

# Electro-organic reactions. Part 54.† Quinodimethane chemistry. Part 2.‡ Electrogeneration and reactivity of *o*-quinodimethanes§

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The electrochemical generation and characterisation of a variety of *o*-quinodimethanes (*o*-QDMs) are described together with the outcome of preparative experiments in which they are key intermediates. The quinodimethanes are conveniently formed, in DMF, by both direct and redox-catalysed electroreduction of 1,2-bis(halomethyl)arenes. Their predominant reaction is polymerisation to poly(*o*-xylylene) (*o*-PX) polymers. In the presence of dienophiles the electrogenerated *o*-QDMs may undergo efficient cycloaddition reaction and distinctions between the possible mechanisms have been attempted on the basis of voltammetric, preparative and stereochemical experiments. Contrary to the precedent of the corresponding methyl ester, diphenyl maleate radical-anion isomerises only slowly to the fumarate radical-anion, yet co-electrolysis of 2,3-bis(bromomethyl)-1,4-dimethoxybenzene and diphenyl maleate or diphenyl fumarate gives exclusively the corresponding *trans*-adduct. Co-electrolysis of dimethyl maleate with either 1,2-bis(bromomethyl)benzene (more easily reduced) or 2,3-bis(bromomethyl)-1,4-dimethoxybenzene (less easily reduced) gave only *o*-PX polymer. The results are rationalised in terms of a double nucleophilic substitution mechanism where electron transfer between dienophile radical-anion and dihalide is relatively slow. Where electron transfer from maleate or fumarate radical-anions is likely to be fast *o*-quinodimethanes are formed by redox-catalysis and they polymerise rather than undergo Diels–Alder reaction. Dimerisation of the dienophile radical-anions, with  $k_2 = 10^4$  to  $10^5 \text{ M}^{-1} \text{ s}^{-1}$ , does not apparently compete with nucleophilic substitution or, where relevant, electron transfer.

## Introduction

*o*-Quinodimethanes (*o*-QDMs), derivatives of 5,6-bis(methylene)cyclohexa-1,3-diene **4a**, are highly reactive intermediates. The parent species **4a** dimerises spontaneously<sup>1</sup> above  $-80^\circ\text{C}$  Cava and Napier<sup>2</sup> first suggested the participation of an *o*-QDM in the conversion of 1,2-bis(dibromomethyl)benzene to *trans*-dibromocyclobutabenzene, a reaction earlier reported by Finkelstein.<sup>3</sup> Jensen and Coleman<sup>4</sup> also proposed the intermediacy of an *o*-QDM in the preparation of 1,2-diphenylbenzocyclophane.

*o*-Quinodimethanes undergo Diels–Alder cycloaddition with dienophiles. Recently it was shown<sup>5,6</sup> that *o*-QDMs generated by cathodic reduction of 1,2-bis(halomethyl)arenes may react *in situ* with dienophiles to give good yields of adducts, even where the dienophile is sterically hindered. Furthermore relatively long-lived radical-anions generated from the dienophiles mediate the cathodic elimination from the 1,2-bis(halomethyl)-arenes.

We here report on the reactions and characterisation of *o*-QDMs formed by direct or mediated cathodic reduction in the absence as well as in the presence of dienophiles. The 1,2-bis(chloromethyl)arenes **2a**, **b** are more difficult to reduce than the corresponding quinodimethanes, as was found<sup>7</sup>

for reduction of 1,4-bis(chloromethyl)benzene and the corresponding *p*-quinodimethanes. In these last cases *p*-QDMs could be generated by redox catalysis in the presence of suitable organic mediators.<sup>7</sup>

We have also explored the stereochemistry of cycloaddition for reaction between fumarate and maleate dienophiles and *o*-QDMs generated by either direct or mediated electrolysis. Radical-anions generated from dialkyl maleate esters are known<sup>8,9</sup> to isomerise to the fumarate species on the time scale of cyclic voltammetric or rotating ring-disk electrode experiments. On a preparative electrolysis time-scale such isomerisation would, if significant, be expected to compete with electron transfer to the 1,2-bis(halomethyl)arene and be reflected in the stereochemistry of the resulting adduct.

## Results and discussion

### Quinodimethane precursors

*o*-Quinodimethanes were cathodically generated from 1,2-bis(halomethyl)arenes (**1a–1d**, **2a**, **2b**) that were mostly prepared by modification of literature methods. 1-( $\alpha$ -Bromobenzyl)-2-( $\alpha$ -bromo- $\alpha$ -phenylbenzyl)benzene **1c** was prepared by treatment of the known diol with hydrobromic acid and with hydrochloric acid for the corresponding chloride **2b**.

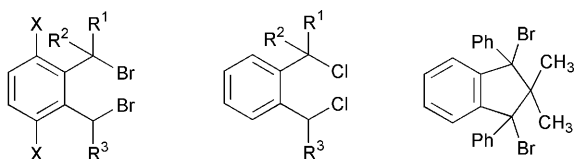
### Characterisation of quinodimethanes by cyclic voltammetry

*p*-Quinodimethanes (*p*-xylylenes), intermediates in the formation of poly(*p*-xylylene) (PPX) polymers, are relatively

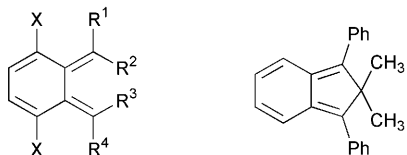
† For part 53, see ref. 27.

‡ For part 1, see ref. 7.

§ Further experimental details are available as supplementary data. For direct electronic access see <http://www.rsc.org/suppdata/p2/b0/b007476o/>



- 1a**  $R^1 = R^2 = R^3 = H, X = H$     **2a**  $R^1 = R^2 = R^3 = H$   
**1b**  $R^1 = R^3 = Ph, R^2 = H, X = H$     **2b**  $R^1 = R^2 = R^3 = Ph$   
**1c**  $R^1 = R^2 = R^3 = Ph, X = H$   
**1d**  $R^1 = R^2 = R^3 = H, X = OMe$



- 4a**  $R^1 = R^2 = R^3 = R^4 = H, X = H$   
**4b**  $R^1 = R^4 = Ph, R^2 = R^3 = H, X = H$   
**4c**  $R^1 = R^2 = R^3 = Ph, R^4 = H, X = H$   
**4d**  $R^1 = R^2 = R^3 = R^4 = H, X = OMe$

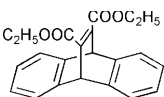
long-lived on a voltammetric time-scale and have been detected and characterised.<sup>7</sup> The 1,4-bis(bromomethyl)arene precursors are reducible at potentials less negative than those required for reduction of the QDMs, which allows their formation and detection by direct reduction. The corresponding chlorides reduce, irreversibly, at more negative potentials and the QDMs are rapidly further reduced following their generation by reductive 1,4-elimination of halide. However, the *p*-QDMs could be generated at less negative potentials through redox catalysis by mediators and this enabled generation from chloride precursors. Cathodic generation at lower temperature ( $-15^\circ\text{C}$ ), combined with relatively fast scan cyclic voltammetry ( $160\text{ V s}^{-1}$ ), resulted in chemically reversible reduction for the parent *p*-QDM and hence measurement, in DMF solution, of its  $E^\circ$  value ( $-1.94\text{ V vs. SCE}$ ). Similar approaches are here described for the detection and characterisation of *o*-QDMs.

Cyclic voltammetry of 1,2-bis(bromomethyl)benzene **1a** [Hg/Pt cathode, DMF– $\text{Et}_4\text{NBr}$  (0.1 M)] gave a peak at  $E_p = -1.22\text{ V vs. SCE}$  ( $1\text{ V s}^{-1}$ ) corresponding to halide cleavage with a subsequent peak at  $E_p = -1.74\text{ V vs. SCE}$  that was chemically irreversible at scan rates up to  $100\text{ V s}^{-1}$ . By analogy with the results<sup>7</sup> for the *p*-QDMs the second peak is assigned to reduction of the parent *o*-QDM (*o*-xylylene) **4a**. The radical-anion of *o*-QDM **4a**, formed at *ca.*  $-1.74\text{ V}$  ( $1\text{ V s}^{-1}$ ), is, like that of the *p*-QDM,<sup>7</sup> too reactive at room temperature (*ca.*  $22^\circ\text{C}$ ) to show chemically reversible reduction at up to  $100\text{ V s}^{-1}$ . In contrast to the *p*-xylylene, reversible reduction of the *o*-QDM **4a** was not achieved at a lower temperature ( $-15^\circ\text{C}$ ).

