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Electro-organic reactions. Part 50.† Quinodimethane chemistry. Part 1. Electrochemical generation and characterisation of *p*-quinodimethanes

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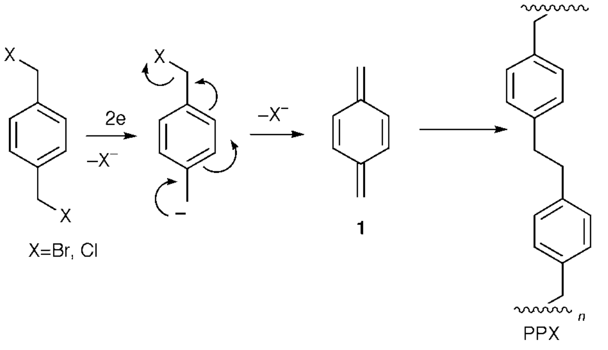
Quinodimethanes (QDMs) were generated cathodically from 1,4-bis(halogenomethyl)arenes, either by direct or by mediated reduction, and characterised using cyclic voltammetry in the 0.1 to 200 V s^{-1} range. Formal redox potentials ($E°$) were determined, including that, at −15 °C, for the parent quinodimethane. Redox catalysis with organic mediators proved to be a convenient method for the generation of quinodimethanes from 1,4-bis(chloromethyl)arenes, either for electroanalytical study of the intermediates or for preparative purposes. The quinodimethanes electrogenerated from bis(chloromethyl)arenes in the presence of an organic mediator react to give good yields of poly(*p*-xylylenes) (PPXs). A copolymer, proposed to be random, is obtained by mediated co-electrolysis of 1,4-bis(chloromethyl)benzenes and 2,5-bis(chloromethyl)-1,4-dimethoxybenzene.

Introduction

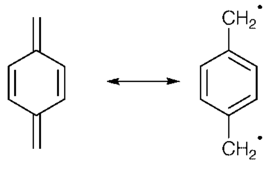
Quinodimethanes (QDMs) are important intermediates in synthesis. Szwarc[1,2] first reported on the *p*-QDM **1** which was formed in high temperature pyrolysis of *p*-xylene in the gas phase. Upon condensation from the gas phase, polymerisation gave a white solid film of poly(*p*-xylylene) (PPX). Szwarc[1,2] proposed that the high reactivity in the condensed phase is due to the significant electron availability at the terminal methylene group, *i.e.* structure **2**, leading to 1,6-addition by a free radical chain mechanism. The inconvenience of dealing with a short-lived species present in the vapour phase at high temperatures limited the early study of the chemistry of *p*-QDM. Errede and Landrum[3] were the first to trap *p*-quinodimethane, formed by pyrolysis, in hexane at −78 °C; it was stable for several hours. Williams *et al.*[4] obtained an ^{1}H NMR in d_8-THF where the sharpness of the signals, taken together with the absence of an EPR signal, indicated the existence of *p*-xylylene in the quinonoid **1** rather than the diradical form **2**.

Covitz[5] and Gilch[6] were the first to study the electrochemical reduction of 1,4-bis(bromomethyl)benzene **3a** which gave PPX **9a**, presumed to arise *via* 1,6-elimination with formation of *p*-quinodimethane (Scheme 1). Since it uses conditions less drastic than for pyrolysis (room temperature, atmospheric pressure) the electrochemical route has extensively been investigated for the formation[7,8] of PPXs and poly(*p*-phenylvinylenes) (PPVs). Furthermore, *o*-quinodimethanes, important intermediates for cycloaddition reactions, may be generated in the presence of dienophiles, and thus effect useful synthetic conversions.[9,10] A limitation of this electrochemical reduction route was that with few exceptions bis(bromomethyl)arenes must be used as the cheaper and less lachrymatory chloro derivatives are more difficult to reduce and in many cases give cathodic hydrogenolysis.

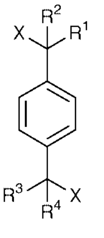
We investigated in more detail the electrochemical behaviour of 1,4-bis(halogenomethyl)arenes **3a**–**f**, **4**, **5a**,**b** with a view to characterising the quinodimethane intermediates. The major follow-up reaction is polymerisation and, for co-electrolysis, co-polymerisation to give PPXs.



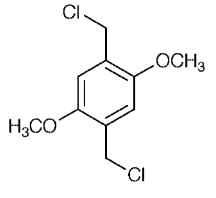
Scheme 1 Cathodic 1,4-elimination.



1 **2**



3a R^1=R^2=R^3=R^4=H, X=Br
3b R^1=R^2=R^3=R^4=H, X=Cl
3c R^1=R^3=Ph R^2=R^4=H, X=Br
3d R^1=R^3=Ph R^2=R^4=H, X=Cl
3e R^1=R^2=R^3=Ph R^4=H, X=Br
3f R^1=R^2=R^3=Ph R^4=H, X=Cl



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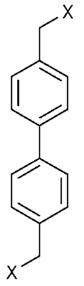

5a X=Br
5b X=Cl

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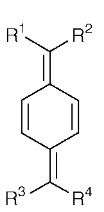
Results and discussion

Preparation of the precursors

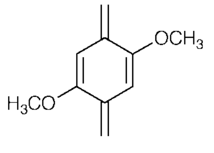
Routes to compounds **4** and **5a** had previously been developed[7,8] in our laboratory. The α,α′-phenyl substituted precursors were prepared by modifications of reported methods based on reaction between an appropriate equivalent of phenylmagnesium halide and either terephthalaldehyde or methyl 4-formylbenzoate (see Experimental section). Compound **5b** was obtained by chloromethylation of biphenyl.

