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Electro-organic Reactions. Part 41. Diels-Alder Reactions of *o*-Quinodimethanes from the Cathodic Reduction of α,α'-Dibromo-1,2-dialkylbenzenes[1]

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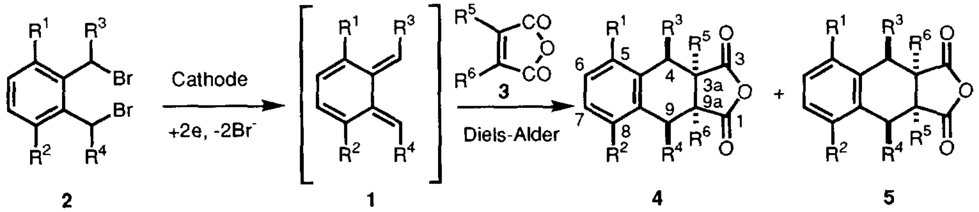
Abstract: Cathodic reduction of α,α'-dibromo-1,2-dialkylbenzenes in DMF containing $Et_4N^+ Br^-$ as supporting electrolyte, in the presence of dienophiles (*e.g.* maleic anhydride derivatives), yielded Diels-Alder adducts of *o*-quinodimethanes. Selective reduction of the benzylic dibromides was often possible even when their irreversible cyclic voltammetric reduction peak potentials were more negative than the E^o values for the anhydrides. This might be a consequence of redox catalysis, with the anhydrides having a dual role as mediators and dienophiles.

Introduction

o-Quinodimethane derivatives **1** are synthetically useful and highly reactive intermediates that are particularly noted for their ability to act as dienes in the Diels-Alder reaction.[2] There are a number of established methods for generating *o*-quinodimethanes, including the reductive debromination of α,α'-dibromo-1,2-dialkylbenzenes using finely divided metallic zinc[3,4] or nickel.[5] Recently[6] we described the preparation of three Diels-Alder adducts of *o*-quinodimethanes by the *cathodic* reduction of dibromides in the presence of maleic anhydride. Since the electrochemical method avoids the production of potentially harmful inorganic residues, we were prompted to investigate the scope of this new approach (Scheme 1).



Scheme 1. Substituents are defined in Table 3.

RESULTS AND DISCUSSION

(i) Cyclic Voltammetry

Because *o*-quinodimethanes are transient species, which readily undergo dimerisation and polymerisation, they must normally be generated in the presence of the substance with which they are required to react. The trapping agent (dienophile) for the Diels-Alder reaction usually contains an electron-poor C=C bond and so may itself be susceptible to cathodic reduction.[7] In order to assess the relative ease of the two competing reductive processses, cyclic voltammetry (c.v.) was used to determine the reduction peak potentials for a selection of dibromides (Table 1); reversible reduction potentials for some of the dienophiles have been made available[8] (Table 2).

The peak potentials measured at 0.3 V s^{-1} are for irreversible reduction of the dibromides; of the dienophiles only dimethylmaleic anhydride exhibits even quasi-reversible behaviour at this sweep rate. Comparisons of irreversible with reversible potentials should be made with caution, although some significance can be attached to large differences. 1,2-Bis(bromomethyl)benzene (**2a**) was found to have a first reduction peak potential of -0.92 V (relative to Ag/AgBr). The reduction is irreversible, implying that the radical anion of **2a** undergoes a rapid follow-up reaction, presumably by loss of Br^- to give a 2-(bromomethyl)benzyl radical, which is then further reduced to the *o*-quinodimethane **1a**. By analogy with other benzylic halides it is likely that concerted electron transfer and halide cleavage is involved.[9] Substituted dibromides **2b**-**2h** gave rise to similar c.v. traces, but with some displacements of the peak potentials relative to those for **2a**.

For the dienophiles **3a**-**3i** (Table 2) the peak potentials show a clear division between the easily reducible maleic anhydride and maleimide derivatives **3a-f**, where two electron-withdrawing substituents are present on the C=C bond ($E_{p,c} > -1.0$ V), and the less electron deficient **3g-i** which have only one such substituent ($E_{p,c} \leq -1.7$ V). The cyclic voltammetric peaks for reduction of the dienophiles are mostly irreversible at sweep speeds between 0.3 and 10 V s^{-1}, but that of dimethylmaleic anydride (**3c**) is quasi-reversible in this range of sweep speeds, implying that the corresponding radical anion is relatively unreactive under the conditions used for c.v. The *reversible* reduction potentials (E^o) of the anhydrides **3a**-**3d** *relative to SCE* have recently been determined elsewhere[8] and are included in Table 2 for comparison. Both sets of data show similar trends, particularly that substitution of the C=C bond by methyl groups makes reduction more difficult; only the E^o values, of course, have thermodynamic significance.