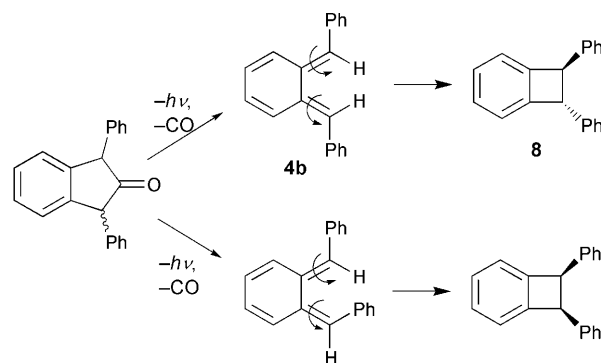
In the *p*-QDM cases stabilisation of the radical-anions, and hence reversible reduction of the phenyl-substituted QDM, was achieved by phenyl substitution at the methylene terminal positions and shown<sup>7</sup> to be the result of extended delocalisation of the charge and spin. However, for reduction of 1,2-bis(*o*-bromobenzyl)benzene **1b** this stratagem fails. Cyclic voltammetry gives an initial reduction wave ( $-1.46\text{ V}$ ,  $1\text{ V s}^{-1}$ ) followed by a broad irreversible peak at a very negative potential ( $-2.11\text{ V}$ ). Constant potential electrolysis of **1b** gave *trans*-1,2-diphenyl-1,2-dihydrocyclobutabenzene **8**, and this was shown by cyclic voltammetry to be responsible for the peak at  $-2.11\text{ V}$ . The formation of **8** is rationalised in terms of the known<sup>10,11</sup> ring closure of the *o*-QDM when formed photochemically (Scheme 1). The exclusive formation of the *trans*-isomer, by conrotatory ring closure, is good evidence that the first-formed intermediate is the more stable (*E,E*)-isomer of the *o*-QDM **4b**.

Ring closure is unlikely for the *o*-QDM **5**, which is expected to be formed by reduction of 1,3-diphenyl-2,2-dimethyl-1,3-di-

**Table 1** Mediators for the cleavage of 1,2-bis(chloromethyl)benzene **2a**

Mediator	$-E^\circ/\text{V vs. SCE}^a$
	1.61
Dimethyl terephthalate	1.61
Diethyl terephthalate	1.63
Perylene	1.63

<sup>a</sup> Formal potentials measured by cyclic voltammetry at  $0.3\text{ V s}^{-1}$  as 2 mM solutions in DMF– $\text{Bu}_4\text{NPF}_6$  (0.1 M) at an Hg/Pt electrode with reference to SCE—calibrated against  $E^\circ$  for anthracene—see Experimental section for details.



**Scheme 1**

bromoindane **3**. This precursor is a single isomer (sharp melting point, clean  $^1\text{H NMR}$ ), probably the more stable *trans*-isomer based on the method of preparation (Grignard addition to 2,2-dimethylindane-1,3-dione followed by treatment of the 1,3-dihydroxy intermediate with HBr), although no assignment was given in the literature.<sup>12</sup> Cyclic voltammetry of **3** indicates a small reversible peak at *ca.*  $-1.5\text{ V vs. SCE}$  followed by a large irreversible peak at  $-1.99\text{ V}$  ( $1\text{ V s}^{-1}$ ). In the presence of a redox mediator (2,3-dimethylmaleic anhydride,  $E^\circ = -1.13\text{ V}$ ) the cyclic voltammogram of **5** developed and the formal redox potential was measured ( $E^\circ = -1.47\text{ V}$ ). Thus the small peak at  $-1.5\text{ V}$  is due to the QDM **5**; either the first reduction wave for **3** is ill-defined, as is common at Hg cathodes with benzyl bromides, or the peak at  $-1.99\text{ V}$  corresponds to direct reduction of **3**, at an unexpectedly negative potential. One explanation for such a difficult reduction would be that dibromide **3** is rigid and highly hindered.

The redox behaviour of 1,2-bis(chloromethyl)benzene **2a** is similar to that reported for 1,4-bis(chloromethyl)benzene.<sup>7</sup> Reduction is at more negative potentials than required for reduction of the corresponding QDM. Consequently redox mediators were sought to enable measurement of the peak potential of the *o*-QDM **4a**. Those mediators that were effective are presented in Table 1; others that were tried but were ineffective were 2,3-dimethylmaleic anhydride, fluorenone, 4-ethoxycarbonylbenzophenone, and 1,4-diacetylbenzene. Both dimethyl terephthalate and perylene were particularly effective in allowing generation of **4a**, and observation of its chemically irreversible reduction peak and measurement of its  $E_p$  value of  $-1.74\text{ V}$ , comfortably identical to that measured by direct reduction of the bromo precursor. The  $E_p$  and  $E^\circ$  values measured for the *o*-QDMs by voltammetry involving generation by direct or mediated reduction are collected in Table 2. The parent *o*-QDM, **4a**, is more easily reduced than the analogous *p*-compound.<sup>7</sup>

Substitution by phenyl groups at the termini of the methylene functions, as in **1c**, lowers the reversible reduction potential of the corresponding QDM, **4c**, relative to the peak potential for irreversible reduction of **4a**, by about 180 mV but in this

**Table 2** Reduction peak potentials<sup>a</sup> of *o*-QDM precursors and the corresponding QDMs

Substrate	$-E_p(1)/V^b$	QDM	$-E^\circ$ or $E_p/V$	$-E^\circ/V$ for corresponding <i>p</i> -QDM <sup>7</sup>
<b>1a</b>	1.22	<b>4a</b>	1.74 ( $E_p$ ) <sup>b</sup>	1.94
<b>2a</b>	2.08	<b>4a</b>	1.74 <sup>c</sup> ( $E_p$ ) <sup>b</sup>	1.94
<b>1b</b>	1.46	<b>(8)</b>	2.11 ( $E_p$ ) <sup>b</sup>	—
<b>1c</b>	0.88 <sup>d</sup>	<b>4c</b>	1.56 ( $E^\circ$ )	1.56
<b>2b</b>	1.88	<b>4c</b>	1.56 <sup>c</sup> ( $E^\circ$ )	1.56
<b>3</b>	[1.99] <sup>e</sup>	<b>5</b>	1.47 <sup>c</sup> ( $E^\circ$ )	—

<sup>a</sup> Potentials measured by cyclic voltammetry at 1–200 V s<sup>-1</sup> as 2 mM solutions in DMF–Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) at an Hg/Pt electrode with reference to SCE—calibrated against  $E^\circ$  for anthracene—see Experimental section for details. <sup>b</sup> Peak potential at 1 V s<sup>-1</sup>. <sup>c</sup> Determined in the presence of mediator. <sup>d</sup> Peak potential at 0.3 V s<sup>-1</sup>. <sup>e</sup> Not clear that this is the first reduction potential, see text.

**Table 3** Products of controlled potential electrolysis<sup>a</sup> in the absence and presence of a mediator

Substrate	Mediator	Charge/F <sup>b</sup>	Product (%) [% yield of recovered mediator]
<b>1a</b>		2.0	<b>6</b> (33)
<b>2a</b>		2.0	<b>6</b> (24) <i>ortho</i> -Xylene (4.7) <b>7</b> (5.7) <b>2a</b> (17)
<b>2a</b>		3.7 <sup>c</sup>	<b>6</b> (30) <i>o</i> -Xylene (33) <b>7</b> (7)
<b>2a</b>	Diethyl 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate	2.0	<b>6</b> (42) [24]
	Dimethyl terephthalate	2.0	<b>6</b> (42) [62]
	Diethyl terephthalate	2.0	<b>6</b> (29) <i>o</i> -Xylene (14) [94]
<b>1b</b>	Perylene	2.0	<b>6</b> (43) [90]
<b>1c</b>		2.0	<b>8</b> (74)
		2.0	<b>9</b> (37)
		2.0	<b>10</b> (7)
<b>3</b>	2,3-Dimethylmaleic anhydride	1.6	<b>11</b> (37)
<b>3</b>			<b>13</b> (23)
			<b>11</b> (37)
			<b>14</b> (9)

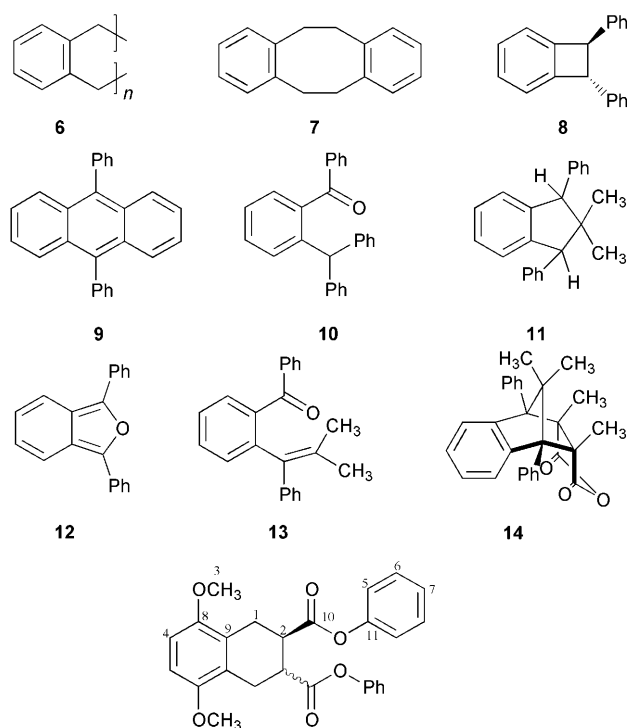
<sup>a</sup> Divided cell, Hg pool cathode, DMF–Et<sub>4</sub>NBr (0.1 M); potential used corresponds to the reduction peak of the mediator (indirect electrolysis) or the first reduction peak of the substrate (direct electrolysis)—see Experimental section for details. <sup>b</sup> Based on the dihalide. <sup>c</sup> At foot of reduction peak.

case the *o*-QDM and its *p*-analogue<sup>7</sup> have identical  $E^\circ$  values (–1.56 V). For the *p*-QDMs, where it was also possible to measure<sup>7</sup> the relative effects of substitution by two and three phenyl groups, it was found that the third phenyl substituent did not participate in delocalising charge and spin because it is sterically prevented from achieving co-planarity with the relevant  $\pi$ -system. It seems that the radical-anion of *o*-xylylene, **4a**, formed at –1.74 V, is more reactive than that of *p*-xylylene, formed at –1.94 V. In cyclic voltammetry, reversibility for the reduction of *p*-xylylene can be achieved relatively easily. Reversibility in the reductions of both **4c** and of the analogous *p*-QDM is easily observed, so presumably the radical-anions of these species are similarly unreactive by virtue of a combination of steric hindrance and delocalisation and there would seem therefore to be little intrinsic difference in their reduction potentials.