Electrochemical behaviour of 1,4-bis(halogenomethyl)arenes and 1,4-bis(halogenobenzyl)arenes

The quinodimethanes **1**, **6a–c** formed by reduction of the 1,4-bis(bromomethyl)arene precursors are detectable by CV at modest scan rates at an Hg cathode in DMF solution. The cyclic voltammograms in Fig. 1 illustrate the scope for detection and characterisation of the quinodimethane intermediates. In some cases the first wave is poorly defined, probably a consequence of the use of a Hg cathode; with halogeno compounds it is not uncommon for surface formation of organomercury compounds to complicate the electrode response.



1 R^1=R^2=R^3=R^4=H
6a R^1=R^4=Ph R^2=R^3=H
6b R^1=R^2=R^3=Ph R^4=H
6c R^1=R^2=R^3=R^4=Ph



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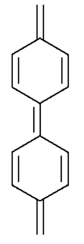

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At room temperature the reduction of quinodimethane **1** (second reduction peak, Fig. 1a) is chemically irreversible at scan rates up to 100 V s^{-1} but using cyclic voltammetry at low temperature (−15 °C) gave sufficient reversibility to allow determination of the $E°$ value (see later, Fig. 2a). Cyclic voltammetry of 1,4-bis(α-bromobenzyl)benzene **3c** (Fig. 1b), at 100 V s^{-1}, shows a clear quasi-reversible second reduction wave and also a well defined third wave. These correspond to the formation of the QDM radical anion, **6a**$^{\bullet -}$, and dianion, **6a**$^{2-}$, respectively. Reversibility is sufficient to allow measurement of the $E°$ value. For the chloro derivative, 1,4-bis(α-chlorobenzyl)benzene **3d**, the expected quinodimethane **6a** is more easily reduced than the precursor, **3d** (Fig. 1c). Consequently **6a**, if formed, will be immediately reduced and preparative experiments show[7] that in such cases the product is that of hydrogenolysis. However, by continuous cycling at 100 V s^{-1} with switching at the foot of the initially observed reduction peak, the characteristic quasi-reversible couple for redox of the quinodimethane **6a** develops (Fig. 1d). The identical $E°$ for the couple generated from both bromo- and chloro-precursors (**3c** and **3d**) is compelling confirmation that the intermediate formed is indeed the corresponding quinodimethane.

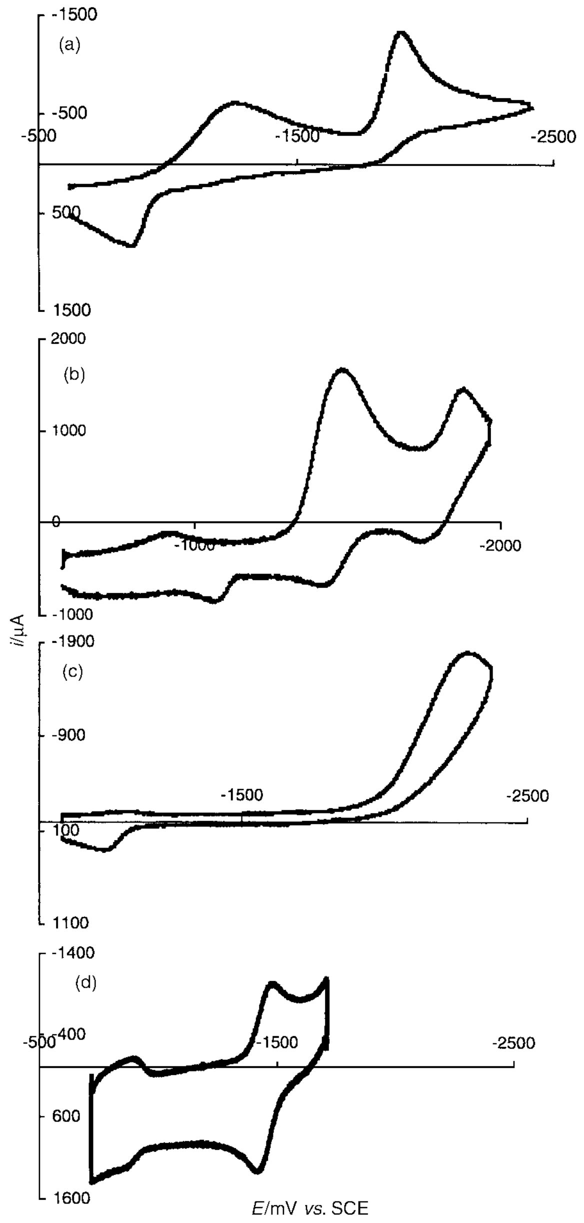


Fig. 1 Cyclic voltammetry of 1,4-bis(halogenomethyl)arenes [2 mM in DMF–Bu_4NPF_6 (0.1 M), Hg/Pt cathode]. (1a) 1,4-Bis(bromomethyl)benzene (**3a**), 100 V s^{-1}. (1b) 1,4-Bis(α-bromobenzyl)benzene (**3c**), 100 V s^{-1}. (1c) 1,4-Bis(α-chlorobenzyl)benzene (**3d**), 100 V s^{-1}. (1d) 1,4-Bis(α-chlorobenzyl)benzene (**3d**), 100 V s^{-1}, continuous cycling.

