

Review Article

Selectivity in Electroreductive Carbon–Carbon Bond Forming Reactions: Redox Chemistry of Activated Alkenes, Quinonemethides and Quinodimethanes

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Dedicated to Professor Lennart Ebersson on the occasion of his 65th birthday

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Electroreductive carbon–carbon bond forming reactions are surveyed with emphasis on those which involve combination of radical-anions cathodically generated from electron-poor alkenes and from quinonemethides. Carbon–carbon bond forming reactions of quinodimethanes formed by 1,4-electroreductive elimination of halides are included. Recent advances in the understanding of the formation, characterisation and reactivity of these intermediates are described with special attention to chemical and stereoselectivity. Several general conclusions are drawn. Radical-anion/radical-anion combination is the rule for electrohydrodimerisation reactions, and the stereochemical consequences of the required orthogonal approach to the transition state are highlighted. The cathodic generation of *p*-quinodimethanes, either by direct reduction or via redox catalysis, is the basis of clean and convenient routes to poly-*p*-xylylenes (PPXs) and poly(*p*-phenylenevinylenes) (PPVs). Similar generation of *o*-quinodimethanes is mediated by easily reducible dienophiles which, when used *in situ*, participate in subsequent and preparatively useful cycloaddition.

Carbon–carbon bond-forming reactions are probably the single most important set of reactions in organic synthesis. It is not surprising, therefore, that the most significant and enduring electrosynthetic reactions are those in which carbon–carbon bonds are formed. The seminal importance of the (anodic) Kolbe reaction and of (cathodic) electrohydrodimerisation (EHD) is well established. Other prominent C–C bond-forming electro-organic reactions include the anodic formation of *N*-acyliminium cations which react with carbon nucleophiles, reductive alkylation and acylation, anodic coupling (e.g. of phenols), the anodic polymerisation of electron-rich arenes such as pyrroles and thiophenes, and the cathodic formation of polymers such as poly-*p*-phenylene (PPP), poly-*p*-xylylene (PPX) and poly(*p*-phenylenevinylene) (PPV).

This article is concerned entirely with reductive methods, especially types of electrosynthetic reaction for carbon–carbon bond formation, the review of which is

timely because their study is also giving new insights into mechanism and stereoselectivity. There is much relevant activity worldwide but this article is presented largely as an account of recent work from the Queen Mary (London) group, hopefully with adequate acknowledgement of that work from other groups which impinges on the topics covered. But I trust that those whose work may not have been included will appreciate the constraints on length for an article such as this.

1. Classification of electroreductive C–C bond-forming reactions and structure of the review

There are many plausible routes for carbon–carbon bond formation following cathodic reduction of an organic molecule. Almost all of them follow initial formation of a radical-anion. Most of the routes available are set out in Scheme 1 and some require special mention. Route A, usually described as the radical-anion/radical-anion

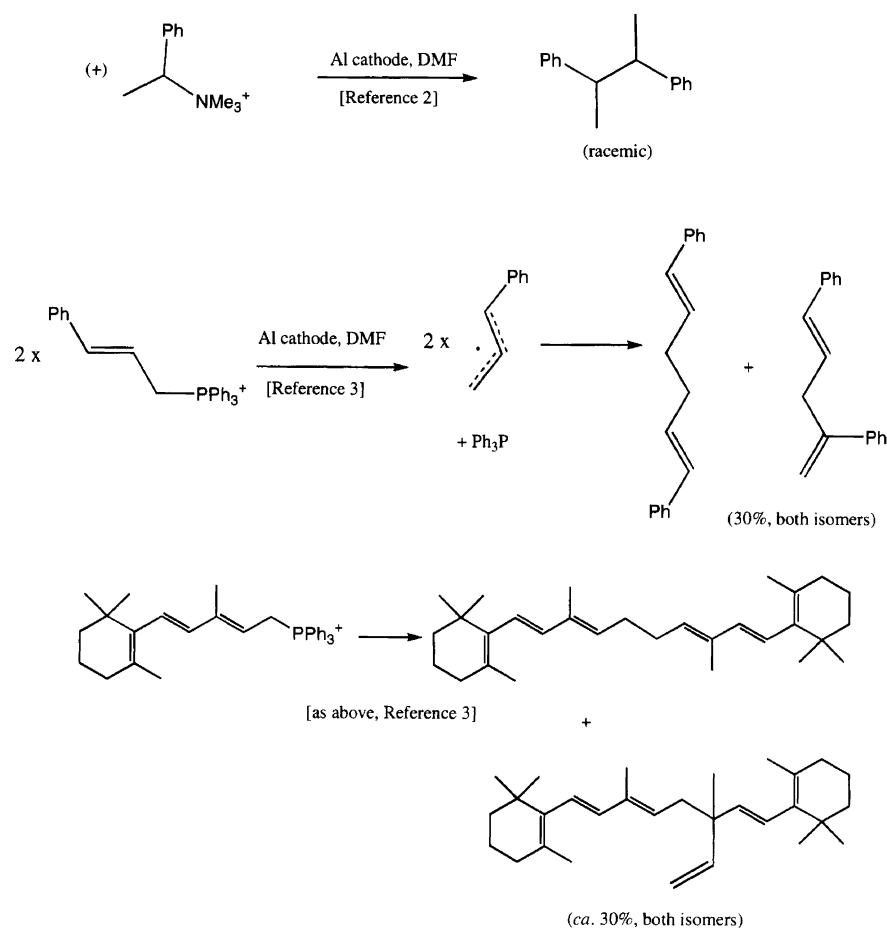


Fig. 1. Coupling via cathodically generated benzylic and allylic radicals.

