EtOH), 376 (45.20, *M* − 2 × EtOH − CO), 348 (58.55, *M* − 2 × EtOH − 2 × CO), 303 (*M* − 2 × EtOH − 2 × CO − OEt), 276 (*M* − H − 3 × CO_2Et), 248 (*M*/2), 247, 231 (*M* − EtOH − 3 × CO_2Et), 203 (100, *M* − H − 4 × CO_2Et), and appropriate peaks at lower *m/e*.

αα′-Bis(ethoxycarbonyl)-2,2′bis(ethoxycarbonylmethyl)bibenzyl (7a).—This had m.p. 110—112 °C, δ_H (CCl_4) 7.8—6.8 (8 H, m, ArH), 4.53 (2 H, s, 2 × CH), 4.05 (4 H, q, *J* 7 Hz, 2 × OCH_2), 3.85 (4 H, q, *J* 7 Hz, 2 × OCH_2), 3.7 (4 H, apparently s, 2 × CH_2), 1.23 (6 H, t, *J* 7 Hz, 2 × CH_3), and 0.84 (6 H, t, *J* 7 Hz, 2 × CH_3). The signals at δ 3.85 and 0.84 are to be attributed to the αα′-(ethoxycarbonyl) CH_2 and CH_3 respectively and are characteristic of the *meso* structure; *m/e* 498 (4.5%, M^+), 452 (18.7, *M* − EtOH), 406 (21.00, *M* − 2 × EtOH), 379 (11.00), 333 (23.1), 305 (13.65 *M* − 2 × EtOH − 2 × CO − OEt), 287 (14.52), 277 (6.00, *M* − 3 × CO_2Et − 2 × H), 249 (100, *M*/2), and appropriate peaks at lower *m/e* (Found: *m/e*, 498.215 ± 0.011. $C_{28}H_{34}O_8$ requires *M*, 498.225).

Trimer (8).—This was a quasi-solid substance which failed to crystallize, δ_H (CCl_4) 7.8—7.0 (12 H, m, ArH), 5.0 (1 H, d, *J* 12 Hz, CH), 4.7 (1 H, d, *J* 12 Hz, CH), 4.9 (1 H, d, *J* 12 Hz, CH), 4.6 (1 H, d, *J* 12 Hz, CH), 3.7 (4 H, apparently s, 2 × CH_2), 4.1 and 3.6 (12 H, 2q, *J* 7.5 Hz, 6 × OCH_2), 1.43, 1.40, 1.37, 1.1, 1.08, and 0.8 (total 18 H, 6 overlapping t, *J* 7.5 Hz); *m/e* 746 (M^+), 700 (*M* − EtOH), 673 (*M* − CO_2Et), 672 (*M* − EtOH − CO), 654 (*M* − EtOH − EtOH), 608 (*M* − 2 × EtOH − EtOH), 600 (*M* − 2 × CO_2Et), 582 (*M* − $PhCH_2CO_2Et$), 581, 580, 562 (*M* − 3 × EtOH − EtOH), 554 (582 − CO), 534 (580 − EtOH), 497 (*M* − 249), and 249 (100%) with metastable peaks for the transitions 746 ⟶ 700 (656.84), 700 ⟶ 672 (655.12), 700 ⟶ 654 (611.02), 654 ⟶ 608 (565.24), 608 ⟶ 562 (519.48), 582 ⟶ 554 (527.35), and 580 ⟶ 534 (491.65) (Found: *m/e*, 746.341 ± 0.012. $C_{42}H_{50}O_{12}$ requires *M*, 746.330).

Results and Discussion

The cyclic voltammetry of diethyl αα′-dibromobenzene-1,2-diacetate (1) (Figure 1a) † and of diethyl α-bromobenzene-1,2-diacetate (2) (Figure 1b) is typical of irreversible electrode processes, E_p −1.05 and −1.09 V at *v* 0.020 V s^{-1} and *C* 5 × 10^{-4}M, respectively. If the i_p *versus* *C* (Figure 2) or the i_p *versus* $v^{\frac{1}{2}}$ plots (Figure 3) for (1) are considered, it can be seen that the situation is apparently simple, In fact, linear behaviour is observed, according to the known equation (1) [8]

$$i_p = 2.9847 \times 10^8 n(\alpha n_\alpha)^{\frac{1}{2}} A D^{\frac{1}{2}} v^{\frac{1}{2}} C \qquad (1)$$

where i_p/μA = peak current, *A*/cm^2 = electrode area, *D*/cm^2 s^{-1} = diffusion coefficient, *v*/V s^{-1} = sweep rate, *C*/M = concentration of the substrate, *n* = number of electrons transferred in the reduction process, α = transfer coefficient, and n_α = number of electrons transferred in the rate-determining step, in the case of totally irreversible electrode processes.