Quinodimethanes **6a–c** are sterically stabilised by phenyl groups attached at the methylene groups. The lower reactivity of the phenyl-substituted quinodimethane **6a** may be a consequence of stabilisation through extended conjugation or of steric hindrance to the follow-up reaction (polymerisation). The fact that the measured $E°$ is less negative than that of the parent quinodimethane **1** (Table 1) argues in favour of extended conjugation stabilising the radical anion. Further phenyl substitution, as in **6b** and **6c**, has little effect on the $E°$ values (Table 1). This is consistent with the greater hindrance to coplanarity of the phenyl groups in the radical anions. Effectively the two phenyl groups in the radical anion of **6a** can achieve planarity and hence delocalise charge and spin whereas additional phenyl groups, as in triphenylmethane, cannot be coplanar and therefore do not add significantly to stabilisation through delocalisation.

Low temperature cyclic voltammetry was carried out on compound **3a**, at a gold cathode. At 160 V s^{-1} quasi-reversible reduction was observed allowing measurement of $E°$ for **1** (Fig. 2, Table 1). As discussed above the chlorides **3b**,**d**, **f**, **5b** are more difficult to reduce than the corresponding quinodimethanes. However, the voltammogram of 1,4-bis(chloromethyl)benzene **3b** shows a small pre-peak (Fig. 2b) which is due to the reduction of the quinodimethane **1** formed by redox catalysis. A low concentration of the quinodimethane will be formed by direct reduction at the foot of the first reduction wave and the corresponding radical anion is probably responsible for further and major formation of the quinodimethane by redox catalysis. This is consistent with the experiment performed using **3d** (Fig. 1d) in which continuous cycling with switching of potential just into the foot of the first wave causes a build-up of the quino-

Table 1 Reduction potentials[a] of starting materials and of the quinodimethanes formed

Substrate	$-E_{red}(1)/V^b$	$-E°(QDM)/V$
3a	1.27	$1.93^b/1.935^c$ (**1**)
3b	2.11	1.93^b (**1**)
3c	0.80	1.495 (**6a**)
3d	1.96	1.495 (**6a**)
3e	0.88	1.560 (**6b**)
3f	2.20	1.56 (**6b**)
4	2.05	1.923^b (**7**)
5a	1.35	1.992^b (**8**)
5b	2.19	1.992^b (**8**)
6c		1.493 (**6c**)

[a] Formal potentials with reference to SCE measured by cyclic voltammetry at 1–200 V s^{-1} in 2 mM solutions in DMF–Bu_4NPF_6 (0.1 M) at an Hg/Pt electrode, at room temperature, see experimental section for details. [b] Peak potential at 1 V s^{-1}. [c] $E°$ at −15 °C, Au cathode, 160 V s^{-1}.

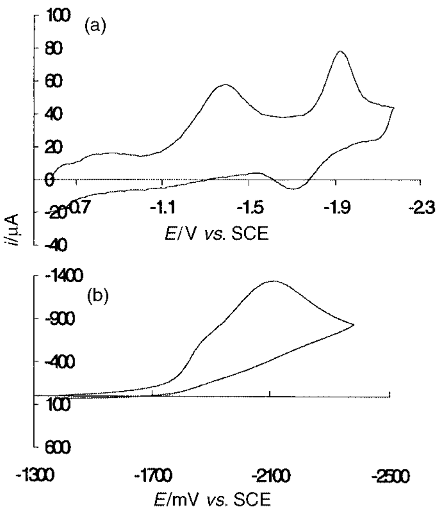


Fig. 2 Cyclic voltammetry of 1,4-bis(halogenomethyl)arenes [2 mM in DMF–Bu_4NPF_6 (0.1 M), Au cathode]. (2a) 1,4-Bis(bromomethyl)benzene (**3a**), −15 °C, 160 V s^{-1}. (2b) 1,4-Bis(chloromethyl)benzene (**3b**), −15 °C, 10 V s^{-1}.

dimethane which at 100 V s^{-1} is reduced reversibly. Deliberate addition of an appropriate mediator that is more easily reduced than either the quinodimethane or precursor (see Table 2) results in development of the quinodimethane reduction peak. This is illustrated (Fig. 3) for the case where **3d** is the precursor and 1,4-diacetylbenzene is the mediator. Fig. 3(a) shows that in the presence of **3d** catalytic currents are well in excess of a two-fold increase, indicating true catalytic activity and not a chemical reaction between mediator radical anion and the halide precursor. Fig. 3b demonstrates the concomitant formation of the quinodimethane **6a**. The peak potentials of the quinodimethanes could be determined using the chlorides as the substrate and they are identical to those obtained through direct reduction of the bromides.

The chloride **3b** in the presence of an organic mediator gives poly(*p*-xylylene) **9a** in good yield. With few exceptions electrogenerated PPXs are waxy solids, insoluble in all common solvents. They have been thoroughly studied[7] by solid state ^{13}C NMR, direct pyrolysis mass spectrometry, thermal analysis and infrared spectroscopy. Examination by FT-IR shows a clear and characteristic absorption at 821 cm^{-1}. The PPX obtained by mediated electrolysis of **3b** appeared to be identical with that formed by direct reduction of 1,4-bis(bromomethyl)benzene **3a**. Direct electrolysis of 1,4-bis(α-bromobenzyl)benzene **3c** and mediated electrolysis of the corresponding chloride **3d** each gave a yellow waxy solid with a softening point at 264 °C. In this case the product was soluble in organic solvent and the broad ^1H NMR signal is evidence for at least an oligomeric structure. Gel permeation chromatography in DMF, and using polystyrene standards, revealed a bimodal distribution of molecular weight with two peaks of similar area. The low molecular weight peak had $M_w = 1297$, with a polydispersivity of 1.3 and the higher molecular weight peak had $M_w = 3.3 \times 10^5$, with a polydispersivity of 2.6. The latter corresponds to a degree of polymerisation of about 1300. Pyrolysis mass spectrometry and Matrix-Assisted Laser Desorption Ionisation Time of Flight (MALDI-TOF) MS gave no fragments at $n > 2$. Similar behaviour was observed in the case of the triphenyl-substituted precursor **3e**.