## Controlled potential electrolysis

Direct electrolyses were typically carried out in DMF–Et<sub>4</sub>NBr (0.1 M) on a 0.5–1 g scale in a divided cell with a mercury pool cathode and an Ag wire reference (see Experimental section for the relationship with SCE). For indirect electrolysis the redox catalyst (mediator) was present in 10 mol%. The results are summarised in Table 3.

1,2-Bis(chloromethyl)benzene **2a** was electrolysed in the presence of various redox mediators selected on the basis of the data in Table 1. Constant potential electrolysis at the potential of the mediator (see Table 1) gave poly(*o*-xylylene) **6**. Using diethyl terephthalate as mediator 5,6,11,12-tetrahydrodibenzo[*a,e*]cyclooctene **7** was formed as a side product. Perylene is the most efficient mediator, as it gave good yields of polymer [poly(*o*-xylylene) **6**] with almost complete recovery of mediator.

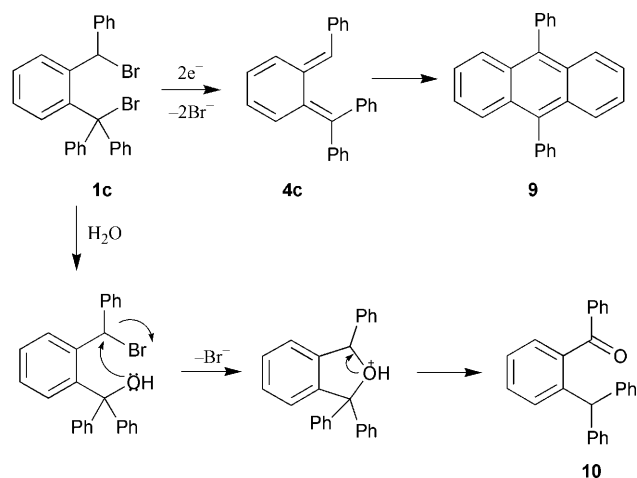


*cis*- and *trans*-**17** ( $R^1 = H$ ,  $R^2 = Ph$ ,  $X = OMe$ ) numbering for NMR data, Tables 6 and 7

For comparison, direct electrolysis of **2a** was performed at  $E_{red} = -2.10$  V vs. Ag, *i.e.* at the foot of the reduction wave. As in the *para* case the electrolysis was either stopped after 2 F or when the background current was reached. The yield of the poly(*o*-xylylene) **6** at 2 F was not as high as in the *para* case and unreacted starting material was present (17.5%). Exhaustive electrolysis (to 3.7 F) gives more polymer but also significant further reduction, consistent with the relatively easy reduction of *o*-xylylene **4a**.

Constant potential electrolysis of 1,2-bis(*o*-bromobenzyl)benzene **1b** resulted in the formation of *trans*-1,2-diphenyl-1,2-dihydrocyclobutabenzene **8**. Quinkert *et al.*<sup>10,11</sup> investigated the stereochemistry of the isomeric 1,2-diphenyl-1,2-dihydrocyclobutabenzene adducts that were obtained from the photodecarboxylation of 1,3-diphenylindanone (Scheme 1). The reported <sup>1</sup>H NMR spectrum of the *trans*-isomer **8** showed a narrow absorption region for the aromatic signals and the phenylmethine protons (PhCH) were at higher field than for the corresponding *cis*-isomer. Comparing these data with those obtained for the product isolated from the controlled potential electrolysis of **1b** confirmed formation of the *trans*-1,2-diphenyl-1,2-dihydrocyclobutabenzene, **8**, the valence tautomer of the *o*-QDM.

1-( $\alpha$ -Bromobenzyl)-2-( $\alpha$ -bromo- $\alpha$ -phenylbenzyl)benzene **1c** was electrolysed exhaustively at  $-1.2$  V vs. Ag wire. A yellow solid was isolated after ether extraction, which was neither a polymer nor 1,1,2-triphenyl-1,2-dihydrocyclobutabenzene<sup>13</sup> but was found by TLC to be mixture of two products. Separation by column chromatography on silica gel gave, as one product, 9,10-diphenylanthracene **9**, identified by its melting point, <sup>1</sup>H NMR and MS. This product has also been found<sup>14</sup> in photolysis of 1,1,3-triphenylindan-2-one. The photolytic reaction is also believed<sup>14</sup> to produce the *o*-QDM **4c** which decays by two competing cyclisation pathways leading to 9,10-diphenylanthracene **9** and 1,1,2-triphenyl-1,2-dihydrocyclobutabenzene. The other product proved to be 2-(diphenylmethyl)benzophenone **10**, a compound produced in the photolysis<sup>15</sup> of phenyl-substituted *o*-QDM **4c**. The *o*-QDM cyclises to 9,10-diphenylanthracene **9**, and 2-(diphenylmethyl)benzophenone **10** is probably a hydrolysis product of the starting material, indicating low current efficiency in the electrochemical reaction. A rationalisation of the results is given in Scheme 2.

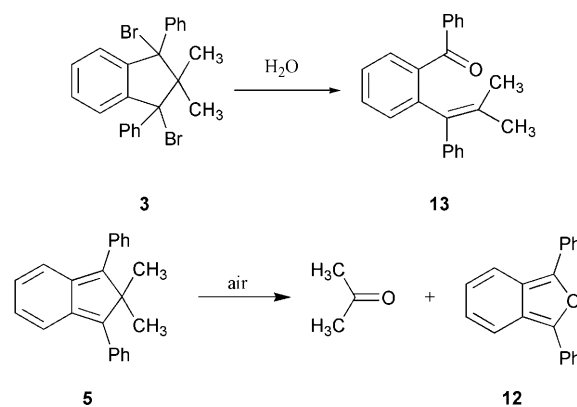


Scheme 2

For 1,3-diphenyl-2,2-dimethyl-1,3-dibromoindane **3**, constant potential electrolysis at  $E_p = -1.55$  V vs. Ag wire resulted in the formation of 1,3-diphenyl-2,2-dimethylindane **11** (37%), which indicates that the initially formed quinodimethane is rapidly reduced further at the electrolysis potential. In contrast, mediated electrolysis of 1,3-diphenyl-2,2-dimethyl-1,3-dibromoindane **3** at  $E_p = -0.95$  V vs. Ag wire, in the presence of 2,3-dimethylmaleic anhydride, gave several products. Separation by column chromatography and characterisation showed one product to be 2-(2-methyl-1-phenylpropenyl)-benzophenone **13** (23%) together with a small amount of 1,3-diphenylisobenzofuran **12**, the hydrogenated product **11** (37%) and a Diels–Alder product **14** (9%). This last product was also reported by Alder and Fremery<sup>12</sup> and Johansson and Skramstad.<sup>16</sup> Part of the starting material (23%) is probably converted chemically into the ring-opened ketone **13**. This side reaction can account for the consumption of only 1.6 F. The formation of the 1,3-diphenylisobenzofuran **12** from **5** has been claimed<sup>16</sup> in the context of the lability of **5**, which on exposure to air at ambient temperature changed colour from orange to colourless. The pathways are summarised in Scheme 3.