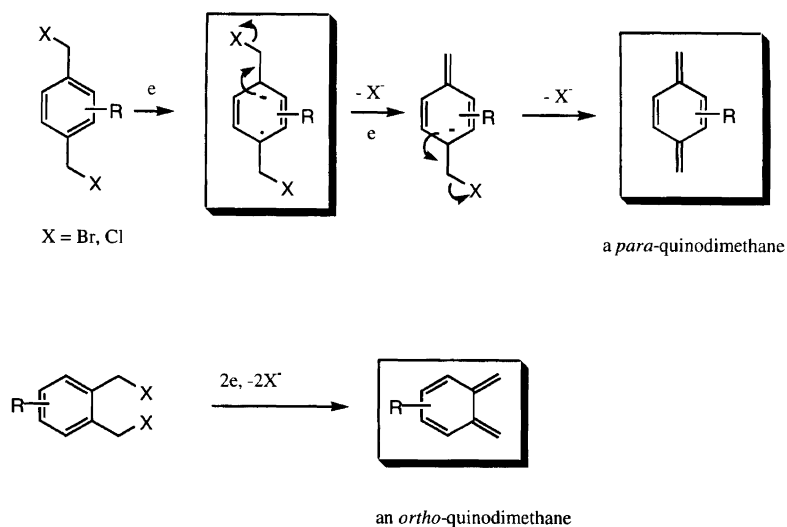


Fig. 2. Cathodic generation of quinodimethanes.

between the electrodes, and the journey time may be varied by varying the interelectrode distance. The relevant theory is in place⁸ and application to the EHD of acrylonitrile shows⁹ unambiguously second-order kinetics with respect to radical-anion and that the

radical-anions undergo very fast dimerisation [$k_2 = (6 \pm 3) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$]. One argument deployed against radical-anion/radical-anion coupling *vis à vis* the rival radical-anion/substrate hypothesis was that coulombic repulsion between radical-anions would be prohibitively

severe and nucleophilic addition to the neutral starting material would be favoured. The speed of the dimerisation of acrylonitrile radical-anions makes it difficult to maintain this argument.

However it is true that EHD reactions tend to be faster the more the charge is delocalised and it tempting to regard this as a lessening of coulombic forces. A qualitative example¹⁰ is the reaction of dimethyl maleate to give, eventually, butane 1,2,3,4-tetracarboxylic acid (Fig. 3a). However, this view is not entirely consistent with the observation¹¹ that dimethyl maleate radical-anions isomerise to the more stable fumarate radical-anions (at ca. 10 s^{-1}) which couple at ca. $34 \text{ M}^{-1} \text{ s}^{-1}$ whereas the maleate radical-anions (which are less stable and in which charge is presumably less well delocalised) couple much more quickly (ca. $4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$). It will become apparent that radical-anion dimerisations are quite sensitive to steric effects and it may be that in this case the orthogonal approach necessary for dimerisation of the fumarate radical-anions is hindered *vis à vis* that of maleate radical-anions. The rapid coupling of maleate radical-anions is presumably one reason why dimethyl maleate is the favoured starting material for production¹⁰ of butane 1,2,3,4-tetracarboxylic acid.

Several recent examples of preparatively interesting EHD and related reactions are collected together in Fig. 3, including the above example. In some cases they also form the basis for discussion of recent developments concerning our understanding of mechanism and stereoselectivity.

The EHD of esters of cinnamic acid has been much studied, partly because there were early indications that the reactions were highly stereoselective (Fig. 3b). In the event studies of these compounds have resulted in a comprehensive re-examination of likely routes for EHD and the outcome is of considerable general significance. The products of cathodic reduction of alkyl cinnamates were early recognised¹² to involve EHD followed by Dieckman condensation under the alkaline conditions of electrolysis. The products are exclusively the all-*trans* esters of (\pm)-5-oxo-2,3-diphenylcyclopentanecarboxylic acid (**2**) and their stereochemistry was firmly established¹³ by assignment of ^1H NMR coupling constants and later confirmed¹⁴ by X-ray crystallography. The further observation that chiral cinnamate esters (**1**) in Fig. 3b led to diastereoselectivity in the range 0–95% d.e. (Table 1) meant that these compounds were ideal substrates for a thorough mechanistic re-evaluation¹⁵ using both kinetic and stereochemical approaches.