Table 2 Redox potentials[a] for mediators used in the cleavage of 1,4-bis(chloromethyl)benzene **3b**

Mediator	$-E°/V$ *vs.* SCE
Fluorene	1.16
Benzophenone	1.75
9-Phenylanthracene	1.88
9,10-Diphenylanthracene	1.83
1,3-Diphenylisobenzofuran	1.84
Perylene	1.63

[a] For conditions see footnote to Table 1.

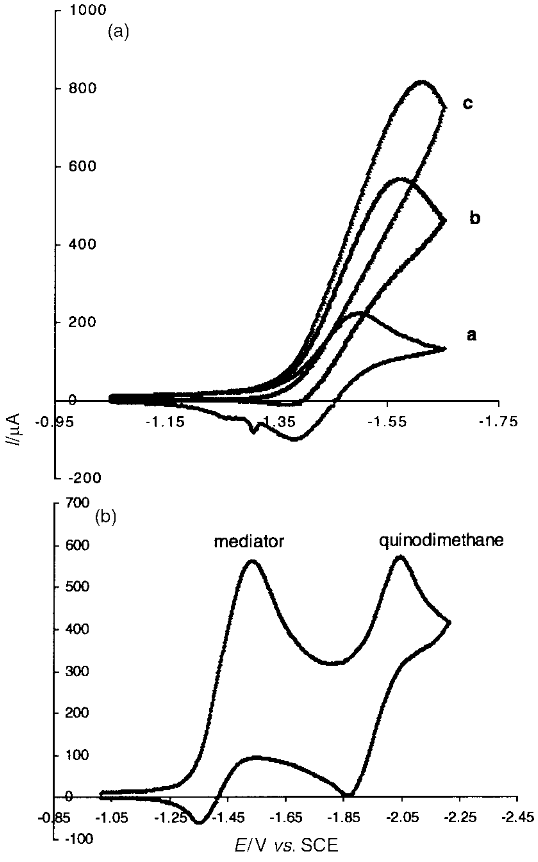
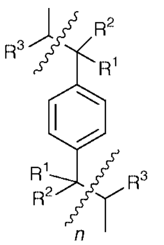
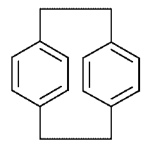


Fig. 3 (a) Cyclic voltammetry of (**a**) 1,4-diacetylbenzene [2 mM in DMF–Bu_4NPF_6 (0.1 M), Hg/Pt cathode] and (**b**) and (**c**) with addition of 1,4-bis(α-chlorobenzyl)benzene (**3d**), 1 and 2 equivalents respectively. (b) As for (**c**) with sweep extended to show development of reduction peak for **6b**.

Provided that the reaction was halted at 2 F, direct electrolysis of the chlorides, at the peak potential, gave insoluble PPXs which were isolated by filtration; the mother liquor contained a small amount of the [2,2]paracyclophane **10**. The yield of the biphenyl-containing PPX, **13**, was, contrary to expectation,[7] greater from careful electrolysis of the chloride **5b** than from the bromide **5a** (Table 4). In contrast exhaustive electrolysis of 1,4-bis(chloromethyl)benzene **3b** gave a substantial yield of **10**. Direct electrolysis of 4,4′-bis(chloromethyl)biphenyl **5b** gave





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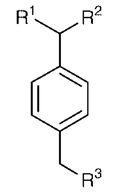
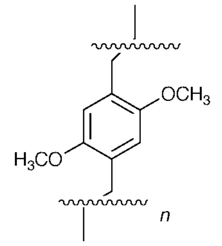


9a $R^1=R^2=R^3=H$
9b $R^1=R^3=Ph, R^2=H$
9c $R^1=R^2=R^3=Ph$

11a $R^1=R^2=R^3=H$
11b $R^1=R^3=Ph, R^2=H$
11c $R^1=R^2=R^3=Ph$



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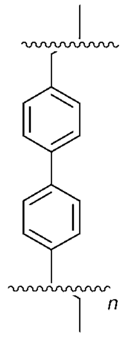

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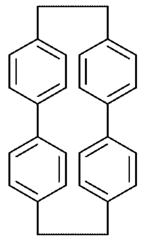

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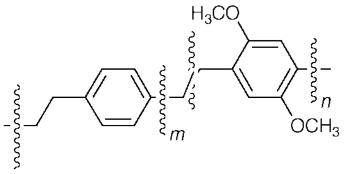
[2.0.2.0]paracyclophane **14** as a minor side product which was separated from 4,4-dimethylbiphenyl by preparative thin layer chromatography.

Mediated copolymerisation

Compound **3b** is more difficult to reduce than the 2,5-dimethoxy analogue **4** by *ca.* 0.7 V. However, mediated co-electrolysis of **3b** and **4** at the peak potential of the mediator (9-phenylanthracene at −1.7 V *vs.* Ag) gave the copolymer, proposed to be the random copolymer **15**, which was insoluble in all common solvents.