† 1 : 1 *meso*- and DL-mixture of isomers (see Experimental section).

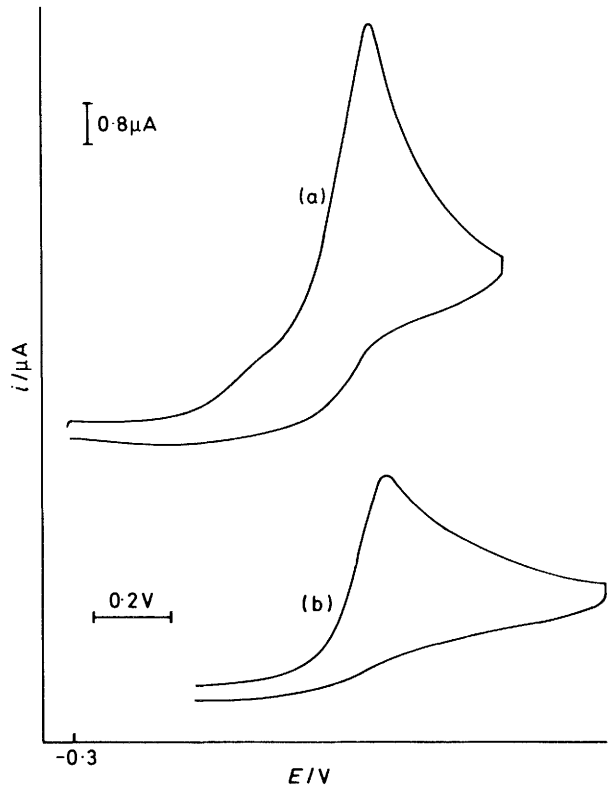


Figure 1. Cyclic voltammograms for (a) dibromo-ester (1) and (b) bromo-ester (2) (both 5.0 × 10^{-4}M) in dimethylformamide containing Et_4NClO_4 (0.1M) as supporting electrolyte. Sweep rate 20 mV s^{-1}, glassy carbon electrode of area 8.2 × 10^{-2} cm^{-1}, *E*/V *versus* s.c.e.

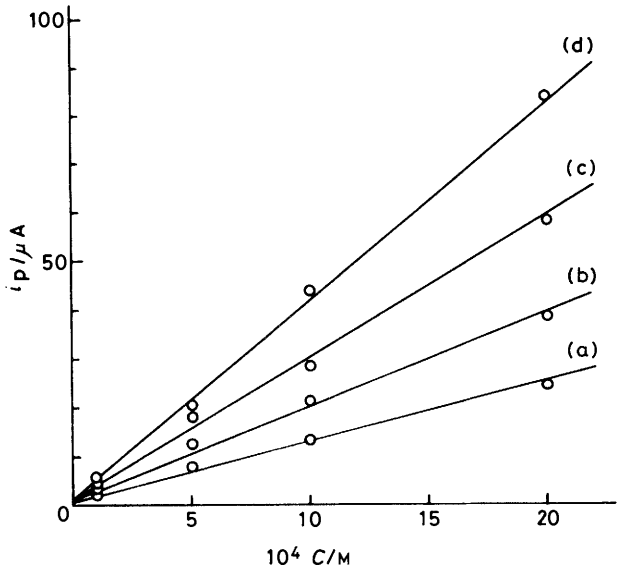


Figure 2. Effect of the concentration (*C*) of (1) on the peak current (i_p) in the cyclic voltammetry of (1) at various sweep rates *v*: (a) *v* = 20 mV s^{-1}; (b) *v* = 50 mV s^{-1}; (c) *v* = 100 mV s^{-1}; (d) *v* = 200 mV s^{-1}; solvent and electrode as in Figure 1