Although the first reduction peak potential of 1,2-bis(bromomethyl)benzene (**2a**) is 0.4 V more negative than that of maleic anhydride (**3a**), electrolysis of a mixture of these two substances gives an acceptable yield of the Diels-Alder adduct **4aa** of maleic anhydride and *o*-quinodimethane, implying that selective reduction of the dibromide is possible. Whatever the follow-up reaction of the radical anion of maleic anhydride which makes its reduction irreversible, it is clear that this radical anion can be intercepted by reaction with the dibromide **2a**. In the absence of reversible redox potentials (E^o) for the dibromides it is difficult to interpret the results with certainty. For dissociative electron-transfer it is not possible to measure E^o, but an appropriate potential may be estimated.[9] However, it is significant that not only does maleic anhydride retain its dienophilic character in the presence of the less easily reduced dibromide **2a**, but so does the quasi-reversibly reduced dimethylmaleic anhydride (**3c**). Furthermore, the reduction of **3c** becomes irreversible upon gradual addition of the dibromide **2a** (up to 1 molar equivalent). It is therefore possible that the radical anion of the dienophile can act as an electron transfer mediator[10] with the outcome of the reaction being decided by the rate and irreversibility of the cleavage to the *o*-quinodimethane (Scheme 2). The fact that halide cleavage is likely to be very fast, probably concerted with electron transfer,[9] and that electron transfer to the anhydrides is fast,[8] argues in favour of a redox catalysis mechanism; the dienophile is regenerated in this process so is available for adduct formation. The position of the equilibrium (Equation 2 in Scheme 2) is determined by the difference between E° for the anhydrides and the appropriate potential for the dihalides. The second electron transfer can be effected either directly at the cathode or, more probably, by single electron transfer from the dienophile radical-anion.

Table 1. Cyclic voltammetric peak potentials[a] ($E_{p,c}$) for irreversible reduction of dibromides **2a-h**.

Dibromide	R^1	R^2	R^3	R^4	$-E_{p,c}(1)$	$-E_{p,c}(2)$	$-E_{p,c}(3)$
2a	H	H	H	H	0.92	1.30	1.88
2b	OMe	H	H	H	1.00	1.53	
2c	OMe	OMe	H	H	0.93	1.45	
2d	OCO^{t}Bu	H	H	H	0.97	1.26	1.88
2e	F	H	H	H	0.82	1.13	
2f	CN	H	H	H	1.10		
2g	H	H	Me	H	1.03	1.71	
2h	H	H	Me	Me	0.88	1.63	

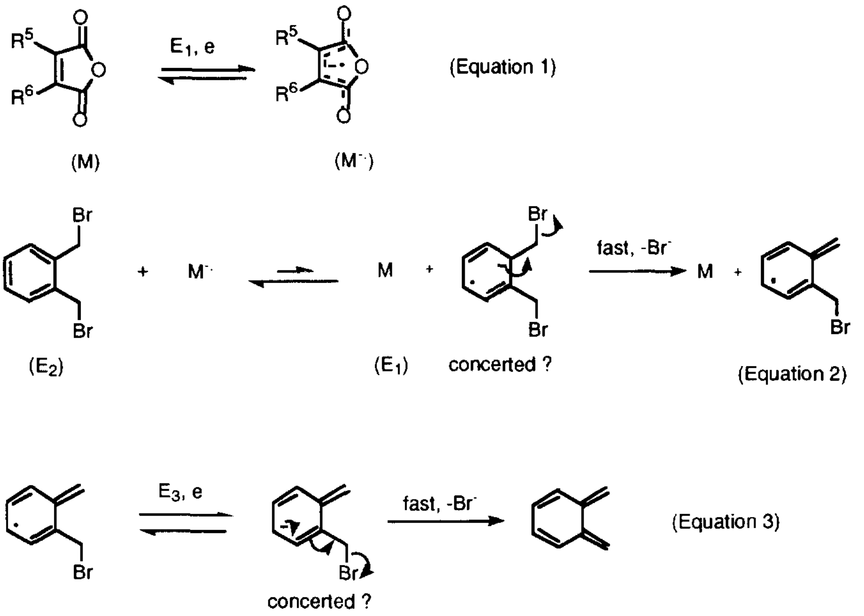
Note: *a*. Hg bead cathode, DMF-Et_4NBr (0.1 M), 0.3 V s^{-1}, V *vs* Ag/AgBr.

Table 2. Cyclic voltammetric peak potentials[a] ($E_{p,c}$) for reduction of dienophiles **3a-i**.

Dienophile number	Dienophile name	Irreversible reduction (note *a*)			Reversible reduction (note *b*)
		$-E_{p,c}(1)$	$-E_{p,c}(2)$	$-E_{p,c}(3)$	$-E^{\circ}$
3a	Maleic anhydride	0.50	1.18	1.67	0.84
3b	Methylmaleic anhydride	0.77	1.54		0.99
3c	Dimethylmaleic anhydride	0.85	1.80		1.13
3d	Phenylmaleic anhydride	0.45	1.25	1.62	0.76
3e	Bromomaleic anhydride	0.34	0.84		
3f	*N*-Phenylmaleimide	0.61	1.43	1.75	
3g	Methyl vinyl ketone	1.70			
3h	Methyl acrylate	1.74			
3i	Methyl methacrylate	1.91			

Notes: *a*. Hg bead cathode, DMF-Et_4NBr (0.1 M), 0.3 V s^{-1}, V *vs* Ag/AgBr.

b. Hg bead cathode, DMF-Bu_4NPF_6 (0.1 M), sweep speeds in the range 1-500 V s^{-1}, V *vs* SCE (taken from reference 8). The E° value of **3c** was estimated from the midpoint of the forward and backward peaks in our quasi reversible c.v. (obtained at 5 V s^{-1}) to be *ca* -0.79 V *vs* Ag/AgBr, so E° (*vs* Ag/AgBr) is approximately 0.34 + E° *vs* SCE.

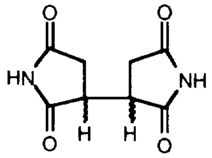


Scheme 2. Proposed mechanism of *o*-quinodimethane formation involving mediated electron transfer.