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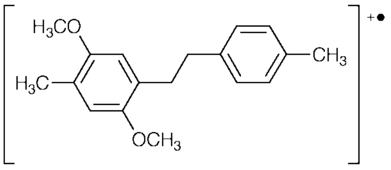

15a

Data from differential scanning calorimetry (DSC), solid state ^{13}C NMR and direct pyrolysis mass spectrometry (DPMS) were used to distinguish between copolymerisation and a possible mixture of the two homopolymers (Table 3) and structure **15**. Detection of the fragment **15a** by DPMS is good evidence for copolymerisation; the ^{13}C NMR spectrum indicates for the proposed copolymer a chemical shift for the CH_2CH_2 link signal significantly different from those determined for the homopolymers **9a** and **12**. A mixture would be expected to display signals at the chemical shifts characteristic of both of homopolymers. A similar result would be expected for a block copolymer. The distinctly different signal observed for **15** is consistent with it being a random copolymer with the CH_2CH_2 link in a different environment.

The melting transitions observed by DSC also point to genuine copolymerisation. The proposed copolymer **15** shows a clear melting transition very different from those exhibited by the homopolymers (Table 3).

Table 3 ^{13}C NMR and DSC data for homo- and co-polymers

Substrate	δ (CH_2)[a]	mp/°C[b]
9a	40.7	269, 432
12	32.7	240
15	36.0	460

[a] From ^{13}C NMR, CH_2CH_2 link between aryl units. [b] Through DSC.

Experimental

Materials and general procedures

Solvents and supporting electrolytes. General-purpose reagent (GPR) grade solvents were used unless stated otherwise. For preparative electrolyses DMF (Aldrich Chemical Co. Ltd.) was used without further purification. For cyclic voltammetry and controlled potential coulometry HPLC grade DMF was used and stored over freshly baked (150 °C) 4 Å molecular sieves. Tetraethylammonium bromide (TEABr, Aldrich GPR grade) and tetraethylammonium hexafluorophosphate ($TEAPF_6$, Aldrich GPR grade) were used without further purification but oven-dried.

Instruments. Melting points (uncorrected) were determined on an Electrothermal capillary tube melting point apparatus. The following instruments were used: ^1H NMR (Bruker WP80 or AM250); FTIR (Perkin-Elmer 1600); mass spectrometry (Kratos MS50RF/Kratos DS90 Data system); Perkin-Elmer PC series DSC7 calorimeter. Solid-state ^{13}C NMR spectra were recorded at 75 MHz on a Bruker MSL-300 multinuclear NMR spectrometer of the University of London Intercollegiate Research Service (ULIRS).

Gel permeation chromatography. A Hewlett-Packard HP1100 series liquid chromatograph, operated by HP ChemStation software, was employed with a quaternary gradient pump and UV detector. Polymer molecular weights were calculated using Polymer Laboratories PL caliber GPC System, version 4.01. Polymer Laboratories PL-gel (polystyrene–divinylbenzene copolymer gel) mixed C (5 µm, two 300 × 7.5 mm and guard) columns were used, enclosed in constant temperature ovens. A calibration curve was constructed using narrow standard polystyrene (molecular weight range 580 to 3×10^6). The mobile phase was DMF at 1.0 ml min^{-1} and 70 °C.

Electrochemical experiments

Cyclic voltammetric experiments at QMW were run using either an EG&G PAR VersaStat potentiostat or an EG&G PAR Model 263A potentiostat with controlling EG&G software (Model 270/250 Research Electrochemistry Software v 4.00). Some of the faster scan rate experiments (1–100 V s^{-1}) used a DT 2101 (Hi-Tek Instruments, UK) potentiostat connected to a waveform generator (PP R1, Hi-Tek Instruments, UK), with data collected by a digital storage oscilloscope (Nic-310, Nicolet). Low temperature measurements (CV, CPE) were run in an H-shaped electrolysis cell contained in a copper-foil cylinder mounted on a refrigerated block and surrounded by polystyrene insulation. The temperature was monitored with a Cu/Ni thermocouple and, at steady state, a constant and evenly distributed temperature was established. A thermometer in the secondary compartment of the cell measured the actual temperature in the cell. In Copenhagen, the electrodes cells and the electrochemical instrumentation as well as the measurement and data handling procedures for voltammetry were identical to those previously described.[11]

Glass cells for cyclic voltammetry were undivided and equipped with a mercury coated platinum disk (0.1–0.6 mm) working electrode (cathode), Ag-wire reference electrode and platinum coil counter electrode (anode). The experiments were carried out in 0.1 M Et_4NBr–DMF or 0.1 M Bu_4NPF_6–DMF solutions. The concentration of the substrate was 2–3 mM and the scan rate varied from 0.1 to 200 V s^{-1}. Since the potential of the Ag-wire reference electrode can vary over a relatively short timescale, the $E°$ value for anthracene was measured at the beginning and at the end of a series of measurements, against the Ag-wire electrode, so that reduction potentials could be consistently referred to the SCE electrode ($E°$ for anthracene = −1.92 V *vs.* SCE in DMF[12]).