#### A comparison of Diels–Alder reactions between dienophiles and *o*-QDMs generated either by redox catalysis or by direct reduction

The electrogeneration of *o*-QDMs in the presence of dienophiles has been extensively used as a preparative route to



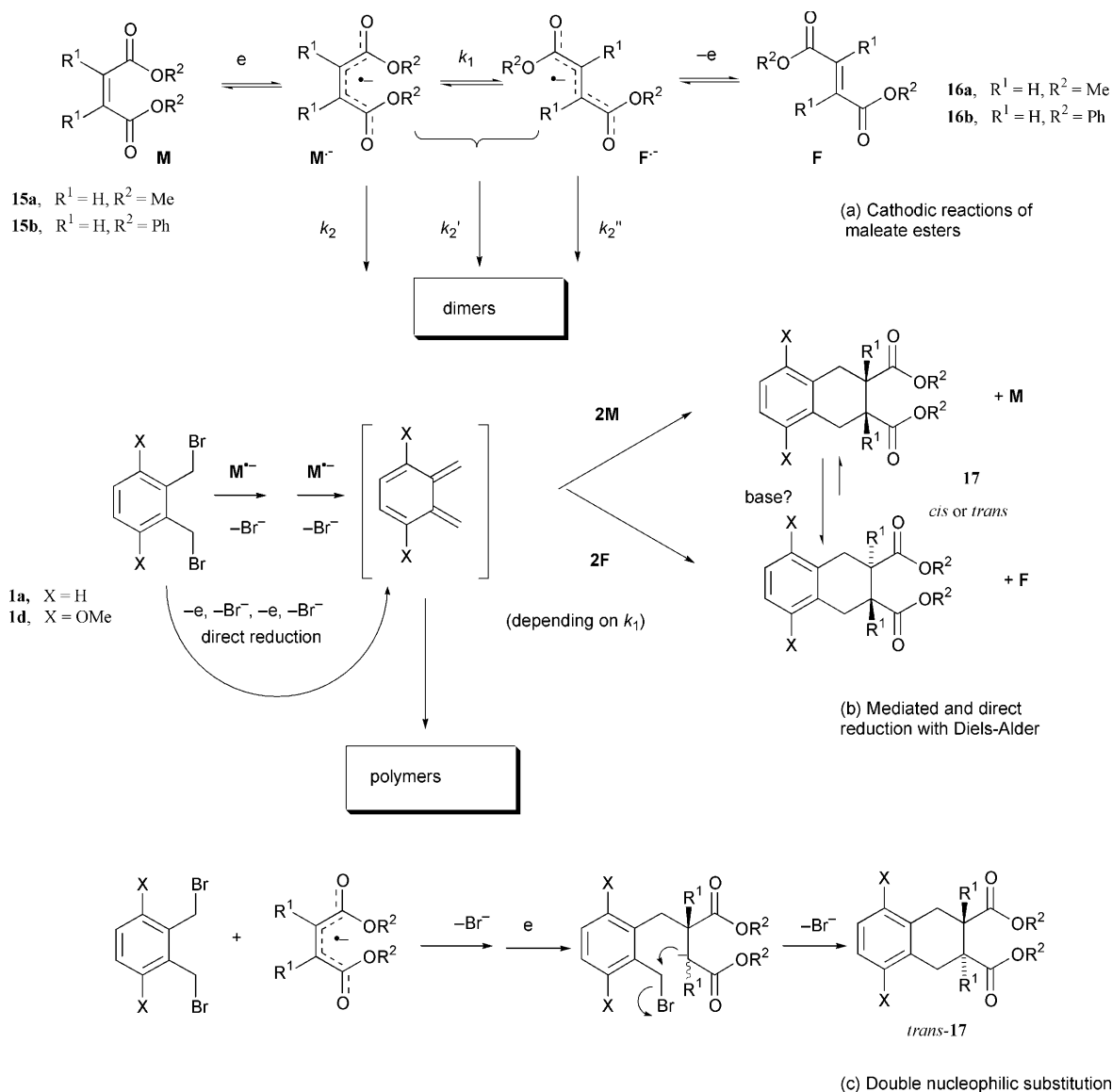
Scheme 3

the corresponding Diels–Alder adducts.<sup>5,6</sup> Typically maleic anhydride or maleimide derivatives have been used as dienophiles and they are more easily reducible than the 1,2-bis(bromomethyl)arenes with which they are co-electrolysed. Consequently the mediated electrolysis of the halomethyl compounds predominates, as has been demonstrated<sup>6</sup> by cyclic voltammetric experiments, which display characteristic catalytic currents associated with redox catalysis and, in coulometric experiments,<sup>17</sup> a change from 1 F reduction of the dienophiles to 2 F reduction in the presence of 1 equivalent of the less easily reduced 1,2-bis(bromomethyl)arenes. We find<sup>17</sup> that *o*-QDMs are similarly generated by mediated reduction in aqueous electrolyte where reduction of the 1,2-bis(bromomethyl)arenes, followed by *in situ* Diels–Alder follow-up reaction, completely suppressed the very fast electrohydrodimerisation of the dienophile (*N*-methylmaleimide) radical-anion. In this case it is proposed that a pre-complex is formed by “hydrophobic packing” between the 1,2-bis(bromomethyl)arene and the dienophile. Although the cases studied to date involve redox catalysis by dienophile, *o*-QDMs can in principle be generated by direct electrolysis and trapped as Diels–Alder adducts by dienophiles less easily reduced than the 1,2-bis(bromomethyl)arenes. In these cases the competing reaction would be polymerisation.

We have attempted to demonstrate the direct reduction route, and at the same time assess the relative reactivity of *o*-QDMs towards cycloaddition *vis à vis* polymerisation. Co-electrolysis of combinations of derivatives of 1,2-bis(bromomethyl)arenes and of maleates and fumarates has been examined for cases where substitution in either or both components is used to manipulate reduction potentials. Thus it is possible to have the maleates and fumarates more easily reduced than the 1,2-bis(bromomethyl)arenes and *vice versa*. Maleate and fumarate will be trapped by *o*-QDMs as *cis*- or *trans*-adducts respectively, but should electron transfer to the dienophiles be the first step then the *trans*-adduct may result irrespective of the dienophile if there is fast isomerisation<sup>8,9</sup> of maleate radical-anions to the more stable fumarate radical-anions.

It is of course possible that electron transfer from maleate radical-anion, to produce the *o*-QDMs with subsequent Diels–Alder reaction, is faster than isomerisation of the maleate radical-anion although this competition also depends on substrate concentration. We therefore also examined the stereochemistry of adducts formed in cases where the maleates are more easily reduced than are the 1,2-bis(bromomethyl)arene precursors. However, even if formed initially the *cis*-Diels–Alder adducts might epimerise under the usually basic conditions of cathodic reduction and this possibility was also tested.

The possible pathways for cathodic reaction of the fumarate and maleate esters alone and in the presence of 1,2-bis(bromomethyl)arene are outlined in Scheme 4, in which the particular substrates used in this study are labelled.



Scheme 4

### The reactivity of maleate radical-anions

The radical-anions of dialkyl maleates are known<sup>8,9</sup> to isomerise to the corresponding fumarate species and, furthermore, they undergo dimerisation, eventually to yield<sup>18</sup> tetraalkylbutane-1,2,3,4-tetracarboxylate. For bimolecular dimerisation in DMF at ambient temperature (*ca.* 24 °C) of dimethyl maleate radical-anions Yeh and Bard<sup>9</sup> reported  $k_2 = 1.9 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  and for unimolecular isomerisation a value of  $k_1 = 2.2 \text{ s}^{-1}$ , both values estimated on the basis of simulation of rotated ring-disk electrode experiments. The corresponding fumarate radical-anion was reported to dimerise<sup>9</sup> with  $k_2 = 110 \text{ M}^{-1} \text{ s}^{-1}$ . The greater rate for reductive dimerisation of the maleate esters is the reason for their choice in the large-scale production<sup>18</sup> of butane-1,2,3,4-tetracarboxylic acid.

In cyclic voltammetry, at low scan rates, the reduction of dimethyl maleate (2–5 mM) gives a single peak that is chemically irreversible because of the dimerisation follow-up reactions. However, at  $10 \text{ V s}^{-1}$  (Fig. 1a and 1b) the appearance of the voltammograms is changed; the dimerisation is partly outrun but isomerisation to the less reactive dimethyl fumarate radical-anion is evident in the re-oxidation peak at *ca.* 0.3 V less negative than the forward reduction peak. This has been shown<sup>8</sup> previously to correspond to oxidation of the dimethyl fumarate radical-anion, a result reproduced here by overlaying

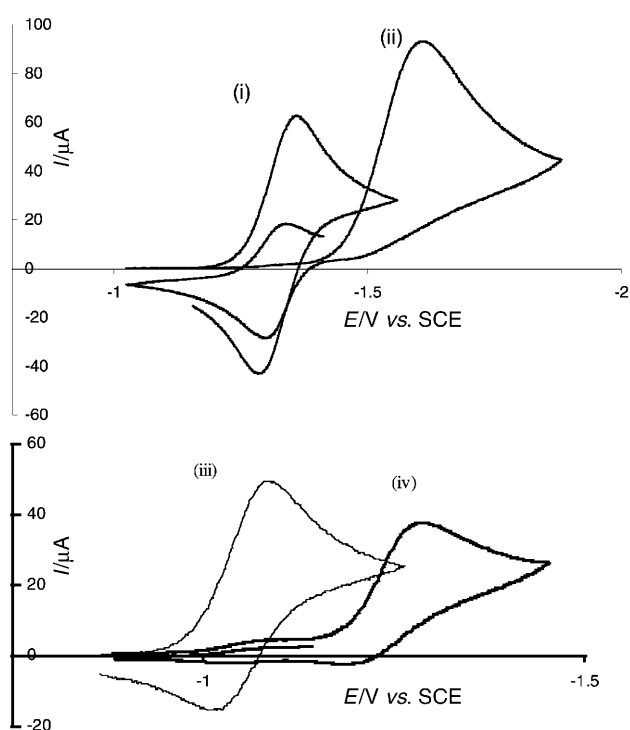
the voltammograms for dimethyl maleate and dimethyl fumarate (Fig. 1a).