The second-order rate constants for dimerisation¹⁵ of the radical-anions derived from the esters (**1**) cover a surprising range given that the changes in substitution are at the alkoxy oxygen. The slowest (*tert*-butyl cinnamate) reacts in DMF with $k_2 = 4 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$, for phenyl cinnamate $k_2 = 8 \times 10^3$ and the fastest dimerisation is for the radical-anion of 4-cyanophenyl cinnamate at $k_2 = 6 \times 10^4$. Furthermore the $\log k_2$ values correlate linearly with E° values for the esters. This is apparently

Table 1. Diastereoisomeric excesses in EHD products^a (**2**) from chiral cinnamates (**1**).

Starting chiral cinnamate	Diastereoisomeric excess, d.e. (%)	
	By ^1H NMR	By HPLC
Menthyl cinnamate	0	0.86
Ethyl <i>O</i> -cinnamoyllactate	33	32
Methyl <i>O</i> -cinnamoylmandelate	44	47
Isopropyl <i>O</i> -cinnamoylmandelate	40	41
<i>O</i> -Cinnamoyl- <i>N</i> -tosylephedrine	34	36
<i>O</i> -Cinnamoyl- <i>N</i> -methylephedrine	36 ^c	— ^b
<i>endo</i> -Bornyl cinnamate	(>95) ^d	(>95) ^d

^aElectrolysis in DMF–LiClO₄ (0.1 M). ^bNot separable by HPLC.

^cElectrolysis in DMF–TEAB (0.1 M). ^dOnly one diastereoisomer was isolated, in high yield (98%).

another manifestation of more stabilised radical-anions having enhanced rates of combination and the generality of this effect is discussed¹⁶ elsewhere.

From a mechanistic and stereochemical point of view the effect of small amounts of water in the DMF electrolyte is revealing.¹⁵ The dimerisation reactions of the cinnamate esters are slow enough to be easily measurable and, in cyclic voltammetry, reduction of the alkyl cinnamates is chemically reversible at 10 V s^{-1} . However, the energies of activation are small (ca. 11 kJ mol^{-1}) and the measured rates are approximately doubled on going from nominally dry DMF to DMF containing 0.28 M of water. The burden of evidence is therefore in favour of formation of relatively persistent radical-anions which complex reversibly with water; temperature changes will influence the position of the equilibrium and the rates of dimerisation in opposite ways, a classical explanation¹⁷ of anomalously low energies of activation. Furthermore the templating effect of water in the complex is the reason why the radical-anions are held in such a way that coupling at C-3 gives the (\pm) isomer rather than the *meso* isomer which would entail eclipsing of the phenyl groups (Fig. 4). The constraints in the transition state for combination of the templated radical-anions also provides the conditions for asymmetric induction under the influence of the chiral alkoxy groups.

In protic solvents EHD competes with the 2 F hydrogenation of the double bond. But a thorough investigation of the reduction of methyl cinnamate (**1**, R = Me) in methanol reveals that linear hydrodimers are amongst the products and that there is no discrimination between (\pm) and *meso* coupling at C-3. And, significantly, for reduction in MeOH *vis à vis* DMF the rates of reaction of the radical anions are increased by 2–3 orders of magnitude. The changes are rationalised¹⁸ in a mechanism which crucially involves, for methyl cinnamate, initial reduction of the substrate hydrogen-bonded at the carbonyl oxygen to MeOH to give the protonated radical-anion as the species which combines in the rate-determining step (see Fig. 4). But templating is not possible here