From the data of Figure 2, we obtained equation (2). From

$$D^{\frac{1}{2}} n(\alpha n_\alpha)^{\frac{1}{2}} = 3.8 \times 10^{-3} \text{ cm s}^{-\frac{1}{2}} \qquad (2)$$

the relation $(E_p - E_{p/2})^{25°} = 0.048/\alpha n_\alpha$ V (E_p, $E_{p/2}$ = potenti-

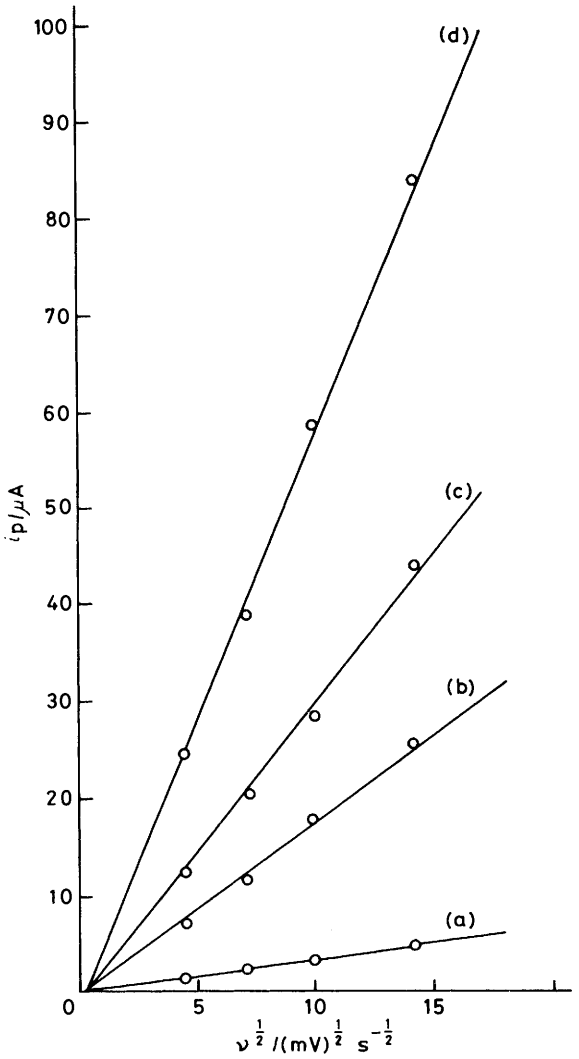


Figure 3. Effect of the sweep rate (v) on the peak current (i_p) in the cyclic voltammetry of (1) at various concentrations C of (1): (a) $C = 1 \times 10^{-4}$M; (b) $C = 5 \times 10^{-4}$M; (c) $C = 1.0 \times 10^{-3}$M; (d) $C = 2 \times 10^{-3}$M; solvent and electrode as in Figure 1

als corresponding to the peak current and to the half-peak current respectively, at a given sweep rate) or from $E_{p/2}$ *versus* log v plots [8] the value αn_α *ca.* 0.5 for (1) was obtained. This corresponds to $n_\alpha = 1$ with $\alpha = 0.5$ or $n_\alpha = 2$ with $\alpha = 0.25$, the last figure being the more reliable. Now, both D and n, the number of electrons transferred in the time scale of the voltammetric experiment, are unknown. To circumvent this difficulty, we compared, at first, the peak current values of (1) with those of diphenylanthracene (A) ($A + e \rightleftharpoons A^{\cdot -}$) under the same concentration and sweep rate, and assuming D (1) $\cong D$ (A) we have equation (3). Some results are collected in the Table.

$$i_p(1)/i_p(A) = 1.11\ n(1)(\alpha n_\alpha)^{\frac{1}{2}}[D(1)/D(A)]^{\frac{1}{2}} \qquad (3)$$

Thus, a value $2 < n < 3$ is suggested. Figure 4 shows how the addition of a proton donor (3,4-dimethylphenol, HA) affects the voltammetric curves of (1). Unusual behaviour is observed, in that the maximum enhancement is reached at the molar ratio C(HA)/C(ester) = 0.5. Further addition of acid lowers the peak current, until, with excess of HA, the peak current is raised only by *ca.* 15% of the original value. Considering, for the moment, the maximum peak current value