(ii) Coulometry

Coulometry was performed on the dibromide **2h** at controlled potentials of -1.0 and -1.6 V (*i.e.* close to the first and second peak potentials observed in c.v.). In each case 2 F were consumed, consistent with reduction to the corresponding *o*-quinodimethane **1h**.

Controlled potential coulometry on dimethylmaleic anhydride **3c** at -0.9 V resulted in the consumption of 1 F, implying that a reductive dimerisation occurs. Such processes are well established for electron deficient alkenes:[7] for example, the one-electron reduction of maleimide in water gave a quantitative yield of hydrodimer **6** as a mixture of (±) and *meso* isomers.[11] However, when phenylmaleic anhydride was subjected to controlled potential coulometry at -0.5 V, it was found that only 0.56 (±0.06) F was consumed, suggesting that a higher degree of oligomerisation had occurred. This was supported by the mass spectrum of the solid product from the electrolysis of phenylmaleic anhydride in the absence of dibromide, which had a base peak at *m*/*z* 522 and other peaks up to *m*/*z* 693.



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(iii) Preparative Scale Generation of o*-Quinodimethanes with Diels-Alder Trapping*

(a) Maleic Anhydride Derivatives as Dienophiles

The results of Diels-Alder reactions between electrochemically generated *o*-quinodimethanes and maleic anhydride derivatives are given in Table 3. The reductions were performed at constant potentials which were close to the second peak potentials determined from c.v. on the dibromides, since this led to the reasonably rapid production of Diels-Alder adducts **4** and **5** (typically within a few hours on the 5 mmol scale). The dienophiles were used in up to three-fold excess and the electrolyses were stopped when the current had fallen to approximately 10% of its initial value, usually after the passage of 4 F relative to the dibromide.

In reactions where both the *o*-quinodimethane and the dienophile were unsymmetrically substituted, the two possible regioisomeric cycloadducts **4** and **5** were formed in a *ca* 1:1 ratio (as determined by ^{1}H NMR spectroscopy), even in the case of the dibromide **2d** which contains the bulky pivaloyloxy group; in no case could these pairs of regioisomers be separated, neither by flash chromatography nor by crystallisation. Compounds **4ag**, **4ah**, **4bh**, **4cg** and **4ch** were obtained as single diastereomers, to which structures were assigned on the assumption that the Diels-Alder reactions occurred with the usual stereospecificity and preference for the *'endo'* mode of cycloaddition, and also that the *o*-quinodimethanes derived from **2g** and **2h** have *E* geometry at the exocyclic C=C bond(s).[12] ^{1}H NMR spectroscopy confirmed that the adducts **4ah** and **4ch** have symmetrical structures: the equivalent methyl groups must therefore be *cis* to one another, as expected from concerted cycloadditions of an (*E*,*E*)-diene. For both adducts **4ag** and **4ah** the coupling constants $J_{3a,9a}$ between the bridgehead protons are 10 Hz, suggesting that boat-like conformations are adopted. For compound **4ag** the two $J_{9,9a}$ values are 7 and 3 Hz. The larger of these values probably corresponds to the coupling between two pseudoaxial hydrogens, with the smaller value arising from the coupling of the pseudoequatorial 9-H with the bridgehead 9a-H. Since compound **4ag** has $J_{3a,4}$ = 6 Hz, it appears that the 4-H is also pseudoequatorial and is therefore *cis* to the bridgehead 3a-H as required for the *'endo'* adduct. Compound **4ah** has $J_{3a,4} = J_{9,9a}$ = 6 Hz, and compound **4bh** has $J_{9,9a}$ = 5 Hz, thus supporting the *'endo'* assignment in these cases also.

When an attempt was made to perform a reaction between bromomaleic anhydride (**3e**) and the electrochemically generated *o*-quinodimethane (**1a**), the unsubstituted adduct **4aa** was obtained in 46% yield, indicating that a reductive debromination had occurred α to a carbonyl group.

The attempted cycloadditions to maleic anhydride of *o*-quinodimethanes from the fluoro- and cyano-substituted dibromides **2e** and **2f** gave complex mixtures of products with little or none of the desired addducts. The aromatic fluoride and cyanide groups are expected to be inert to the mildly reductive conditions used, but the presence of these electron withdrawing substituents on the *o*-quinodimethanes would have reduced the rates of the Diels-Alder reactions.

(b) Other Dienophiles

Scheme 3 and Table 4 show the results obtained when dienophiles other than anhydrides were used to trap *o*-quinodimethane (**1a**). With *N*-phenylmaleimide (**3f**), which is doubly activated, a moderate yield of the cycloadduct **7f** was obtained. However, when the singly activated dienophiles **3g**-**3i** were used, the yields of the corresponding Diels-Alder adducts **7g-i** were poor and there were substantial quantities of hydrocarbon products. Thus it appears that the Diels-Alder trapping of **1a** by singly activated dienophiles was too slow to compete efficiently with the dimerisation and polymerisation of **1a**. A control experiment was performed in which 1,2-bis(bromomethyl)benzene was electrolysed in the absence of any added dienophile: this gave a similar mixture of hydrocarbons, as judged by ^{1}H NMR spectroscopy.