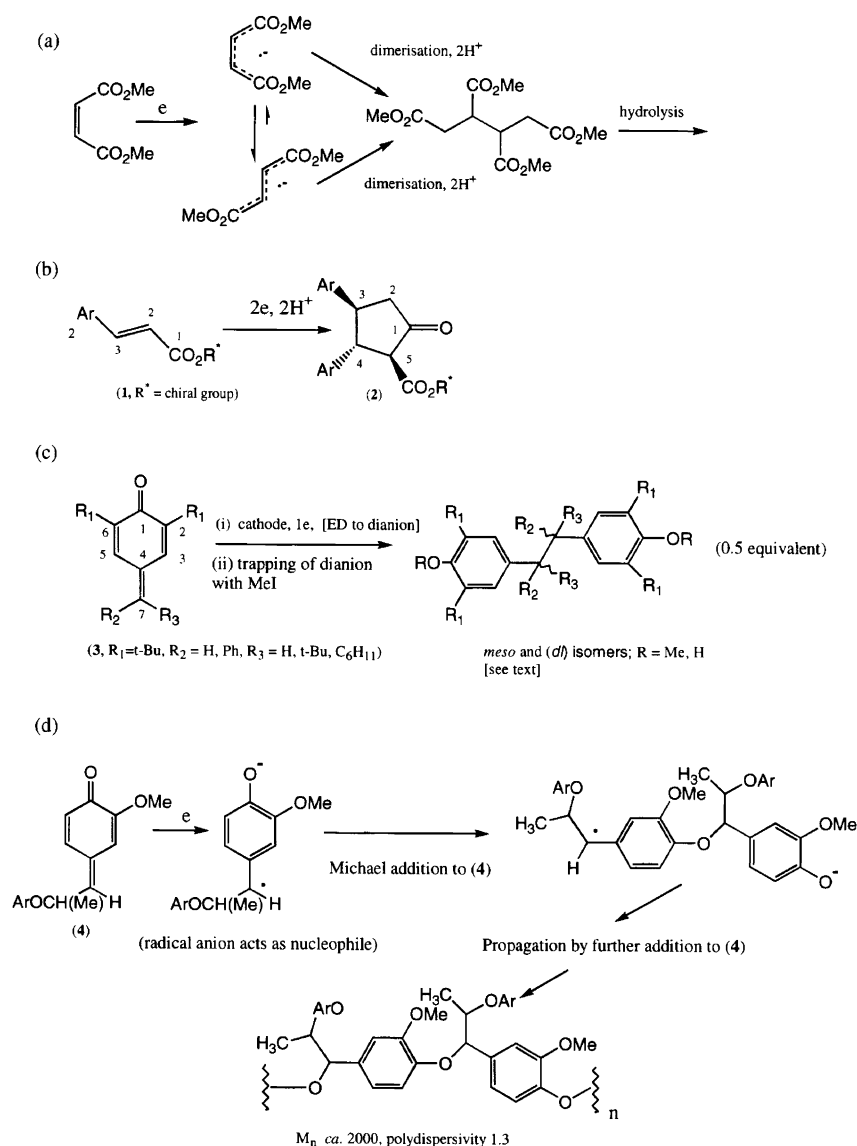


Fig. 3. Electrohydrodimerisation and related reactions (3a–3c) and cathodically induced polymerisation (3d).

and the reason for discrimination between the (\pm) and *meso* isomers is lost.

Although this discussion has been restricted to the electrochemical reactions of alkenes activated by ester functions almost any strongly electron-withdrawing function will activate alkenes and make them good candidates for electrohydrodimerisation. There could well be synthetic advantage in reversible activation of alkenes for EHD and this approach has been demonstrated¹⁹ but not exploited. The example is given in Fig. 5 and relates to reversible activation by the formation of arene–chromium tricarbonyl complexes. The $\text{Cr}(\text{CO})_3$ group is often held to have an electron-withdrawing effect similar to that of the nitro group. In the example given the reduction potential of stilbene is moved on complexation with $\text{Cr}(\text{CO})_3$ from $E_p = -1.80$ V to -1.22 V [quasi-reversible reduction in both cases, V vs. Ag/AgI at an Hg cathode in propylene carbonate– Bu_4NI (0.1 M) at 0.5 V s^{-1}].

Furthermore preparative-scale 1 F reduction proceeds cleanly as in Fig. 5, although a mixture of stereoisomers of the coupled product is obtained. Without activation by complexation with $\text{Cr}(\text{CO})_3$ stilbene undergoes cathodic hydrogenation.

An intriguing type of electrochemical dimerisation reaction is emerging which almost certainly proceeds via a radical-anion/substrate route although not the usual Michael addition variation in which a nucleophilic radical-anion is held to add to the starting material (Scheme 1, route B). Two examples are given in Fig. 6. They are similar in that formation of cyclobutane rings is the most interesting feature and that overall this does not represent reduction of the starting alkenes but cycloaddition! They differ in that the formation of the cyclobutane from the vinyl sulfone²⁰ is only initiated cathodically and there is no significant consumption of charge, whereas the reaction of 2-vinylpyridine²¹ can be

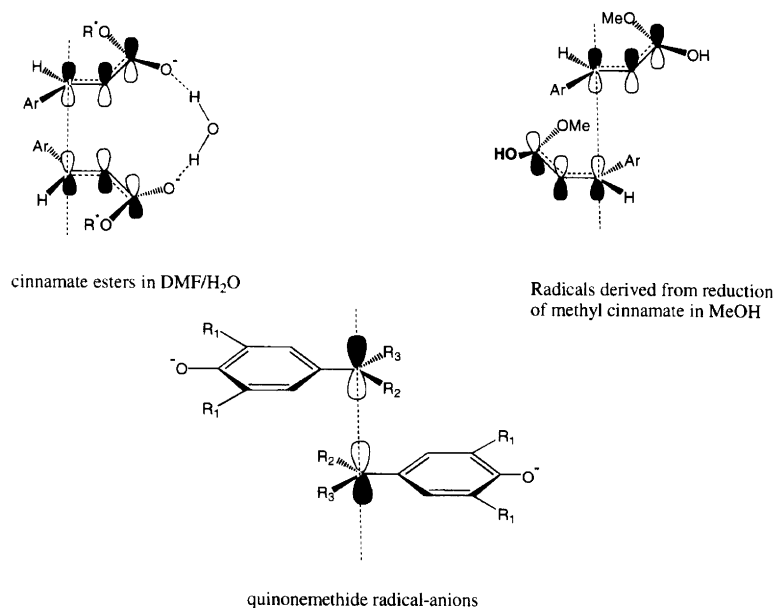


Fig. 4. Stereoelectronic control of key steps in examples of the coupling of radical-anions in electrohydrodimerisation reactions.