Contrary to expectation we find that under comparable conditions the radical-anion of diphenyl maleate does not isomerise rapidly to the more stable fumarate species. Over a scan rate range of 0.1 to  $50 \text{ V s}^{-1}$  no re-oxidation of diphenyl fumarate radical-anion was seen clearly (Fig. 1b(iv)), whereas for the reduction of dimethyl maleate the re-oxidation of the corresponding fumarate radical-anion is prominent (Fig. 1a). The voltammogram in Fig. 1b(iv) reveals a small impurity peak, probably due to diphenyl fumarate, that distorts comparison of the peak heights. We have determined rates of dimerisation for the radical-anions of diphenyl maleate and diphenyl fumarate and, for comparison, have re-examined the corresponding kinetics of the dimethyl esters. The compounds used in this part of the study, together with relevant voltammetric and kinetic data, are included in Table 4. We find that under our reaction conditions the radical-anion of diphenyl maleate dimerises about an order of magnitude faster than does the diphenyl fumarate radical-anion. The radical-anions of both diphenyl maleate and fumarate are considerably more reactive than the corresponding dimethyl species; this is not evident from Fig. 1 because of the different intervals between peak potential and switching potential in the two examples. Our result for the dimerisation of the radical-anion

**Table 4** Components of co-electrolyses, of reduction potentials<sup>a</sup> and kinetic data (Scheme 4)

Compound <sup>b</sup>	$-E_p(1)^c$	$-E^\circ$	Scan rate/ $V^{-1} s^{-1}$	Concn./ mM	$10^{-4} k_2^d/M^{-1} s^{-1}$	$k_1/s^{-1}$
<b>15a</b> , R <sup>1</sup> = H, R <sup>2</sup> = Me	—	1.59	30	2	1.22	[2.2] <sup>g</sup>
				5	1.30	
			40	2	1.21	
				5	1.29	
					$1.26 \pm 0.05$ $[1.9 \times 10^5]^g$	
<b>15b</b> , R <sup>1</sup> = H, R <sup>2</sup> = Ph	—	1.24	20	0.88 <sup>e</sup>	12.0	
				1.76	12.2	
			30	0.88	11.7	
				1.76	12.2	
					$12.0 \pm 0.2$ 0.109	
<b>16a</b> , R <sup>1</sup> = H, R <sup>2</sup> = Me	—	1.30	0.8	5	0.118	
				5	$0.114 \pm 0.005$ $[1.1 \times 10^2]^g$	
			<b>16b</b> , R <sup>1</sup> = H, R <sup>2</sup> = Ph	—	1.07	10
2	1.52					
<b>1a</b> , X = H	1.22	—	20	1	1.53	
				2	1.52	
<b>1b</b> , X = OMe	1.90	—	20	1	1.53	
				2	$1.53 \pm 0.001$	

<sup>a</sup> Hg/Pt cathode, DMF–Bu<sub>4</sub>PF<sub>6</sub> (0.1 M), 0.8–40 V s<sup>-1</sup>, substrate 1–5 mM [second-order rate constants acceptably independent of substrate concentration]. <sup>b</sup> See Scheme 4. <sup>c</sup> Potentials wrt. SCE, calibrated against E° for anthracene—see Experimental section for details. <sup>d</sup> By cyclic voltammetry with digital simulation (BioAnalytical Systems DigiSim v2.1), details of simulations, including parameters used, are available as supplementary data. <sup>e</sup> After allowance for an impurity, probably diphenyl fumarate, see Fig. 1b.



**Fig. 1** Cyclic voltammetry in DMF–*n*-Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M); Hg/Pt cathode, 10 V s<sup>-1</sup>, substrate 2 mM, of dimethyl fumarate [1a(i)] and dimethyl maleate [1a(ii)] and of diphenyl fumarate [1b(iii)] and diphenyl maleate [1b(iv)]—see Table 4 for data and the text for details.

of dimethyl fumarate is not in good accord with that found earlier by Yeh and Bard<sup>9</sup> who used a different technique (experiments at rotating ring-disk electrodes) and who took steps rigorously to dry the solvent (DMF). In our case the electrolyte was dried in a heated vacuum pistol and the DMF was freshly distilled and both solvent and electrolyte were introduced into the cell after passage through a column of activated alumina. However, it is likely that the solutions still contained adventitious water, known<sup>19</sup> to accelerate hydro-

dimerisation reactions. Examination of the voltammograms in Fig. 1a shows that the forward reduction peak for dimethyl maleate has, by comparison with the reversible peak for dimethyl fumarate,  $n > 1$ . It seems that, in addition to hydrodimerisation, another reaction is taking place, probably hydrogenation ( $n = 2$ ) involving trace acidic impurities in the DMF. This explanation does not account, however, for our observation of a lower rate of dimerisation of dimethyl maleate radical-anions. However, the diphenyl esters show no similar abnormality in cyclic voltammetry in the same medium. At 30 and 40 V s<sup>-1</sup> the isomerisation of the maleate radical-anion to the fumarate radical-anion is almost completely outrun although there may still be unquantified competition from protonation in the methyl maleate case. In deriving the rate constants for dimerisation by simulation both possibly competing reactions were ignored.

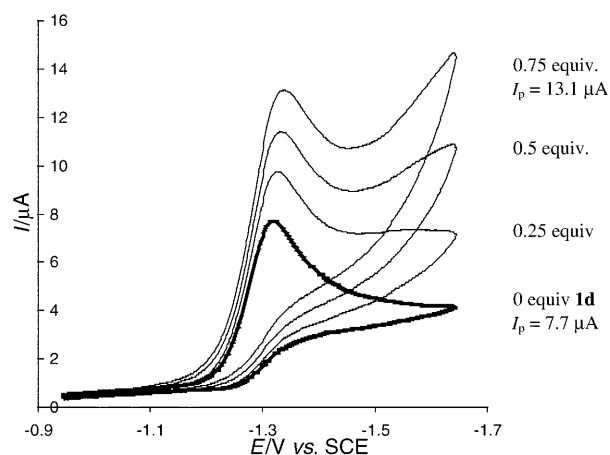
The dialkyl maleates are known<sup>18</sup> efficiently to hydrodimerise under preparative conditions and we also find that controlled potential electrolysis of diphenyl maleate (Hg cathode, DMF–Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M)) proceeds smoothly to 1 F. Aqueous work-up is made difficult by the rapid hydrolysis of the phenyl ester products, but <sup>1</sup>H NMR examination of the crude residue after solvent removal indicates that a substantial product (*ca.* 50%) is a mixture of *meso*- and ( $\pm$ )-isomers of the expected linear hydrodimer (see Experimental section). A second product has not yet been isolated or identified.

Because of the uncertainty over follow-up reactions other than dimerisation, it was not possible to simulate the cyclic voltammogram in Fig. 1a, with a view to determining the rate constant for isomerisation of dimethyl maleate radical-anion to dimethyl fumarate radical-anion. The voltammograms for dimethyl fumarate, and diphenyl maleate and fumarate are not substantially affected by adventitious impurity in the DMF. Consequently, digital simulation provides kinetic data for dimerisation of the radical-anions of diphenyl maleate and diphenyl fumarate. We did not find conditions in the scan rate range 1–50 V s<sup>-1</sup> where a fumarate re-oxidation peak was significant on reduction of diphenyl maleate. A comparison of Figs. 1a and 1b clearly indicates that isomerisation of the diphenyl maleate radical-anion is much slower than that

**Table 5** Co-electrolysis experiments<sup>a</sup>

QDM precursor	Dienophile	Method	Charge/F	$\Delta E^b$	Product	Yield (%)
<b>1d</b>	Diphenyl fumarate ( <b>16b</b> )	Cathode	3.7	0.86	<i>trans</i> - <b>17</b>	97
<b>1d</b>	Diphenyl maleate ( <b>15b</b> )	Cathode	3.2	0.66	<i>trans</i> - <b>17</b>	85
<b>1d</b>	Diphenyl maleate ( <b>15a</b> )	Cathode	2.3	0.31	<i>o</i> -PX polymer	—
<b>1a</b>	Diphenyl maleate ( <b>15a</b> )	Cathode	2.5	-0.37 <sup>c</sup>	<i>o</i> -PX polymer	—
<b>1d</b>	Diphenyl maleate ( <b>15b</b> )	Zn dust	—	—	<i>trans</i> - <b>17</b>	ca. 60
					<i>cis</i> - <b>17</b>	ca. 6
<b>1d</b>	Diphenyl fumarate ( <b>16b</b> )	Zn dust	—	—	<i>trans</i> - <b>17</b>	67
<b>1a</b>	Diphenyl fumarate ( <b>16b</b> )	Zn dust	—	—	<i>trans</i> - <b>17</b>	46

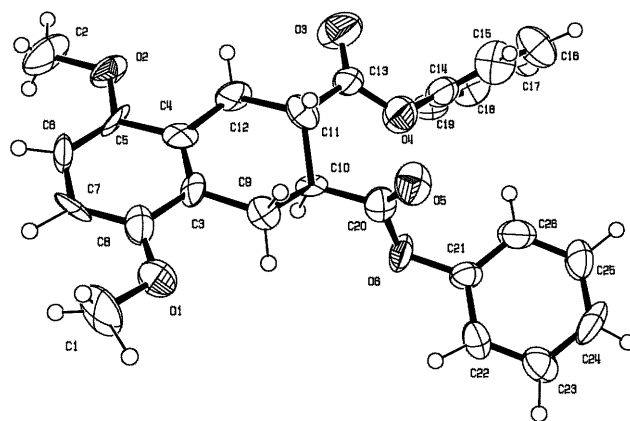
<sup>a</sup> Hg pool cathode, divided cell, DMF-Et<sub>4</sub>NBr (0.1 M), controlled potential (see Experimental for details), substrate concentrations 25–50 mM, dienophile in two-fold excess, charge based on the dihalide. <sup>b</sup> Difference between  $E_p$  for dihalide and  $E^\circ$  for dienophile. <sup>c</sup> *i.e.* Dienophile less easily reduced by 0.37 V.