Table 3. Diels-Alder reactions of electrochemically generated *o*-quinodimethanes with maleic anhydride derivatives.[a]

R^1	R^2	R^3	R^4	R^5	R^6	Adduct(s)[b]	Yield (%)	Molar ratio **2**:**3**	$-E_{red}$/V (note *c*)	F (note *d*)
H	H	H	H	H	H	**4aa**	58[e]	1:3.0	1.40	4.4
OMe	H	H	H	H	H	**4ab**	29	1:2.8	1.50	8.0
OMe	OMe	H	H	H	H	**4ac**	46[e]	1:3.0	1.45	4.0
O_2C^tBu	H	H	H	H	H	**4ad**	14	1:3.0	1.26	4.0
H	H	Me	H	H	H	**4ag**	78	1:1.5	1.71	4.0
H	H	Me	Me	H	H	**4ah**	87	1:1.5	1.63	4.0
H	H	H	H	Me	H	**4ba**	37	1:1.5	1.30	4.0
OMe	H	H	H	Me	H	**4bb + 5bb**	55	1:3.0	1.50	8.0
OMe	OMe	H	H	Me	H	**4bc**	36	1:3.0	1.45	6.0
O_2C^tBu	H	H	H	Me	H	**4bd + 5bd**	9	1:3.0	1.26	8.0
H	H	Me	H	Me	H	**4bg + 5bg**	73	1:1.5	1.71	4.0
H	H	Me	Me	Me	H	**4bh**	83	1:1.5	1.63	3.5
H	H	H	H	Me	Me	**4ca**	54	1:1.5	1.30	3.5
MeO	H	H	H	Me	Me	**4cb**	48	1:1.5	1.50	4.0
MeO	MeO	H	H	Me	Me	**4cc**	56	1:3.3	1.45	4.0
H	H	Me	H	Me	Me	**4cg**	47	1:1.5	1.71	4.0
H	H	Me	Me	Me	Me	**4ch**	69	1:1.5	1.63	4.0
MeO	H	H	H	Ph	H	**4db + 5db**	12	1:2.9	1.50	4.0

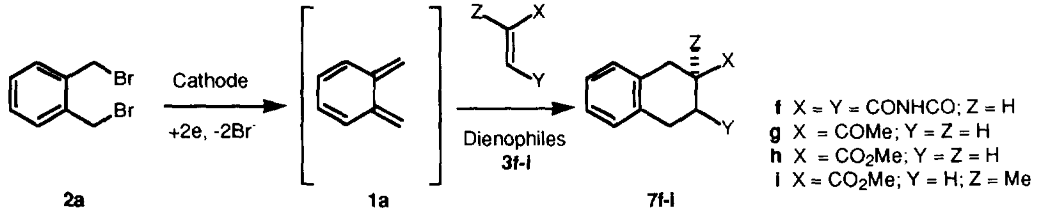
Notes: *a*. Hg pool cathode; divided cell; DMF-Et_4NBr (0.1 M); at *ca* $-E_{p,c}$(2) of the dibromide **2**.

b. In all cases where pairs of regioisomeric products were possible the cycloadducts **4** and **5** were obtained in a *ca* 1:1 ratio (as determined by ^{1}H NMR spectroscopy) and could not be separated.

c. Potential at which the electrolysis was performed relative to Ag/AgBr.

d. Faradays of electricity passed during electrolysis per mole of dibromide **2** used; only 2 F is required for production of the quinodimethane, the excess is presumably used to reduce excess dienophile.

e. This reaction has previously been described by us in reference 6.



Scheme 3.

Table 4. Diels-Alder reactions of electrochemically generated *o*-quinodimethane (**1a**) with dienophiles other than anhydrides.

Dienophile	Adduct	Yield (%)	Molar ratio **2a**:**3**	E_{red}/V (note *a*)	F mol^{-1} (note *b*)
N-Phenylmaleimide (**3f**)	**7f**	51	1:2.0	-1.30	4.0
Methyl vinyl ketone (**3g**)	**7g**	20	1:1.0	-1.30	4.0
Methyl acrylate (**3h**)	**7h**	15	1:1.0	-1.30	4.0
Methyl methacrylate (**3i**)	**7i**	11	1:2.0	-1.30	4.0

Notes: *a*. Potential at which the electrolysis was performed relative to Ag/AgBr.
b. Faradays of electricity passed during electrolysis per mole of dibromide **2a** used.

CONCLUSIONS

Electrochemical reduction of α,α'-dibromo-1,2-dialkylbenzenes leads to the formation of *o*-quinodimethanes and is a useful alternative to the use of dissolving metal reductions. The transient *o*-quinodimethanes may be trapped as their Diels-Alder adducts: this process is particularly efficient when the dienophile is doubly activated (*e.g.* for maleic anhydride derivatives or *N*-phenylmaleimide) and the *o*-quinodimethane does not bear electron-withdrawing substituents. The cycloadducts are obtainable even in cases where the dienophile is more readily reducible than the dibromide and it is proposed that under these circumstances the dienophile acts as an electron transfer mediator as outlined in Scheme 2.

EXPERIMENTAL SECTION

Materials and General Procedures

The following substances were prepared by literature methods: 2,3-bis(bromomethyl)anisole (**2b**),[13] 2,3-bis(bromomethyl)-1,4-dimethoxybenzene (**2c**)[14] and 1,2-bis(bromomethyl)-3-fluorobenzene (**2e**).[15] Melting points were determined on an Electrothermal capillary tube melting point apparatus and are uncorrected. Infra red spectra were recorded on KBr discs using a Perkin-Elmer 1600 series FTIR spectrophotometer. ^1H NMR spectra were recorded on Bruker WP 80 (80 MHz), AM 250 (250 MHz) and AMX 600 (600 MHz) spectrometers and unless indicated otherwise were obtained in $CDCl_3$ solution. Mass spectra was performed using the electron impact technique. Organic extracts were dried over $MgSO_4$ and evaporated under reduced pressure. Merck pre-coated silica gel plates were used for thin layer chromatography. All petroleum ether refers to the fraction of boiling range 40-60°C. *N,N*-Dimethylformamide (DMF) used for voltammetric experiments was dried over $CuSO_4$ for three days and distilled under reduced pressure. CCl_4 was dried by refluxing over P_2O_5 for three hours and distilled. Tetraethylammonium bromide (TEAB) (from Aldrich) was dried in an oven at 90-100°C.