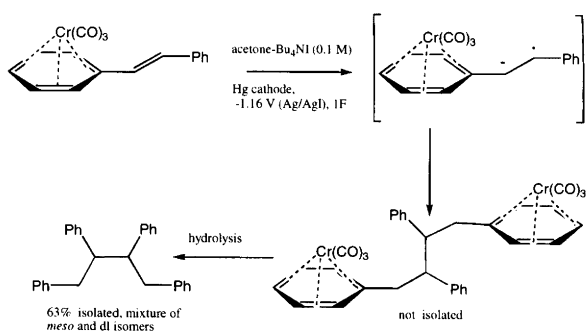


Fig. 5. Electrohydrodimerisation via reversible activation.

shown to consume 0.5 F in a reduction process which gives equivalent amounts of the 0 F cyclobutane derivative (**5**, R = H, structure proved by X-ray crystallography) and the 1 F linear hydrodimer (**6**). In an on-going study there is compelling evidence from the stereochemistry of cyclobutane products from compounds (**5**, R = alkyl) that a SOMO–LUMO cycloaddition is the key step. In the sulfone case it is likely that the cyclobutyl radical-anion formed in such cycloaddition is oxidised by the starting material, hence there is no charge consumption, whereas in the pyridine case disproportionation completes the reaction to give the product(s) **5** and the hydrodimer **6** which is at the 1e reduction level. Therefore 4 mol of starting material consume 2 F giving rise to one mole of the cyclobutane and one mole of **6**, giving a value of 0.5 F for the consumption of starting material. A thorough mechanistic and theoretical study of these reactions is needed but a likely reason for the operation of this route in these cases is that the initially formed cyclobutane radical-anion is considerably stabilised by delocalisation onto either sulfone substituents or

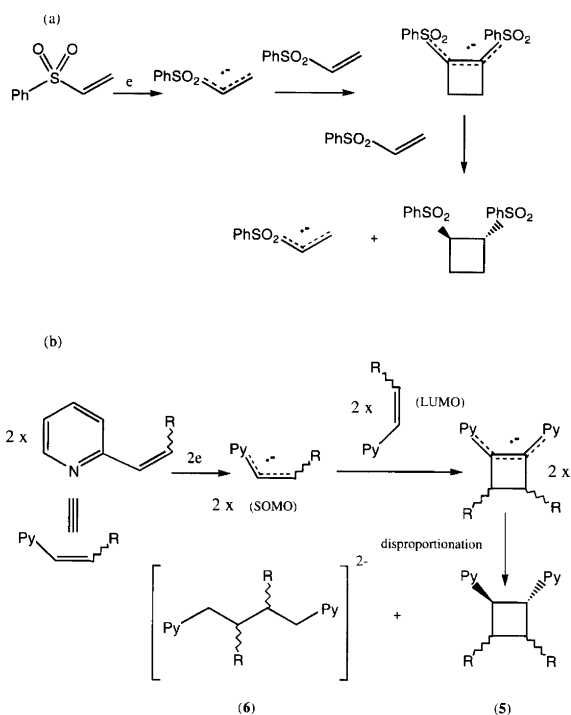


Fig. 6. Hydrodimerisation via radical-anion/substrate cycloaddition.

heteroaromatic rings, thus allowing sufficient time for oxidation or disproportionation. However, these factors could also operate in the electroreduction of other highly electron-deficient alkenes, and this prompts the intriguing possibility that these cycloadditions are common. The

Note added in proof: Careful coulometry now shows the cyclobutanes to arise exclusively from the 0 F catalytic chain route.

cyclobutanes formed from vinylpyridines and vinylquinolines are themselves easily reduced further to give²¹ the linear hydrodimers, so there is a possibility that cyclobutanes may be formed by cycloaddition in other cases but are never isolated because they are further reduced *in situ* to the EHD product. We must recall, however, that in the EHD of acrylonitrile the coupling step is cleanly second-order in radical-anion.⁹

2.2 Quinonemethides. Quinonemethides (**3**) in Fig. 3c are important intermediates in the redox chemistry of phenols and they are implicated as intermediates in both the biosynthesis and oxidative degradation of lignins. Indeed it is possible to produce²² highly regular polymers with lignin-like functionality by the base- or cathodically induced reaction of quinonemethides (Fig. 3d). In this case reaction proceeds by a succession of Michael additions, without significant consumption of charge, and is not a true electropolymerisation.

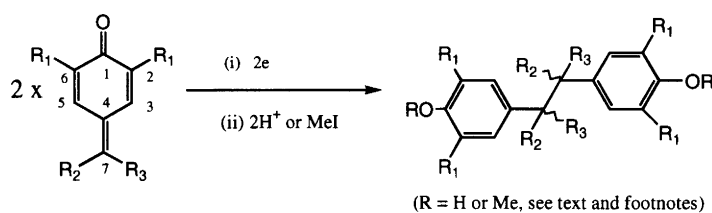
The rich redox chemistry of quinonemethides does, however, include interesting examples of cathodic dimerisation reactions including EHD. One is included in Fig 3, as 3c. The compounds of type **3** form persistent radical-anions where $R_2 = H$ and R_3 is bulky, e.g. Ph or *t*-Bu, but in the presence of an excess of methyl iodide dimerisation takes place.²³ Where $R_2 = R_3 = H$ reduction is chemically irreversible but, in the presence of methyl iodide, high yields of dimers are obtained. Trapping of the anionic products of radical-anion dimerisation by *O*-methylation is a convenient way of producing stable and easily isolated products. However, similar reactions in the absence of methyl iodide work and have been used in a preliminary study²⁴ of the kinetics and stereochemistry of quinonemethide EHD. Key results are collected in Table 2. The effect of steric hindrance to coupling is seen in the two rate constants given in the table: the