Preparative scale electrochemical reductions were performed using conventional glass cells, with the anode and cathode compartments separated by a glass sinter. The reaction took place at a mercury pool working electrode (cathode), the reference electrode was Ag wire and the counter electrode (anode) a carbon rod. Reduction potentials for controlled potential electrolyses were determined by cyclic voltammetry on the solutions immediately prior to electrolysis, *i.e.* at greater than ideal concentrations. Consequently the peak potentials so determined, against the relatively unstable Ag-wire reference, serve to enable reduction at the first reduction wave in an electrolysis immediately following measurement. However, actual values fluctuate from day-to-day and cannot be compared with peak potentials measured at low concentration with reference to SCE (see above). The reactions were kept under inert atmosphere by the slow bubbling of dry nitrogen through the electrolytes. The catholyte was mechanically stirred.

Starting materials

1,4-Bis(α-hydroxybenzyl)benzene. This was prepared by reaction between phenylmagnesium bromide and terephthalaldehyde according to literature precedent.[13] The product was recrystallised from ethyl acetate–hexane by first dissolving the solid in the minimum of ethyl acetate and then adding the same volume of hexane. White crystals were formed after refrigerating for some hours (99.5 g, 44%); mp 158 °C (lit.[13] 163–164 °C); ^1H NMR δ_H (250 MHz, $CDCl_3$) 2.18 (2H, s, OH), 5.83 (2H, s, PhCH), 7.38–7.40 (14H, m, Ph).

1,4-Bis(α-bromobenzyl)benzene 3c. This was prepared by treatment of 1,4-bis(α-hydroxybenzyl)benzene with HBr in a slight modification of a reported method.[14] The solid product was recrystallised from acetone to give the dibromide (1.09 g, 71%); mp 117–119 °C (lit.[14] 114–115 °C); ^1H NMR δ_H (250 MHz, $CDCl_3$) 6.25 (2H, s, PhCH), 7.38–7.45 (14H, m, Ph).

1,4-Bis(α-chlorobenzyl)benzene 3d. This was prepared by treatment of 1,4-bis(α-hydroxybenzyl)benzene with HCl in a slight modification of a reported method.[13] The precipitate obtained was washed several times with diethyl ether to give white crystals (1.3 g, 58%); mp 138 °C (lit.[13] 139–140 °C); ^1H NMR δ_H (250 MHz, $CDCl_3$) 6.10 (2H, s, PhCH), 7.29–7.38 (14H, m, Ph).

1-(α-Hydroxybenzhydryl)-4-(α-hydroxybenzyl)benzene. Phenylmagnesium bromide, prepared in dry ether by the usual method from bromobenzene (31.4 g, 0.20 mol) and magnesium turnings (8.2 g, 0.40 mol), was carefully treated with methyl 4-formylbenzoate (2.0 g, 12 mmol). Steam distillation of the residue removed biphenyl and the crude product was dissolved in ether, washed with water, dried ($MgSO_4$) and the solvent evaporated. Attempted crystallisation failed and an oily product was isolated[15] (4.25 g, 95%); ^1H NMR δ_H (250 MHz, $CDCl_3$) 1.55 (1H, s, OH), 2.23 (1H, s, OH), 5.83 (1H, s, PhCH), 7.30–7.35 (19H, m, Ph).

1-(α-Bromobenzhydryl)-4-(α-bromobenzyl)benzene 3e. 1-(α-Hydroxybenzhydryl)-4-(α-hydroxybenzyl)benzene (1.0 g, 2.7 mmol) was treated with HBr. Crystals precipitated on cooling and the product was recrystallised from petroleum ether (bp 40–60 °C) (0.91 g, 68%); mp 145–150 °C (lit.[15] 142 °C); ^1H NMR δ_H (250 MHz, $CDCl_3$) 6.28 (1H, s, PhCH), 7.20–7.90 (19H, m, Ph).

1-(α-Chlorobenzhydryl)-4-(α-chlorobenzyl)benzene 3f. 1-(α-Hydroxybenzhydryl)-4-(α-hydroxybenzyl)benzene (1.0 g, 27 mmol) was treated with HCl as before. A yellow oil was obtained. Attempts at further purification by chromatography led to degradation (0.40 g, 36%); ^1H NMR δ_H (250 MHz, $CDCl_3$) 6.14 (1H, s, PhCH), 7.30–7.59 (19H, m, Ph); IR (KBr)/cm^{-1}: 3059, 3030, 1597, 1482, 1231, 1010, 738, 699; MS *m/z* (calc.): 402.0949 ($C_{26}H_{20}Cl_2$, 402.0941), 366.1170 ($C_{26}H_{19}Cl$, 366.1174) (Found: C, 77.3; H, 5.1; Cl, 17.3. $C_{26}H_{20}Cl_2$ requires C, 77.6; H, 5.0; Cl, 17.4%).

4,4′-Bis(bromomethyl)biphenyl 5a. 4,4′-Dimethylbiphenyl (1.82 g, 1 mmol), NBS (3.6 g, 2.1 mmol) and a few grains of benzoyl peroxide were added to dry CCl_4 (50 ml). The mixture was heated under reflux for *ca.* 30 minutes and cooled to room temperature. The insoluble succinimide was filtered off and washed with a small amount of CCl_4. The combined filtrate was concentrated under reduced pressure. The white crystals formed were collected and dried in vacuum (2.7 g, 79%); mp 157–160 °C (lit.[16] 169.5–171.5 °C); ^1H NMR δ_H (250 MHz, $CDCl_3$) 4.55 (4H, s, $PhCH_2$), 7.51 (4H, d, $J = 7.5$, Ph), 7.53 (4H, d, $J = 7.5$ Hz, Ph).