Cyclic voltammetric and controlled potential coulometric experiments were run in an undivided cell using a mercury bead working electrode (cathode), Ag/AgBr reference electrode and platinum coil counter-electrode (anode). The experiments were carried out in 0.1 M TEAB/DMF solution. The concentration of substrate was 2-3 mM and the scan speed was 0.3 V s^{-1}. Preparative scale electrochemical reductions were performed using conventional glass cells, with the anode and cathode compartments separated by a microporous polypropylene film (Hoechst-Celanese Celguard 2500). The reactions took place at a mercury pool working electrode (cathode), the reference electrode was Ag/AgBr, and a carbon rod was the counter-electrode (anode). The reactions were kept under an inert atmosphere by the slow bubbling of dry nitrogen through the electrolyte (0.1 M TEAB/DMF). The catholyte was magnetically stirred.

Preparation of the Dibromides 2d, 2f, 2g and 2h.

2,3-Dimethylphenyl pivalate. This was obtained in 91% yield by esterification of 2,3-dimethylphenol with pivaloyl chloride in dry pyridine followed by distribution between ether and water and distillation at 15 mmHg and 140 °C. IR/cm^{-1} 1751; ^1H NMR (250 MHz) 1.39 (9 H, s), 2.06 (3 H, s), 2.29 (3 H, s), 6.80 (1 H, d, J = 7 Hz), 7.01 (1 H, d, J = 7 Hz) and 7.08 (1 H, t, J = 7 Hz). (MS found m/z : 206.1310. $C_{13}H_{18}O_2$ requires M, 206.1307).

2,3-Bis(bromomethyl)phenyl pivalate (**2d**). 2,3-Dimethylphenyl pivalate (0.50 g, 2.4 mmol) and *N*-bromosuccinimide (NBS) (0.74 g, 4.2 mmol) were refluxed in dry CCl_4 (20 ml) for 4h. The reaction mixture was cooled and filtered; the residue was concentrated and recrystallised from ether-petroleum ether to give the title compound (0.68 g, 77%) as a white solid m.p. 56-57 °C; IR/cm^{-1} 1761; ^1H NMR (250 MHz) 1.43 (9 H, s), 4.59 (2 H, s), 4.61 (2 H, s), 7.07 (1 H, dd, J = 8, 1.5 Hz), 7.25 (1 H, dd, J = 8, 1.5 Hz) and 7.25 (1 H, t, J = 8 Hz). (MS found m/z : 365.9475, 363.9498 and 361.9518. $C_{13}H_{16}Br_2O_2$ requires M, 365.9477, 363.9497 and 361.9517).

2,3-Bis(bromomethyl)benzonitrile (**2f**). This was prepared by treatment of 2,3-dimethylbenzonitrile with NBS in CCl_4, by analogy with the preparation of **2d** above. Recrystallisation from MeOH gave **2f** (60%), m.p. 93 °C; ^1H NMR (80 MHz) 4.65 (2 H, s), 4.8 (2 H, s) and 7.3-7.7 (3 H, m).

1-(1-Bromoethyl)-2-(bromomethyl)benzene (**2g**). This was prepared by treatment of 2-ethyltoluene with NBS in CCl_4, by analogy with the preparation of **2d** above. Recrystallisation from petroleum ether gave **2g** as white crystals (83% yield), m.p. 35-37 °C; ^1H NMR (80 MHz) 2.1 (3 H, d, J = 7 Hz), 4.55 (1 H, d, J = 11 Hz), 4.85 (1 H, d, J = 11 Hz), 5.7 (1 H, q, J = 7 Hz) and 7.0-8.0 (4 H, m).

1,2-Bis(1-bromoethyl)benzene (**2h**). This was prepared by treatment of 1,2-diethylbenzene with NBS in CCl_4, by analogy with the preparation of **2d** above. The crude product, which was obtained in quantitative yield and was used in electrochemical reductions without further purification, was found by ^1H NMR spectroscopy to be a *ca* 3:1 mixture of diastereomers. Recrystallisation from CH_2Cl_2 gave colourless, rectangular prisms (63% yield) comprising a *ca* 15:1 mixture of diastereomers. ^1H NMR for major diastereomer (80 MHz) 2.15 (6 H, d, J = 8 Hz), 5.7 (2 H, q, J = 8 Hz) and 7.25-7.75 (5 H, m); ^{1}H NMR for minor diastereomer (80 MHz) 2.1 (6 H, d, J = 8 Hz), 5.6 (2 H, q, J = 8 Hz) and 7.25-7.75 (5 H, m).