presence of a second substituent at C-7 considerably reduces the rate of dimerisation. Furthermore, the proportions of (\pm) to *meso* isomers in these dimerisations are comparable and indicate unselective coupling. This is consistent with the absence of possibilities for the templating effect proposed for the more selective coupling of cinnamate radical-anions in DMF containing small amounts of water.

2.3 The stereochemistry of radical-anion/radical-anion combination. This is a convenient point at which to discuss the manner in which radical-anions dimerise. The approach to the transition state must be orthogonal and in Fig. 4 are the relevant stereochemical arrangements for alkyl cinnamate coupling in DMF and of methyl cinnamate coupling in MeOH (see discussion above) compared with that for quinonemethide coupling. The sensitivity to steric hindrance can be seen from these diagrams; for the non-templated cases the transition state leading to the *meso* isomer is shown and where substituents at the reaction centre are small it is likely that this is the less strained transition state. A convincing example²⁵ of the importance of stereoelectronic factors in EHD reactions is the formation as the major product of the all-axial hydrodimer **8** in EHD of the activated cyclohexene **7**; the crucial axial-axial C-C bond formation occurs because of the stereoelectronic demands for coupling of the radical-anion of **7** – see Fig. 7. The methoxycarbonyl groups end up in axial positions following protonation under thermodynamic control. It turns out that, given the diaxial linking of the cyclohexane rings, axial ester groups are favoured.

Of more synthetic interest is the EHD-related coupling of the vinylquinonemethide **9**. These intermediates are relatively unstable but may be generated in an electrochemical cell by chemical oxidation of the corresponding

Table 2. Cyclic voltammetric^a data for quinonemethide reduction.



R_1	R_2	R_3	$-E^\circ$	$-E_{pc}(1)$	$-E_{pc}(2)$	$-E_{pa}(1)$	Rates of combination of radical anions ($10^{-4}k_2/M^{-1} s^{-1}$)
<i>t</i> -Bu	H	Ph	1.155 ^b	1.205 ^c	1.962 ^c	1.12 ^c	22.5 ^d
Me	H	Ph	—	1.073	1.789	—	—
<i>t</i> -Bu	C ₆ H ₁₁	Ph	1.397	1.436	—	1.359	ca. 5
<i>t</i> -Bu	H	<i>t</i> -Bu	—	1.468 ^f	—	—	—
<i>t</i> -Bu	<i>t</i> -Bu	Ph	1.387 ^e	1.428	1.848	1.348	—
<i>t</i> -Bu	Ph	Ph	1.130	—	—	—	—

^aHg/Pt cathode, DMF-Bu₄NPF₆ (0.1 M), potentials vs. SCE, substrate 2 mM, $v = 0.3 \text{ V s}^{-1}$. ^b $v = 100 \text{ V s}^{-1}$. ^c $v = 9 \text{ V s}^{-1}$. ^dYield of hydrodimer = 80% (R = Me), *meso*: (\pm) ratio = 2 (R = Me) and 1 (R = H). ^e $v = 1 \text{ V s}^{-1}$. ^fQuasi-reversible at 100 V s^{-1} .

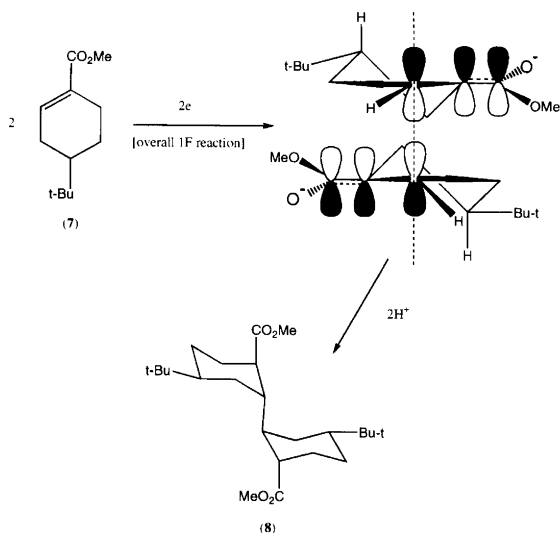


Fig. 7. Stereoelectronic control of coupling of radical-anions of methyl 4-*tert*-butylcyclohex-1-ene-1-carboxylate (**7**)

phenol for *in situ* electrolysis,²⁶ as in Fig. 8. This forms a useful, short route to an analogue (**10**, R = MeO) of ocimin (**10**, R = H), a novel neolignan extracted²⁷ from *ocimum americanum* (basil). In this case the susceptibility of electrodimersation to steric hindrance is an advantage because potentially competitive coupling at C-7/C-7 and C-7/C-9 is not observed, coupling appears to be exclusively, as required, at C-9/C-9, the least hindered option.