**Fig. 2** Cyclic voltammetry of **15b** with incremental addition of **1d**; Hg/Pt cathode, DMF-Et<sub>4</sub>NBr (0.1 M), 0.5 V s<sup>-1</sup>.

of the corresponding dimethyl species, although we cannot say by how much.

On a preparative electrolysis time-scale the dimerisation of dienophile radical-anions could in principle compete with electron transfer to the QDM precursors (mediated reduction). The problem of competing dimerisation must also be considered in the use of maleic anhydride derivatives as redox mediators. They were found<sup>5,6</sup> to be very effective as dual mediators/dienophiles, but the anhydrides give fairly persistent radical-anions in DMF. In the case of diphenyl maleate, because isomerisation to fumarate is slow, rapid electron transfer to give an *o*-QDM, followed by cycloaddition, would preserve in **17** the *cis*-stereochemistry of the maleate dienophile, providing that *cis*-**17** is stable under the reaction conditions.

The reduction potentials of maleate and fumarate esters, and of the 1,2-bis(bromomethyl)arenes **1a** and **1d**, are found to be very sensitive to substitution (Table 4). In particular, the diphenyl esters **15b** and **16b** are more easily reduced than the corresponding methyl esters **15a** and **16a**. In the presence of increasing amounts of the dibromide, **1d**, the cyclic voltammetric reduction current for diphenyl maleate (**15b**) is seen to increase by about two-fold (Fig. 2a). At the scan rate used the reduction of **15b** is not reversible and the current increase probably relates to a switch from 1 F dimerisation to 2 F reductive cleavage, *i.e.* it is not clearly a catalytic current associated with redox catalysis. The manifestation of redox catalysis is typically found for maleic anhydride derivatives as dienophiles/mediators.<sup>6</sup> In these earlier cases where the catalytic current is much greater than a two-fold increase the differences between reduction potentials of the mediator and dibromide [ $\Delta E = E^\circ$  (mediator) -  $E_p$  (dibromide)] were much smaller (typically<sup>5,6</sup> *ca.* 0.3 V) than for the case in Fig. 2a, where  $\Delta E = 0.67$  V. This is at the limit of separations at which redox

**Fig. 3** X-Ray crystallographic structure of *trans*-**17**.

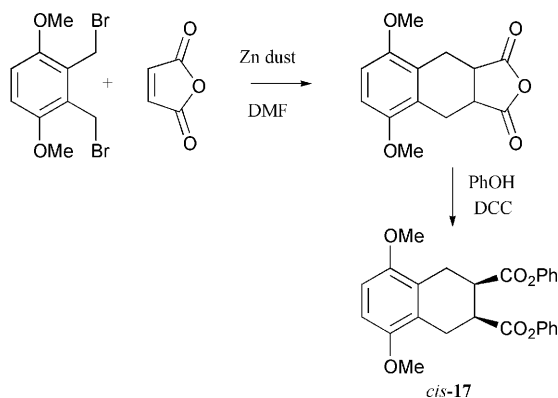
catalysis is usually observed ( $\Delta E \leq 0.5$  V) and electron transfer is likely to be relatively slow. Thus, although it may be that the reduction of **1d** is mediated by the radical-anion of **15b**, a two-fold increase in current would also be consistent with a double nucleophilic attack of radical-anion on the dibromide and this possibility is included in Scheme 4.

**Co-electrolyses where the dienophile is the more easily reduced component.** Co-electrolysis experiments, at controlled potential, were designed in which either the dienophile or the 1,2-bis(bromomethyl)arene could be the more easily reduced component. The results are summarised in Table 5. Preparative-scale exhaustive co-electrolysis of diphenyl maleate, **15b**, and 2,3-bis(bromomethyl)-1,4-dimethoxybenzene, **1d**, with the maleate in two-fold excess, proceeded to 3.2 F (based on the dibromide) and gave *trans*-**17** (85%, R<sup>1</sup> = H, R<sup>2</sup> = Ph) with no trace of the *cis*-isomer. The assignment of *trans*-stereochemistry was made by X-ray crystallography (Experimental section and Fig. 3). Similar co-electrolysis of **1d** with diphenyl fumarate, **16b**, consumed 3.7 F and gave a near-quantitative yield of the adduct, *trans*-**17**.

Isolation of the *trans*-adduct only is consistent with: (a) prior generation of radical-anions of the dienophiles with *cis*-*trans* isomerisation of the maleate radical-anion being faster than electron transfer to the QDM precursor; (b) formation of the *cis*-adduct from maleate with rapid epimerisation by electro-generated base; and (c) double nucleophilic attack by the radical-anions, with equilibrium control. We have shown that the diphenyl maleate radical-anion isomerises rather slowly so possibility (a) is unlikely given that either electron transfer or nucleophilic reaction between maleate radical-anion and 1,2-bis(bromomethyl)arene is sufficiently fast to outrun the competing dimerisation ( $k_2 = 10^5$  M<sup>-1</sup> s<sup>-1</sup>). Route (c) for reaction between **1d** and diphenyl maleate (**15b**) is supported by the large  $\Delta E$  value (Table 5) that presages slow electron transfer;

the lack of a convincing catalytic current (Fig. 2) also favours this explanation.

**Epimerisation of *cis*-17 in the presence of diphenyl maleate radical-anion.** The *cis*-isomer was available for comparison, having been prepared by unambiguous synthesis (see Scheme 5)



Scheme 5

and the corresponding *trans*-isomer was the major product of preparative electrolysis. The adducts also contain convenient aromatic chromophores for detection by UV absorption. Consequently conditions were established for the base-line separation in HPLC of a mixture of *cis*- and *trans*-17 together with diphenyl maleate (**15b**). The extinction coefficients of the *cis*- and *trans*-isomers proved, conveniently, to be identical.

An equimolar mixture of diphenyl maleate (**15b**) and the electrochemically inactive *cis*-17 was electrolysed in DMF–Et<sub>4</sub>NBr (0.1 M) at an Hg cathode at the first reduction potential of **15b**. Analysis at the start of the electrolysis and after the consumption of 0.56 F showed that *cis* to *trans* epimerisation had occurred to the extent of 53%. This is compelling evidence for epimerisation *pro rata* to the formation of diphenyl maleate radical-anions.

**Co-electrolyses where the dienophile is the less easily reduced component.** The *o*-QDM precursor **1a** is more easily reduced than dimethyl maleate, **15a** (Table 4). Consequently, direct reduction at the potential for conversion of **1a** in the presence of unreduced dimethyl maleate should result in formation of *cis*-17, (R<sup>1</sup> = H, R<sup>2</sup> = Me, X = H). Co-electrolysis to just over 2 F yielded copious amounts of the corresponding *o*-PX polymers with no detectable Diels–Alder adduct. The order of reduction is reversed for **1d** *vis à vis* **15a** and mediated reduction of **1d** ( $\Delta E = 0.39$  V) would be expected. The corresponding *o*-PX was also the only detectable product of this co-electrolysis.

**Mechanistic conclusions.** A rationalisation must crucially account for (i) the reaction between the radical-anions of diphenyl maleate and fumarate and 2,3-bis(bromomethyl)-1,4-dimethoxybenzene (**1d**) giving exclusively the *trans*-cycloadducts, despite the fact that the separations of peak potentials are  $>0.5$  V suggesting relatively slow electron transfer and therefore inefficient redox catalysis; and (ii) that where redox catalysis to form the quinodimethane is likely to be favoured, such as in co-electrolysis of **1d** and dimethyl maleate ( $\Delta E = 0.31$  V), cycloaddition is not found and polymerisation of the QDM predominates.

The simplest explanation is that when *o*-QDMs are formed by redox catalysis involving the maleate and fumarate dienophiles Diels–Alder reaction is slower than polymerisation. We do know from the cyclic voltammetric studies (see earlier) that the parent *o*-xylylene does not give reversible redox behaviour at up to 160 V s<sup>-1</sup>, *i.e.* it reacts (polymerises) relatively quickly. For those cases where electron transfer between the dienophile

radical-anions and the dihalides is slow ( $\Delta E \geq 0.5$  V) the double nucleophilic substitution route comes into play. This also accounts for the exclusive formation of *trans*-cycloadducts. The expected isomerisation of diphenyl maleate radical-anions to the fumarate species is surprisingly slow but even had the expected *cis*-adduct been formed initially by the Diels–Alder route it would have rapidly to epimerised in the presence of electrogenerated base, probably the dianion formed by rapid dimerisation of the maleate radical-anions.