Preparative Scale Reductions

5-Methoxy-3a,4,9,9a-tetrahydronaphtho[2,3-c]furan-1,3-dione (**4ab**).–Example of general procedure. 1,2-Bis(bromomethyl)anisole (**2b**) (1.2 g, 4.3 mmol) and maleic anhydride (1.2 g, 12.2 mmol) were co-electrolyzed, using a reduction potential of -1.5V (Ag/AgBr) and passing 8 F mol^{-1} with respect to **2b**. The crude reaction mixture was partitioned between ether and water; the ether extract was washed, dried, evaporated and the residue was recrystallised from toluene (twice) to give **4ab** (0.27 g, 29%) as white crystals, m.p. 172 °C; IR (KBr)/cm^{-1} 1844 and 1780; ^{1}H NMR (250 MHz) 2.64-2.73 (1 H, m), 2.87-2.95 (1 H, m), 3.14 (1 H, dd, J = 15, 3 Hz), 3.50-3.62 (3 H, m), 3.82 (3 H, s), 6.81 (2H, d, J = 8Hz) and 7.17 (1 H, t, J = 8 Hz). (MS found m/z : 234.0794. Required for $M + H_2$ ($C_{13}H_{14}O_4$), 234.0892).

5-Pivaloyloxy-3a,4,9,9a-tetrahydronaphtho[2,3-c]furan-1,3-dione (**4ad**). M.p. 145 °C (from Et_2O); IR (KBr)/cm^{-1} 1844, 1778 and 1745; ^{1}H NMR (250 MHz) 1.41 (9 H, s), 2.70 (1 H, dd, J = 15, 6 Hz), 2.98 (1 H, dd, J = 15, 6 Hz), 3.18 (2 H, dd, J = 15, 3 Hz), 3.50-3.55 (2 H, m), 6.97 (1 H, d, J = 8 Hz), 7.08 (1 H, d, J = 8 Hz) and 7.22 (1 H, t, J = 8 Hz). (MS found m/z : 302.1155. $C_{17}H_{18}O_5$ requires M, 302.1154).

4-Methyl-3a,4,9,9a-tetrahydronaphtho[2,3-c]furan-1,3-dione (**4ag**).[16] M.p. 191-192 °C (from Et_2O); IR (KBr)/cm^{-1} 1846 and 1775; ^{1}H NMR (250 MHz) 1.68 (3 H, d, J = 7 Hz), 2.86 (1 H, dd, J = 15, 7 Hz), 3.09 (1 H, quintet, J = 7 Hz), 3.25 (1 H, dd, J = 15, 3 Hz), 3.47 (1 H, dd, J = 10, 6 Hz), 3.63 (1 H, ddd, J = 10, 7, 3 Hz) and 7.17-7.35 (4 H, m). (MS found m/z : 216.0787. $C_{13}H_{12}O_3$ requires M, 216.0786).

4,9-Dimethyl-3a,4,9,9a-tetrahydronaphtho[2,3-c]furan-1,3-dione (**4ah**). M.p. 247-249 °C (from toluene); IR (KBr)/cm^{-1} 1844 and 1778; ^{1}H NMR (250 MHz) 1.75 (6 H, d, J = 7 Hz), 3.02-3.14 (2 H, m), 3.44-3.53 (2 H, m) and 7.25-7.35 (4 H, m). The 600 MHz ^{1}H NMR spectrum of **4ah** in the region between δ3 and δ4 was obtained and then simulated iteratively as the AA'BB' part of an $AA'BB'X_3X'_3$ spectrum, using the Bruker 'Panic' program running on a Bruker Aspect-3000 computer. The following values were deduced: J_{AB} = 5.9 Hz, $J_{BB'}$ = 9.8 Hz and J_{AX} = 7.1 Hz. (MS found m/z : 230.0942. $C_{14}H_{14}O_3$ requires M, 230.0943).

3a-Methyl-3a,4,9,9a-tetrahydronaphtho[2,3-c]furan-1,3-dione (**4ba**). M.p. 59 °C (from Et_2O); IR (KBr)/cm^{-1} 1870 and 1800; ^{1}H NMR (250 MHz) 1.56 (3 H, s), 2.67 (1 H, d, J = 15 Hz), 2.97 (1 H, dd, J = 15, 7 Hz), 3.12-3.21 (3 H, m) and 7.12-7.24 (4 H, m). (MS found: m/z 216.0786. $C_{13}H_{12}O_3$ requires M, 216.0786).

5-Methoxy-3a-methyl-3a,4,9,9a-tetrahydronaphtho[2,3-c]furan-1,3-dione (**4bb**) and 8-Methoxy-3a-methyl-3a,4,9,9a-tetrahydronaphtho[2,3-c]furan-1,3-dione (**5bb**). Flash chromatography (petroleum ether-dichloromethane, 1:4) gave a 1:1 mixture of regioisomers **4bb** and **5bb** with the following properties: IR (KBr)/cm^{-1} 1851 and 1776 (C=O of anhydride); ^{1}H NMR (250 MHz) 1.54 (3 H, s), 1.56 (3 H, s), 2.37 (1 H, d, J = 14 Hz), 2.63 (1 H, d, J = 14 Hz), 2.69 (1 H, dd, J = 15 Hz, 6 Hz), 2.92 (1 H, dd, J = 15, 7 Hz), 3.09-3.20 (4

H, m), 3.60 (1 H, dd, *J* = 15, 3 Hz), 3.62 (1 H, d, *J* = 15 Hz), 3.81 (3 H, s), 3.82 (3 H, s), 6.77-6.84 (4 H, m), and 7.16 (2 H, t, *J* = 8 Hz). (MS found *m/z* : 246.0890. $C_{14}H_{14}O_4$ requires *M*, 246.0892).