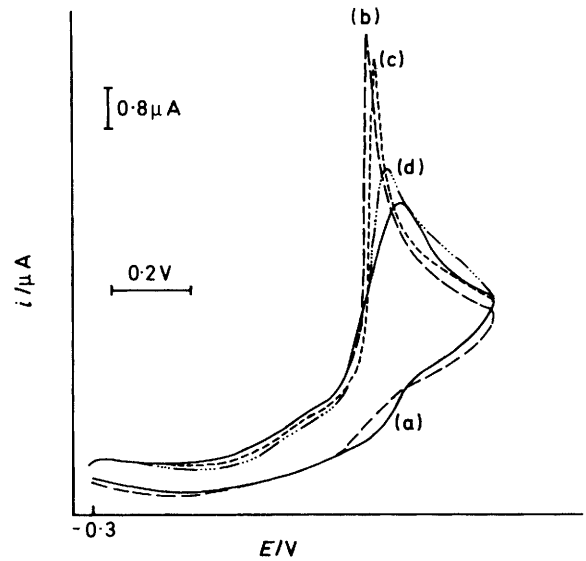


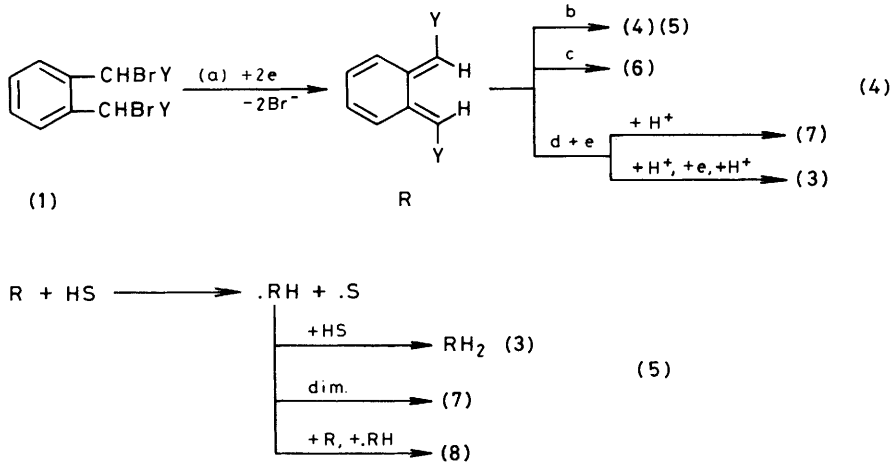
Figure 4. Cyclic voltammograms of dibromo-ester (1) (1.0×10^{-3}M) in the presence of proton donor HA (3,4-xylenol) in DMF–0.1M-Et_4NClO_4 at glassy carbon electrode: (a) C(HA) = 0; (b) C(HA) = 5×10^{-4}M; (c) C(HA) = 1.0×10^{-3}M; (d) excess of HA

Results of the voltammetric measurements of n [a] for the electroreduction of dibromo-ester (1) on a glassy carbon electrode (g.c.e.) in DMF–0.1M-Et_4NClO_4 solution

$10^3\ C$ [b]	v [c]	n [a]
0.1	0.020	3.00
	0.200	2.53
0.5	0.020	3.03
	0.200	2.73
1.0	0.020	2.34
	0.200	2.54
2.0	0.020	2.46
	0.200	2.69

[a] Number of Faradays per mol of substrate as determined using equation (3), see text. [b] C = Concentration of the substrate in mol l^{-1}. [c] v = Sweep rate (V s^{-1}).

obtained in the presence of acid, and the n value obtained in its absence (Table), it is easily verified that the number of electrons transferred to (1) (C 10^{-3}M) is raised to *ca.* 4 when 5×10^{-4}M-acid is present. Furthermore, in this case the peak is sharp and the peak potential is shifted towards more positive values (*ca.* 80 mV) with respect to the normal (*i.e.* in the absence of acid) value. We observed also that the positive shift of E_p is more pronounced at low sweep rates, the 'inverted acid effect' on i_p remaining almost the same at the higher sweep rates. We have ensured that no chemical effects of the acid on the dibromo-ester are operative. Of the several explanations of decreasing effectiveness upon increasing content of acid, the assumption of clustering of the acid at the interface between the electrode and the solution, thus blocking further reduction of the substrate, seems to be the most tenable. At this point, it can be concluded that cyclic voltammetry indicates a two-electron process ($n = 2$) for reduction of RBr_2, in strictly aprotic conditions; the values $2 < n < 3$ (Table) reflect the presence of residual unavoidable proton donors in the solution; proton donors are effective (part of the 'inverted' behaviour cited) indicating that an anionic intermediate is formed. The situation is different for the conditions of the preparative-scale reductions: here the n_{app} value in 'aprotic' DMF (see Experimental section) is