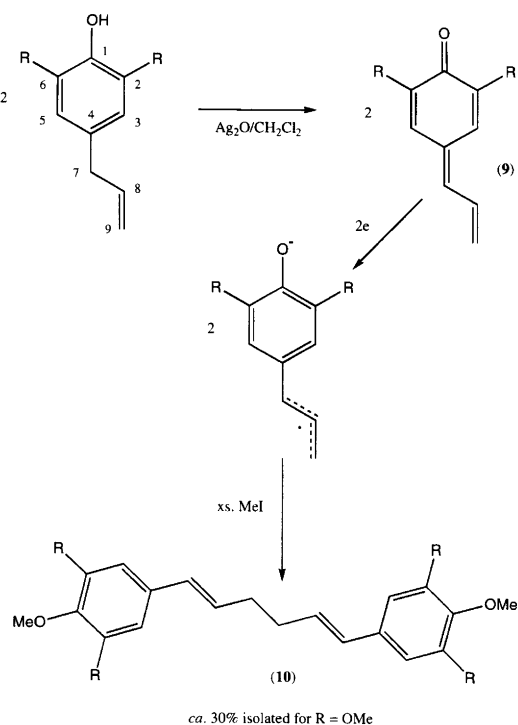


Fig. 8. Reductive dimerisation of a vinylquinonemethide in the preparation of an ocimin analogue (see the text).

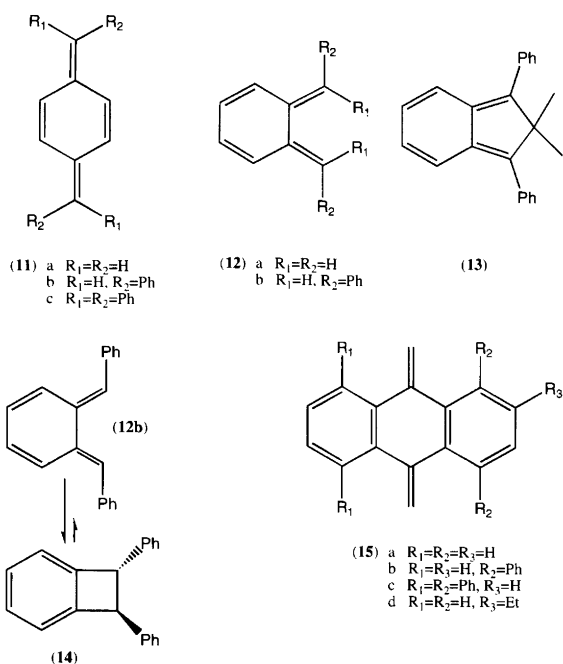


Fig. 9. Quinodimethanes generated by electroreduction of corresponding bis(halomethyl)arenes (see also Table 3).

2.4 Quinodimethanes.

2.4.1 Characterisation. The cathodic generation of *ortho*- and *para*-quinodimethanes from 1,2- and 1,4-bis(halomethyl)arenes has been outlined in Fig. 2. Covitz concluded⁶ quite correctly that the polyxylylene polymers he obtained were evidence of the intermediacy of quinodimethanes; these polymers are also obtained in pyrolysis reactions known to produce quinodimethanes. Direct evidence for their formation comes, in the *ortho* cases, from trapping by Diels–Alder reactions in the presence of dienophiles. This is a synthetically convenient procedure and also mechanistically significant. It is discussed in detail in a subsequent section.

Cyclic voltammetry of 1,2- and 1,4-bis(halomethyl)arenes has proved to be in many cases a method not only for observing quinodimethane formation but for measuring their reduction potentials.²⁸ Several examples of quinodimethanes which have been observed in voltammetric experiments are presented in Fig. 9 and the relevant data are collected in Table 3. Even the parent quinodimethanes **11a** and **12a** are sufficiently long-lived to allow measurement of their reduction potentials although reduction is chemically irreversible at up to 100 V s^{-1} . For many of the examples given reduction may be chemically reversible at less than 100 V s^{-1} and consequently formal reduction potentials (E° values) are measurable. Presumably the driving force for reduction of the quinodimethanes is affected by the restoration of the aromatic ring in the radical-anions formed. Thus they are relatively easily reduced and can be considered to be part of a structural sequence ranging from quinones to quinodimethanes (Fig. 10).

Table 3. Reduction potentials of electrogenerated quinodimethanes.

Quinodimethane	$-E^\circ$ (V vs. SCE) ^a	Comments
11a	[1.93] ^b	Polymerises on preparative electrolysis
11b	1.495 ^c	Thiele's hydrocarbon Polymerises on preparative electrolysis, but reacts with added dienophiles
11c	1.493	
12a	[1.74] ^b	
12b	—	Rapid intramolecular cyclisation to give 14
13	1.470	Polymerises to pentamer on preparative electrolysis
15a	1.974	
15b	1.977	
15c	1.976	
15d	2.018	

^aBy cyclic voltammetry of the corresponding bis(halomethyl)arenes in DMF–Bu₄NPF₆ (0.1 M) at an Hg/Pt electrode. ^bNot chemically reversible at up to 100 V s⁻¹, therefore peak potential at 1 V s⁻¹. ^cAt 100 V s⁻¹.