5,8-Dimethoxy-3a-methyl-3a,4,9,9a-tetrahydronaphtho[2,3-*c*]-furan-1,3-dione (**4bc**). Flash chromatography (petroleum ether-dichloromethane, 1:1) gave **4bc** as white crystals, m.p. 168-170 °C; IR (KBr)/cm^{-1} 1854 and 1786; ^{1}H NMR (250 MHz) 1.55 (3 H, s, Me), 2.38 (1 H, d, *J* = 15 Hz), 2.66 (1 H, dd, *J* = 15, 7 Hz), 3.12 (1 H, dd, *J* = 7, 4 Hz), 3.55 (1 H, d, *J* = 15 Hz), 3.58 (1 H, dd, *J* = 15, 4 Hz), 3.77 (3 H, s), 3.78 (3 H, s), 6.73 (2 H, s). (MS found *m/z* : 276.0998. $C_{15}H_{16}O_5$ requires *M*, 276.0998).

3a-Methyl-5-pivaloyloxy-3a,4,9,9a-tetrahydronaphtho[2,3-*c*]furan-1,3-dione (**4bd**) and 3a-Methyl-8-pivaloyloxy-3a,4,9,9a-tetrahydronaphtho[2,3-*c*]furan-1,3-dione (**5bd**). Flash chromatography (petroleum ether-dichloromethane, 3:1) gave a 1:1 mixture of regioisomers **4bd** and **5bd** with the following properties: IR (KBr)/cm^{-1} 1842, 1776 and 1745; ^{1}H NMR (250 MHz) 1.41 (18 H, s), 1.54 (3 H, s), 1.55 (3 H, s), 2.41 (1 H, d, *J* = 15 Hz), 2.69 (1 H, d, *J* = 15 Hz), 2.71 (1 H, dd, *J* = 14, 6 Hz), 2.92-3.03 (1 H, m), 3.10-3.24 (6 H, m), 6.96-6.84 (2 H, d, *J* = 8 Hz), 7.08 (2 H, t, *J* = 8 Hz) and 7.22 (2 H, 'd', *J* = 8 Hz). (MS found *m/z* : 316.1311. $C_{18}H_{20}O_5$ requires *M*, 316.1311).

3a,4-Dimethyl-3a,4,9,9a-tetrahydronaphtho[2,3-*c*]furan-1,3-dione (**4bg**) and 3a,9-Dimethyl-3a,4,9,9a-tetrahydronaphtho[2,3-*c*]furan-1,3-dione (**5bg**). Flash chromatography (petroleum ether-dichloromethane, 3:2) gave a 1:1 mixture of regioisomers **4bg** and **5bg** with the following properties: IR (KBr)/cm^{-1} 1845 and 1776; ^{1}H NMR (250 MHz) 1.53 (3 H, d, *J* = 7 Hz), 1.56 (3 H, s), 1.60 (3 H, s), 1.71 (3 H, d, *J* = 7 Hz), 2.68 (1 H, d, *J* = 15 Hz), 2.82 (1 H, dd, *J* = 14, 7 Hz), 2.97-3.27 (6 H, m) and 7.15-7.34 (8 H, m). (MS found *m/z* : 230.0943. $C_{14}H_{14}O_3$ requires *M*, 230.0943).

3a,4,9-Trimethyl-3a,4,9,9a-tetrahydronaphtho[2,3-*c*]furan-1,3-dione (**4bh**). Flash chromatography (petroleum ether-dichloromethane, 3:2) gave **4bh** as white crystals, m.p. 90-92 °C; IR (KBr)/cm^{-1} 1845 and 1775; ^{1}H NMR (250 MHz) 1.645 (3 H, d, *J* = 7 Hz), 1.65 (3 H, s), 1.75 (3 H, d, *J* = 7 Hz), 2.78 (1 H, q, *J* = 7Hz), 3.05 (1 H, d, *J* = 5 Hz), 3.12 (1 H, qd, *J* = 7, 5 Hz), and 7.25-7.33 (4 H, m). (MS found *m/z* : 244.1099. $C_{15}H_{16}O_3$ requires *M*, 244.1099).

3a,9a-Dimethyl-3a,4,9,9a-tetrahydronaphtho[2,3-*c*]furan-1,3-dione (**4ca**). M.p. 152-152 °C (from toluene); IR (KBr)/cm^{-1} 1840 and 1780; ^{1}H NMR (250 MHz) 1.46 (6 H, s), 2.69 (2 H, d, *J* = 14 Hz), 3.13 (2 H, d, *J* = 14 Hz) and 7.13-7.26 (4 H, m). (MS found *m/z* : 230.0943. $C_{14}H_{14}O_3$ requires *M*, 230.0943).

3a,9a-Dimethyl-5-methoxy-3a,4,9,9a-tetrahydronaphtho[2,3-*c*]furan-1,3-dione (**4cb**). Flash chromatography (petroleum ether-dichloromethane, 1:1), followed by recystallisation from ether gave **4cb** as white crystals, m. p. 146-147 °C; IR (KBr)/cm^{-1} 1843 and 1781; ^{1}H NMR (250 MHz) 1.45 (3 H, s), 1.47 (3 H, s), 2.37 (1 H, d, *J* = 15 Hz), 2.65 (1 H, d, *J* = 15 Hz), 3.10 (1 H, d, *J* = 15 Hz), 3.63 (1H, d, *J* = 15 Hz), 3.82 (3H, s, OMe), 6.77-6.80 (2H, m) and 7.16 (1H, t, *J* = 8Hz). (MS found *m/z* : 260.1089. $C_{15}H_{16}O_4$ requires *M*, 260.1049).