4,4′-Bis(hydroxymethyl)biphenyl. This was prepared according to a literature method[17] by reduction of biphenyl-4,4′-dicarboxylic acid (1.0 g, 4.13 mmol) with lithium aluminium hydride (5.0 g, 0.13 mol) in dry THF solution. The crude product was recrystallised from ethanol (0.75 g, 85%); mp 190 °C (lit.[17] 188–189 °C); ^1H NMR δ_H (250 MHz, d_6-DMSO) 3.80 (2H, s, br, OH), 4.71 (4H, s, $PhCH_2$), 7.45 (4H, d, $J = 7.5$, Ph), 7.59 (4H, d, $J = 7.5$ Hz, Ph).

4,4′-Bis(chloromethyl)biphenyl 5b. 4,4′-Bis(hydroxymethyl)-biphenyl (1.0 g, 4.62 mmol) was chlorinated by treatment with HCl as before. The crude product was recrystallised from ethanol (0.66 g, 57%); mp 135–137 °C (lit.[18] 136–138 °C); ^1H NMR δ_H (250 MHz, $CDCl_3$) 4.64 (4H, s, $PhCH_2$), 7.48 (4H, d, $J = 7.5$, Ph), 7.59 (4H, d, $J = 7.5$ Hz, Ph).

2,5-Bis(chloromethyl)-1,4-dimethoxybenzene 4. This was prepared by chloromethylation of 1,4-dimethoxybenzene (13.8 g, 0.1 mol) using a modification of the published[19] method. The product was recrystallised from acetone (9.8 g, 42%); mp 163–164 °C (lit.[19] 165–167 °C); ^1H NMR δ_H (250 MHz, $CDCl_3$) 3.85 (6H, s, $PhOCH_3$), 4.64 (4H, s, $PhCH_2$), 6.93 (2H, s, Ph).

Electrolysis

The background current of the cell/electrolyte system was noted and the substrate (0.5–2.0 g for 80 ml cell volume; 0.2–0.5 g for 30 ml cell volume) dissolved in the electrolyte in the working compartment of the cell. For mediated electrolyses 10 mol% of the mediator was added. The electrolyses were judged to be complete after the current had decayed to background level (direct electrolysis) or when 2 F had been consumed (mediated electrolysis). Insoluble products were filtered off and soluble products obtained by adding approximately three times the volume of distilled water to the reaction mixture. If some precipitate was formed it was filtered off and washed with water. The remaining solution was shaken with ether (3 × 20 ml) and the ether layer washed (water, 3 × 30 ml), dried ($MgSO_4$), and the solvent evaporated. The product (Table 4) was purified by

Table 4 Products of controlled potential electrolysis[a] in the absence and presence of a mediator

Substrate	Mediator	Charge/ F mol^{-1}	Product (%)/yield of recovered mediator [%]
3a		2.0	**9a** (90)[7]
3c		2.0	**9b** (65)
3e		1.9	**9c** (28)
3b		2.0	**9a** (70)
			10 (4.5)
			11a (9.5)
			3b (7.2)
3b		2.9	**9a** (73)
			10 (25)
			11a (2)
3b	Benzophenone	2.0	**9a** (58)/[43][b]
	9-Phenylanthracene	2.0	**9a** (37)/[97]
	9,10-Diphenylanthracene	2.0	**9a** (45)/[98]
	1,3-Diphenylisobenzofuran	2.0	**9a** (43)/[93]
	Perylene	2.0	**9a** (50)/[93]
3d		3.9	**11b**(79)
3d	Fluorene	2.0	**9b** (84)/[97]
3f		4.0	**11c** (80)
4	9-Phenylanthracene	2.0	**12** (38)/[98]
5a		2.0	**13** (26)
			4,4′-Dimethylbiphenyl(11)
5b		2.0	**13** (40)
			4,4′-Dimethylbiphenyl(32)
			5b (28)
5b		3.1	**13** (47)
			4,4′-Dimethylbiphenyl(51)
			14 (2)

[a] Divided cell, Hg pool cathode, DMF–Et_4NBr (0.1 M); the reduction potential was controlled with reference to a silver-wire electrode corresponding to the reduction peak of the mediator (indirect electrolysis) or the first reduction peak of the substrate (direct electrolysis), see Experimental section for details. [b] Benzopinacol also formed.