Experiments have also been carried out using chemical generation (Zn dust reduction) of the *o*-quinodimethanes from the 1,2-bis(bromomethyl)arenes in the presence of the maleate and fumarate dienophiles. Generation of **4d** by zinc-dust reduction, in DMF, and in the presence of diphenyl maleate, **15b**, gave a mixture of the adducts **17** (*ca.* 66%) with a *trans*:*cis* ratio of 10:1. The formation of *trans*-isomer in this case is probably also a result of partial epimerisation of the *cis*-isomer through enolisation of *cis*-adduct catalysed by ZnBr<sub>2</sub>, a product of the reaction. In further experiments, using the Zn-dust method, the corresponding *trans*-17 adducts were formed in moderate yields from combinations of **1d** or **1a** with diphenyl fumarate. The electrochemical method is cleaner and more efficient.

It is unlikely that these reactions proceed by the double nucleophilic substitution route, yet if *o*-quinodimethanes are generated they apparently react by Diels–Alder cycloaddition rather than polymerisation—the preservation of some *cis*-stereochemistry supports this. This contention contrasts with the findings for the electrochemical method. The probable reason is that the zinc-dust reductions take place over a considerable period (5–10 hours). Consequently the *o*-QDMs are formed slowly and in low concentration relative to the dienophile. Diels–Alder reaction may therefore compete favourably against polymerisation.

## Experimental

### Materials and general procedures

General-purpose reagents grade solvents (GPR) were used unless stated otherwise. For preparative electrolyses DMF (Aldrich) was used without further purification. For cyclic voltammetry and controlled potential coulometry DMF (Aldrich, HPLC grade) was used and stored over freshly baked (150 °C) 4 Å molecular sieve. Supporting electrolytes were tetraethylammonium bromide (Aldrich) and tetraethylammonium hexafluorophosphate (Aldrich), without any further purification.

Melting points were determined on an Electrothermal capillary tube melting point apparatus and were uncorrected. For polymers the melting points were obtained from DSC experiments using a Perkin-Elmer PC series DSC7 calorimeter. Infrared spectra were recorded on KBr discs using a Perkin-Elmer 1600 series FTIR spectrophotometer. <sup>1</sup>H NMR spectra and <sup>13</sup>C NMR (63 MHz) on a Bruker AM 250 (250 MHz) spectrometer. Solid-state <sup>13</sup>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). Direct pyrolysis mass spectra were recorded on a Kratos MS50RT mass spectrometer.

HPLC experiments were carried out using a Hewlett Packard HP1100 Series Liquid Chromatograph with UV detection at 270 nm. The instrument was equipped with a Zorbax Sil column (5 μm, 4.6 mm ID × 250 mm) and guard, run isocratically with EtOAc–hexane (30:70, Merck HPLC grade) eluent at 1.0 ml min<sup>-1</sup> and an injection volume of 10 μl.

### Crystallography

The intensity data were collected on an Enraf Nonius CAD-4 diffractometer using Mo-Kα radiation ( $\lambda = 0.71069$  Å) with an



$\omega$ -2 $\theta$  scan at 120 K. The unit cell parameters were determined by least-squares refinement on diffractometer angles  $6.4 \leq \theta \leq 11.5^\circ$  for 25 automatically centred reflections.<sup>20</sup> All data were corrected for absorption by semi-empirical methods ( $\psi$  scan)<sup>21</sup> and for Lorentz-polarization effects by XCAD4.<sup>22</sup> The structure was solved by direct methods using SHELXS-97,<sup>23</sup> and refined anisotropically (non-hydrogen atoms) by full-matrix least-squares on  $F^2$  using the SHELXL-97 program.<sup>22</sup> The program ORTEP-3<sup>24</sup> was used for drawing the molecules. WINGX<sup>25</sup> was used to prepare the material for publication.

**Crystal data.** The structure of *trans*-**17**, ( $R^1 = H$ ,  $R^2 = Ph$ ,  $X = OMe$ ) (Fig. 3) was determined by M. Motevalli (QMW Crystallographic Service):  $C_{26}H_{24}O_6$ ,  $M = 432.45$ , orthorhombic,  $a = 18.582(5)$ ,  $b = 10.594(4)$ ,  $c = 22.431(8)$  Å,  $U = 4416(3)$  Å<sup>3</sup>,  $T = 291$  K, space group *Pbca*,  $Z = 8$ ,  $\mu = 0.092$  mm<sup>-1</sup>. The final *R* indices were  $R1 = 0.0656$ ,  $wR2 = 0.0515$ . CCDC reference number 188/281. See <http://www.rsc.org/suppdata/p2/b0/b007476o/> for crystallographic files in .cif format.

### Electrochemical experiments

Cyclic voltammetric experiments (CV) were performed using a VersaStat EG&G Princeton Applied Research potentiostat with Model 270/250 Research Electrochemistry Software v 4.00. For faster scan rates (1–100 V s<sup>-1</sup>) either an assembly of a digital oscilloscope (Nic-310, Nicolet) connected to a waveform generator (PP R1, Hi-Tek Instruments, England), a DT 2101 (Hi-Tek Instruments, England) potentiostat and a XYt-recorder (PM 8271, Philips) or an EG&G Princeton Applied Research potentiostat Model 263A with appropriate software control were used.

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<sub>4</sub>NBr–DMF or 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> DMF solutions. The concentration of the substrate was 2–3 mM and the scan rate varied from 0.1–200 V s<sup>-1</sup>. Because the potential of the Ag wire reference electrode can vary over a relatively short time-scale, the  $E^\circ$  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 ( $E^\circ$  for anthracene =  $-1.92$  V vs. SCE in DMF<sup>26</sup>).

Preparative scale electrochemical reductions were performed using conventional glass cells, with the anode and cathode compartments separated by a glass sinter. The cells were equipped with a mercury pool working electrode (cathode), a Ag wire reference electrode and a carbon rod counter electrode (anode). 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

Many of these are known compounds that were prepared by modification of literature methods. Consequently, descriptions of their preparation, and physical and spectroscopic data are deposited as supplementary data. Only new compounds are described in this section.

**1-( $\alpha$ -Bromobenzyl)-2-( $\alpha$ -bromo- $\alpha$ -phenylbenzyl)benzene (1c).** 1-( $\alpha$ -Hydroxybenzyl)-2-( $\alpha$ -hydroxy- $\alpha$ -phenylbenzyl)benzene (1.0 g, 1.12 mmol) was dissolved in glacial acetic acid (20 ml) and the mixture heated gently until all the diol was dissolved when HBr (5 ml in HOAc (45%)) was added. The mixture was heated under reflux at 120 °C (1 hour), cooled to room temperature, diluted with water (50 ml) and the product extracted into chloroform. The organic layer was washed (H<sub>2</sub>O), dried (MgSO<sub>4</sub>) and the solvent evaporated. Crystals precipitated on cooling (0.91 g, 68%); mp 109 °C; <sup>1</sup>H NMR  $\delta_H$  (250 MHz, CDCl<sub>3</sub>) 6.40 (1H, s, PhCH(Br)Ar), 7.35–8.05 (19H, m, ArH), IR (KBr)/cm<sup>-1</sup> 3058 (m,  $\nu_{arom}$ ·C–H), 3029 (s,  $\nu_{sat}$ ·C–H), 1596 (s, benzene ring), 1482 (s,  $\nu$ C–H), 738 (m,  $\delta$ Ar–H, 2 adjacent H), 700 (m,  $\delta$ C–H); *m/z* 491.9590, C<sub>26</sub>H<sub>20</sub>Br<sub>2</sub> requires 491.957; elemental analysis, found (calcd): C 63.1% (63.4), H 4.1 (4.09), Br 32.8 (32.52).

**1-(Chlorobenzyl)-2-(phenylchlorobenzyl)benzene (2b).** 1-( $\alpha$ -Hydroxybenzyl)-2-( $\alpha$ -hydroxy- $\alpha$ -phenylbenzyl)benzene (1.0 g, 1.12 mmol) was dissolved in glacial acetic acid (20 ml). Concentrated HCl (10 ml) was added and refluxed (120 °C) for 30 minutes. The solution was cooled to room temperature, extracted with ether, washed with water, dried (MgSO<sub>4</sub>) and the solvent evaporated. A yellow oil was obtained (0.40 g, 36%); <sup>1</sup>H NMR  $\delta_H$  (250 MHz, CDCl<sub>3</sub>) 6.14 (1H, s, PhCH(Cl)Ar), 7.15–7.95 (19H, m, ArH); IR (KBr)/cm<sup>-1</sup> 3059 (m,  $\nu_{arom}$ ·C–H), 3030 (s,  $\nu_{sat}$ ·C–H), 1597 (s, benzene ring), 1482 (s,  $\nu$ C–H), 738 (m,  $\delta$ Ar–H, 2 adjacent H), 699 (m,  $\delta$ C–H); *m/z* 402.0949, C<sub>26</sub>H<sub>20</sub>Cl<sub>2</sub> requires 402.0941; elemental analysis, found (calcd): C 77.3% (77.59), H 5.1 (5.01), Cl 17.3 (17.39).