5,8-Dimethoxy-3a,9a-dimethyl-3a,4,9,9a-tetrahydronaphtho[2,3-*c*]furan-1,3-dione (**4cc**). M.p. 140-142 °C (from CH_2Cl_2); IR (KBr)/cm^{-1} 1814 and 1782; ^{1}H NMR (250 MHz) 1.45 (6 H, s), 2.34 (2 H, d, *J* = 15 Hz), 3.58 (2 H, d, *J* = 15 Hz), 3.77 (6 H, s) and 6.72 (2 H, s). (MS found *m/z* : 290.1154. $C_{16}H_{18}O_5$ requires *M*, 290.1154).

3a,4,9a-Trimethyl-3a,4,9,9a-tetrahydronaphtho[2,3-c]furan-1,3-dione (**4cg**). Flash chromatography (petroleum ether-dichloromethane, 2:3) gave **4cg** as white crystals, m.p. 116-118 °C; IR (KBr)/cm^{-1} 1872 and 1800; ^{1}H NMR (250 MHz) 1.46 (3 H, s), 1.47 (3 H, s), 1.60 (3 H, d, *J* = 7 Hz), 2.74 (1 H, d, *J* = 15 Hz), 2.76 (1 H, q, *J* = 7 Hz), 3.16 (1 H, d, *J* = 15 Hz) and 7.14-7.33 (4 H, m). (MS found *m/z* : 244.1099. $C_{15}H_{16}O_3$ requires *M*, 244.1099).

3a,4,9,9a-Tetramethyl-3a,4,9,9a-tetrahydronaphtho[2,3-*c*]furan-1,3-dione (**4ch**). Crystallisation from petroleum ether-dichloromethane gave **4ch** as white crystals, m.p. 174-175 °C; IR (KBr)/cm^{-1} 1846 and 1778; ^{1}H NMR (250 MHz) 1.49 (6 H, s), 1.66 (6 H, d, *J* = 7 Hz), 2.78 (2 H, q, *J* = 7Hz) and 7.24-7.32 (4 H, m). (MS found *m/z* : 258.1255. $C_{16}H_{18}O_3$ requires *M*, 258.1256).

5-Methoxy-3a-phenyl-3a,4,9,9a-tetrahydronaphtho[2,3-*c*]furan-1,3-dione (**4db**) and 8-Methoxy-3a-phenyl-3a,4,9,9a-tetrahydronaphtho[2,3-*c*]furan-1,3-dione (**5db**). Flash chromatography (petroleum ether-dichloromethane, 2:3) gave a 1:1 mixture of regioisomers **4db** and **5db** with the following properties: IR (KBr)/cm^{-1} 1846 and 1776; ^{1}H NMR (250 MHz) 2.78 (1 H, d, *J* = 15 Hz), 2.80 (1 H, dd, *J* = 15, 7 Hz), 3.05-3.15 (2 H, m), 3.32 (1 H, dd, *J* = 15, 3Hz), 3.47 (1 H, d, *J* = 15 Hz), 3.75-3.88 (3 H, m), 3.82 (3 H, s), 3.83 (3 H, s), 4.04 (1 H, d, *J* = 15 Hz), 6.81-6.86 (4 H, m) and 7.16-7.50 (12 H, m). (MS found *m/z*: 308.1055. $C_{19}H_{16}O_4$ requires 308.1049).

2-Phenyl-3a,4,9,9a-tetrahydronaphtho[2,3-*c*]pyrrole-1,3-dione (**7f**). M.p. 114-115 °C (from CH_2Cl_2); IR (KBr)/cm^{-1} 1775 and 1705; ^{1}H NMR (250 MHz) 2.94-3.03 (2 H, m), 3.24 (2 H, dd, *J* = 15, 3 Hz), 3.41-3.50 (2 H, m), 6.82 (2 H, dd, *J* = 8, 2 Hz) and 7.15-7.38 (7 H, m). (MS found *m/z* : 277.1102. $C_{18}H_{15}NO_2$ requires *M*, 277.1103).

2-Acetyl-1,2,3,4-tetrahydronaphthalene (**7g**). Flash chromatography (gradient from petroleum ether to dichloromethane) gave **7g** as an oil, (lit.,[17] oil); IR (film)/cm^{-1} 1709; ^{1}H NMR (80 MHz) 1.6-2.4 (5 H, m), 2.8-3.1(5 H, m) and 7.1-7.2 (4 H, m). The 2,4-dinitrophenylhydrazone of **7g** had m.p. 158 °C (lit.,[17] 157-158 °C).

Methyl 1,2,3,4-tetrahydronaphthalene-2-carboxylate (**7h**).[18] After flash chromatography (petroleum ether-dichloromethane, 3:1) **7h** was obtained as a yellow oil with the following properties: IR (KBr)/cm^{-1} 1736; ^{1}H NMR (80 MHz) 1.80-2.45 (2 H, m,), 2.88-3.15 (5 H, m,), 3.83 (3 H, s) and 7.20 (4 H, s).

Methyl 2-methyl-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**7i**). After flash chromatography (petroleum ether-dichloromethane, 3:1) **7i** was obtained as a yellow oil with the following properties: IR (KBr)/cm^{-1} 1732; ^{1}H NMR (250 MHz, $CDCl_3$) 1.27 (3 H, s,), 1.77 (1 H, dt, J = 13, 7 Hz), 2.16 (1 H, 'dt', J = 13, 7 Hz), 2.65 (1 H, d, J = 16 Hz), 2.82 (2 H, t, J = 7 Hz), 3.23 (1 H, d, J = 16 Hz), 3.65 (3 H, s) and 7.04-7.15 (4 H, m).

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