2, because the residual water present is consumed at the beginning of the controlled potential electrolysis (c.p.e.) (compare the voltammetric experiment) and then the reduction proceeds in virtually aprotic conditions. Preparative-scale reduction of (1) leads to a variety of products after work-up, mainly cyclic dimer (6), dimer (7a), trimer (8), and diester (3). A number of possible pathways may be envisaged for the formation of the products from (1). The possibilities shown in equations (4) and (5) are considered most likely. Hydrogen-atom transfer from the solvent to R (of the diradical type) is likely to compete with paths b—d in equation (4). Thus, it can be understood why n_{app} tends to 2 in the preparative-scale reduction: the following reactions can interfere with reaction (4b—d) in the conditions of c.p.e. When all the acidic substances are consumed during c.p.e., reactions (5) may be the prevailing route leading to hydrogenated products. The fate of the solvent-derived radical .S is not known at present: however, yellow impurities probably derived from it are always present at the end of c.p.e. and they remain fixed on the chromatographic column used in work-up.

Neither voltammetric experiments nor the nature of the products obtained in c.p.e. of (1) can give a definite answer about the question of concerted or stepwise nature of path a in reaction (4). The reduction potentials of (1) and (2), as measured by the peak potential E_p, are very close together (for example, $\Delta E_p = 40$ mV at $v = 0.02$ V s^{-1}) so that (2), if formed, will be almost immediately reduced at the potential applied in c.p.e.

That compound (5) obtained from electrolysis of (1) was a benzocyclobutene was apparent from the mass spectrum (molecular ion at *m/e* 248) and from the simple n.m.r. spectrum, indicative of a *trans*-structure. For example, the aromatic CH signals appear as an apparent singlet (see Experimental section) whereas compound (4) shows a multiplet. Unfortunately, the corresponding *cis*-isomer (4) was characterized only by its n.m.r. spectrum (see Experimental section). Formation of the unstable *cis*-benzocyclobutene (4) is remarkable in that steric interactions between the two ethoxy-carbonyl groups lead probably to a large bond length between the carbon atoms bearing the substituents, and the inefficiency of formation of (4) is not surprising.

It is interesting to note that electrochemical reduction of (1) gave only one dibenzo[*a,e*]cyclo-octene (6), in which the protons of the cyclo-octene ring resonate as a single AB system [δ_H ($CDCl_3$) 4.7 and 5.1 (*J* 8 Hz)], indicative[9] of a distorted tube conformation. Thus, the stereochemical assignment of (6) as the 5,6,11,12-tetrahydro-*r*-5,*t*-6,*t*-11,*c*-12-tetrakis(ethoxycarbonyl)dibenzo[*a,e*]cyclo-octene follows from the δ (CH) values of the cyclo-octene ring which are nearly coincident with those of the corresponding tetramethyl ester described in ref. 9. It can be inferred[9] that (6) originates from an αα′-bis(ethoxycarbonyl)-*o*-quinodimethane intermediate, R in equation (4), which forms a spiro-dimer. This in turn rearranges[9] to the dibenzocyclo-octene (6). The spiro-dimer of R, which may be an intermediate in the formation of (6), was not observed by us, presumably because of rapid conversion into (6) during chromatographic separation.

Little doubt exists about the assignment of *meso*-stereochemistry to compound (7): the methyl resonance of the ' inner ' ethoxycarbonyl groups at δ 0.84 is characteristic, *e.g.* δ 0.89 for *meso*-diethyl 2,3-diphenylsuccinate.[10] In the n.m.r. spectrum of trimer (8) the methine protons appear as two AB systems, δ 5 and 4.7 (*J* 12 Hz) and 4.9 and 4.6 (*J* 12 Hz). The large vicinal coupling suggests a *trans*-relationship between the protons locked in the more populated conformation of (8).

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