***trans*-1,2,3,4-Tetrahydro-5,8-dimethoxynaphthalene-2,3-dicarboxylic acid diphenyl ester (trans-17, R<sup>1</sup> = H, R<sup>2</sup> = Ph, X = OMe).** Activated zinc dust (0.5 g) was suspended in a solution of 2,3-bis(bromomethyl)-1,4-dimethoxybenzene **1d** (0.2 g, 0.0006 mol) and diphenyl fumarate **16b** (0.5 g, 0.002 mol) in DMF (5 ml), under nitrogen. The reaction was followed by TLC (CH<sub>2</sub>Cl<sub>2</sub>) and after 5 hours the mixture was filtered through Celite and the solvent evaporated. The oil obtained was suspended in ethyl acetate (50 ml) and the solution washed with brine (150 ml). After drying (MgSO<sub>4</sub>) and solvent removal flash chromatography (CH<sub>2</sub>Cl<sub>2</sub> 85%, petroleum ether 15%) gave the *trans* product, (0.178 g, 67%); mp 128–130 °C; *m/z* 432.1573, C<sub>26</sub>H<sub>24</sub>O<sub>6</sub> requires 432.1566. Full NMR data (<sup>1</sup>H and <sup>13</sup>C) are deposited as supplementary data, and for the relevant X-ray crystallographic structure, see Fig. 3.

***cis*-1,2,3,4-Tetrahydro-5,8-dimethoxynaphthalene-2,3-dicarboxylic acid diphenyl ester, cis-17 (R<sup>1</sup> = H, R<sup>2</sup> = Ph, X = OMe).** The Zn-dust reduction was carried out as above in the presence of diphenyl fumarate, except that reaction took 10 hours. Flash chromatography (CH<sub>2</sub>Cl<sub>2</sub> 90%, petroleum ether 10%) gave a mixture of *cis* and *trans*-**17** ( $R^1 = H$ ,  $R^2 = Ph$ ,  $X = OMe$ ), approximately 1 : 10.

### Unambiguous preparation of *cis*-1,2,3,4-tetrahydro-5,8-dimethoxynaphthalene-2,3-dicarboxylic acid diphenyl ester, cis-17 (R<sup>1</sup> = H, R<sup>2</sup> = Ph, X = OMe)

The *cis*-adduct expected for cycloaddition involving diphenyl maleate was prepared by first reacting the appropriate QDM with maleic anhydride and the ensuing *cis*-adduct was then converted into the corresponding diphenyl ester.

***cis*-5,8-Dimethoxy-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic anhydride.** 2,3-Bis(bromomethyl)-1,4-dimethoxybenzene **1d** (0.2 g, 0.0006 mol) and maleic anhydride (0.3 g, 0.003 mol) in DMF (15 ml), under nitrogen, were reacted with Zn dust (0.4 g, 0.006 mol). Work-up as above gave *cis*-5,8-dimethoxy-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic

anhydride as a white solid (0.105 g, 65%); mp 209–210 °C (lit.<sup>29</sup> 210–211 °C);  $\delta_{\text{H}}$  (250 MHz, CDCl<sub>3</sub>) 2.62 (2H, m, CH<sub>ax</sub>-H<sub>eq</sub>), 3.34 (2H, m, CH<sub>ax</sub>-H<sub>eq</sub>), 3.68 (2H, m, CHCO), 3.72 (6H, s, OCH<sub>3</sub>), 6.82 (2H, s, ArH).

**cis-5,8-Dimethoxy-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic acid diphenyl ester, cis-17** (R<sup>1</sup> = H, R<sup>2</sup> = Ph, X = OMe). To a cooled (0 °C) solution of *cis*-5,8-dimethoxy-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic anhydride (see above) (0.1 g, 3.8 × 10<sup>-4</sup> mol) and phenol (0.01 g, 0.001 mol) in CH<sub>2</sub>Cl<sub>2</sub> was added 1,3-dicyclohexylcarbodiimide (DCC, 0.17 g, 8 × 10<sup>-4</sup> mol) and 4-(dimethylamino)pyridine (DMAP, 0.01 g, 4 × 10<sup>-4</sup> mol). The reaction was run at 0 °C and followed by TLC. After 4 hours the dicyclohexylurea was filtered off and the product isolated by flash chromatography (CH<sub>2</sub>Cl<sub>2</sub>-petroleum ether, 3:1) to give *cis*-5,8-dimethoxy-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic acid diphenyl ester (0.103 g, 62%); mp 132–133 °C; *m/z* 432.1585, C<sub>26</sub>H<sub>24</sub>O<sub>6</sub> requires 432.1590; NMR data (<sup>1</sup>H and <sup>13</sup>C) are deposited as supplementary data.

## Electrolysis

### a. *ortho*-Quinodimethane formation with polymerisation.

**General procedure.** The substrate (0.5–2.0 g for 80 ml cell 0.2–0.5 g for 30 ml cell) and mediator, if appropriate, were dissolved in the previously de-oxygenated (N<sub>2</sub> bubbling) electrolyte in the cathode compartment of a divided cell. After electrolysis at controlled potential reaction was considered complete after the current had decayed to the background level (direct electrolysis) or when 2 F had passed through the cell (mediated electrolysis). Insoluble (polymeric) products were then filtered off and soluble products were obtained by adding distilled water to the reaction mixture. Any precipitate formed was filtered off and washed with water. The remaining solution was extracted three times with 20 ml diethyl ether and then washed at least three times with 30 ml water, the ether extract was dried (MgSO<sub>4</sub>) and the solvent evaporated. The next purification step was crystallisation or column chromatography. Physical and spectroscopic data (FTIR, NMR and MS) for products obtained in these experiments are available as supplementary data.

### b. *ortho*-Quinodimethane formation with cycloaddition. The following example may be taken to represent the typical procedure.

*Co-electrolysis of 2,3-bis(bromomethyl)-1,4-dimethoxybenzene, 1d, with diphenyl maleate, 15b.* 2,3-Bis(bromomethyl)-1,4-dimethoxybenzene (**1d**, 0.45 g, 0.0014 mol) and diphenyl maleate (**15b**, 0.75 g, 0.0028 mol) were added to the catholyte (ca. 80 ml DMF-Et<sub>4</sub>NBr (0.1 M)) in a divided cell equipped with a stirred mercury pool cathode, a silver wire reference electrode and a carbon rod anode. After electrolysis at -1.1 V the current fell from 130 mA to 8 mA and 3.7 F had been consumed. The catholyte was removed and DMF evaporated under reduced pressure. The residue was dissolved in ethyl acetate (70 ml) and washed with brine (3 × 50 ml). The ethyl acetate layer was dried (MgSO<sub>4</sub>) and after solvent removal flash chromatography (CH<sub>2</sub>Cl<sub>2</sub>-petroleum ether, 3:1) gave (*trans*-**17**, R<sup>1</sup> = H, R<sup>2</sup> = Ph, X = OMe) as a white solid (0.580 g, 97%).

*Controlled potential reduction of diphenyl maleate, 15b.* Diphenyl maleate (0.268 g, 0.001 mol) was electrolysed at -1.3 V vs. Ag wire in DMF-Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M), according to the general procedure, until the background current was reached (0.94 F). The catholyte was evaporated to dryness and the water (50 ml) added. The beige precipitate was filtered and dried (1.07 g, containing ca. 90 mg of diphenyl maleate-derived product, according to <sup>1</sup>H NMR). Attempts at normal aqueous work-up and extraction failed, probably due to rapid hydrolysis

of the phenyl esters and consequent formation of the tetraalkylammonium salt, which is soluble in both organic and aqueous phases. Examination of the <sup>1</sup>H NMR spectrum of the precipitated mixture of electrolyte and organic product was problematical because signals from the large excess of electrolyte obscured important parts of the spectrum. However, according to accessible parts of the spectrum, and relative integration, two products appear to be present, compound A (55%), proposed as the *meso*- and ( $\pm$ )-isomers (in the ratio 6:1, or 1:6) of [RO<sub>2</sub>CCH<sub>2</sub>CH(CO<sub>2</sub>R)CH(CO<sub>2</sub>R)CH<sub>2</sub>CO<sub>2</sub>R], the linear hydrodimer, and an as yet unidentified compound B (45%). Only two signals are visible for compound B, two separate double doublets in the ratio 7:1. Compound A (major isomer, *meso* or ( $\pm$ ))  $\delta_{\text{H}}$  (600 MHz, CDCl<sub>3</sub>) 3.50 (1H, dd, *J* 16.48, 8.92 Hz, CH<sub>2</sub>CH), 2.89 (1H, dd, *J* 16.30, 9.42 Hz, CH<sub>2</sub>CH); (minor isomer, ( $\pm$ ) or *meso*) 3.65 (1H, dd, *J* 19.60, 8.71 Hz). Compound B (major isomer) 4.42 (1H, d, *J* 7.32 Hz) (minor isomer) 4.47 (1H, d, *J* 8.45 Hz).

*Co-electrolysis of cis-5,8-dimethoxy-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic acid diphenyl ester (cis-17) with diphenyl maleate, 15b.* Compound *cis*-**17** (0.114 g, 0.25 mmol) and diphenyl maleate (0.069 g, 0.25 mmol) were co-electrolysed in DMF-Et<sub>4</sub>NBr (0.1 M) until 0.6 F had passed. The catholyte was evaporated to dryness, water added and the product extracted into CH<sub>2</sub>Cl<sub>2</sub>. The combined organic extract was dried (MgSO<sub>4</sub>) and evaporated to dryness. The syrup so obtained was analysed by HPLC at room temperature [column, Zorbax sil (4.6 mm ID × 25 cm), isocratic, EtOAc-hexane (30:70), detector wavelength of 270 nm].

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