Table 5 Spectroscopic data for the products

Product	mp/°C	FTIR/cm^{-1}	δ_H(250 MHz, $CDCl_3$)	δ_C(250 MHz, $CDCl_3$)
9a	425–432 (lit.[7] 420)	3044 (m, ν_{arom} C–H), 2920 (s, ν_{sat} C–H), 1510 (s, benzene ring), 821 (s, $\delta_{Ar–H,}$ 2 adjacent H)		40.56 (2 × CH_2), 130.15, 142.05, 185.41
9b	264	3024 (s, ν_{arom} C–H), 2899 (m, ν_{sat} C–H), 1600 (s, benzene ring), 730, 740 (s, $\delta_{Ar–H}$, 2 adjacent H), 697 (s, $\delta_{C–H}$)	4.60 (2H, d, broad, $J \approx 25$ Hz, PhC*H*), 6.85–7.16 (14H, m, broad, ArH)	56.2 (2 × CH), 125.7, 126.6, 127.9, 128.4, 128.7, 140.9, 143.5
9c	252	3024 (s, ν_{arom} C–H), 2931 (w, ν_{sat} C–H), 1600 (s, benzene ring), 1491, 1446 (s, $\delta_{C–H}$), 740 (s, $\delta_{Ar–H}$, 2 adjacent H), 699 (s, $\delta_{C–H}$)	3.93 (1H, s, PhC*H*), 6.70–7.55 (19H, m, broad, Ar*H*)	
10	285 (lit.[20] 283–285)		3.05 (8H, s, CH_2), 6.48 (8H, s, Ar*H*)	
Benzopinacol	185 (lit.[21] 184–186)		3.00 (2H, s, O*H*), 7.10–7.45 (20H, m, Ar*H*	
11b	86 (lit.[22] 85.5)		3.97 (4H, s, PhCH_2), 7.13 (4H, s, Ar*H*), 7.22 (10H, s, Ar*H*)	
11c	140–142 (lit.[15] 142)		3.90 (s, 2H, CH_2), 5.50 (s, 1H, C*H*), 7.0–7.21 (m, 19H, Ar*H*)	
12	239–245	3028 (m, ν_{arom} C–H), 2931 (s, ν_{sat} C–H), 2823 (s, νOCH_3), 1507 (s, benzene ring), 1212, 1044 (s, νC–H), 860 (m, $\delta_{Ar–H}$, 2 adjacent H), 654 (m, $\delta_{C–H}$)		32.7 (2 × CH_2), 53.5 (CH_3), 112.8, 127.9 , 151.3
13	>330 (lit.[7] 343)	3022(m, ν_{arom} C–H), 2920 and 2851 (m, ν_{sat} C–H), 1497 (s, benzene ring), 815 (s, $\delta_{Ar–H}$, 2 adjacent H)		
4,4′-Dimethyl-biphenyl	125 (lit.[22] 125–128)		2.40 (6H, s, CH_3), 7.28 (8 H, d, $J = 8$ Hz, ArH_a), 7.51 (8 H, d, $J = 8$ Hz, ArH_b)	
14[a]	248 (lit.[24] 247–249		2.96 (8H, s, CH_2), 6.77 (8H, d, Ar*H*, $J = 8$ Hz), 6.61 (8H, d, Ar*H*, $J = 8$ Hz)	
15	153–157	3022 (m, ν_{arom} C–H), 2931 (s, ν_{sat} C–H), 2825 (s, νOCH_3), 1507 (s, benzene ring), 1212 and 1044 (s, νC–H), 860 (s, $\delta_{Ar–H}$, 2 adjacent H), 654 (s, $\delta_{C–H}$)		36.0 (CH_2), 53.5 (OCH_3), 112.6, 127.5, 138.9

[a] Paracyclophane separated from the 4,4′-dimethylbiphenyl on a silica gel glass plate eluted with cyclohexane–benzene (1 : 1).

Table 6 Direct pyrolysis mass spectrometric fragments of polymers

Product	n	Fragment	m/z found	m/z calculated	Intensity (%)
9a	1	$C_8H_9^+$	105.0727	105.0704	100
	2	$C_{16}H_{17}^+$	209.1271	209.1330	16.7
	3	$C_{24}H_{26}^+$	314.1954	314.2034	6.9
	4	$C_{32}H_{34}^+$	418.2593	418.2661	2.5
9b	1	$C_{20}H_{16}^+$	257.1259	256.1264	100
	2	$C_{40}H_{32}^+$	512.2506	512.2504	20.3
9c	1	$C_{26}H_{20}^+$	333.1615	332.1580	100
	2	$C_{52}H_{40}^+$	664.3194	664.3160	24.3
12	1	$C_{10}H_{13}O_2^+$	165.0874	165.0901	69.1
	2	$C_{20}H_{22}O_4^+$	330.1700	330.1837	18.7
	3	$C_{28}H_{26}O_6^+$	466.2358	466.2442	21.1
	4	$C_{37}H_{44}O_8^+$	616.3033	616.3046	8.2
13	1	$C_{14}H_{13}^+$	181.1012	181.1017	100
	2	$C_{28}H_{26}^+$	362.2065	362.2035	14.3
15	PX	$C_8H_9^+$	105.0701	105.0707	100
	PY	$C_9H_{11}O_2^+$	151.0765	151.0762	22.1
	PX-PY	$C_{17}H_{18}O_2^+$	254.1351	254.1311	2.8
Benzopinacol		$C_{26}H_{20}O_2^+$	364.1464	364.1445	6.7
		$C_{13}H_{11}O^+$	184.0847	184.0801	21.9

Table 7 Elemental analyses of polymers

Polymer	Ideal formula	%C (%calc.)	%H (%calc.)	%Balance (%calc.)	C:H (calc.)
9a	$(C_8H_8)_n$	87.69 (92.26)	7.32 (7.74)	4.99 (0)	11.98 (11.92)
9b	$(C_{20}H_{16})_n$[a]	89.70 (93.70)	6.40 (6.29)	3.90 (0)	14.02 (14.98)
9c	$(C_{26}H_{20})_n$	89.50 (93.93)	5.80 (6.07)	4.70 (0)	15.43 (15.47)
12	$(C_{10}H_{13}O_2)_n$[a]	70.93 (73.13)	7.80 (7.37)	22.09 (19.49)	9.10 (9.92)
13	$(C_{14}H_{13})_n$[a]	90.34 (93.28)	6.34 (6.72)	3.32 (0)	14.25 (13.88)
15	$(C_{17}H_{18}O_2)_n$[a]	79.90 (80.55)	7.12 (7.04)	12.98 (11.92)	11.22 (11.44)

[a] Traces of N found in the sample, **9b** (2.17), **12** (0.24), **13** (0.25), **15** (0.23%).

crystallisation or column chromatography and characterised (Tables 5–7).

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