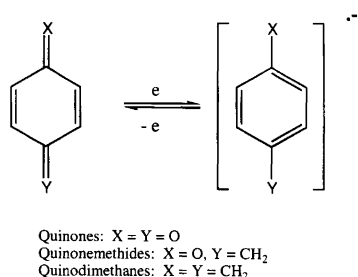


Fig. 10. The relationship between quinones, quinonemethides and quinodimethanes.

The similarity of E° values for the quinodimethanes **11b** and **11c** is explained by the inability of the extra phenyl group in the radical-anion of **11c** to accept delocalised spin or charge because it cannot achieve planarity in a species that is analogous to a triphenylmethyl radical (or anion!). Similarly the phenyl groups in the anthracene-9,10-quinodimethanes **15b** and **15c** are prevented from becoming coplanar by steric hindrance at the *peri* positions. In most cases the bis(bromomethyl)arenes are required as starting materials – the quinodimethane reductions take place at more negative potentials than required for halide cleavage and elimination. However, for the anthracene intermediates the corresponding chlorides may be used. The generation of **11b** was found to be possible by continuous sweeping to the foot of the reduction peak for the precursor 1,4-bis(chloromethyl)arene. This was interpreted in terms of the radical-anion thus generated, probably by reduction of the quinodimethane product **11b**, being sufficiently persistent to promote mediated electrolysis in these systems by catalysing further cleavage of the more difficult to reduce chloro compound. This approach to quinodimethane

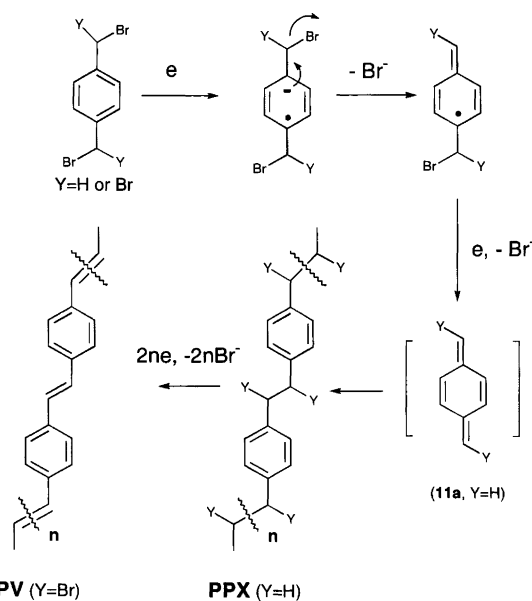


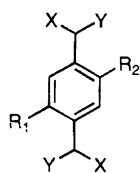
Fig. 11. Linear polymers via electrogenerated quinodimethanes.

dimethane production is elaborated upon elsewhere (section 2.4.3).

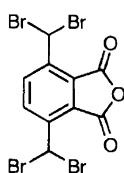
2.4.2 Electropolymerisation via quinodimethanes. The polymerisation of thermally generated *para*-quinodimethanes to give poly-*p*-xylylenes (PPXs) is a commercial process. The polymers are valuable coating materials and they are normally deposited directly onto surfaces. The electrochemical approach, summarised in Fig. 11, proved to be not only versatile but also capable of producing materials soluble in organic solvents²⁹ and also, using bis(dihalomethyl)arenes, of leading to the poly(*p*-phenylenevinylens) (PPVs).³⁰ These may be doped to give conducting polymers and they are also key materials for the development of electrochemiluminescent devices.

The major advantages of the cathodic method here are: (i) a considerable range of nuclear substituents may be tolerated in the starting materials; (ii) the use of a stirred mercury pool cathode means that as polymer is formed it does not foul the electrode and stop electrolysis; and (iii) the polymers formed are linear and highly regular. Their structural characterisation^{29,30} was by ¹³C NMR (solution and solid-state), ¹H NMR where appropriate in solution, thermal analysis and direct pyrolysis mass spectrometry. Because conditions may be manipulated to give good proportions of polymers soluble in the electrolyte (DMF) many of these reactions can also be carried out at a suitable solid electrode material such as lead. A representative sample of the considerable variety of precursors for this electropolymerisation is given as formulae **16–28** and details concerning their reduction and the products are listed in Table 4.

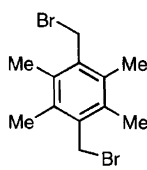
The availability of soluble PPXs allowed an interesting test of the chemical reactivity of the electrogenerated quinodimethanes. Co-electrolysis of equivalent amounts



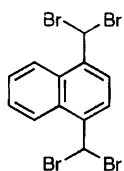
- (16) X=H, Y=Br, R₁=H, R₂=OCOMe
 (17) X=Y=Br, R₁=H, R₂=OCOMe
 (18) X=H, Y=Br, R₁=R₂=H
 (19) X=Y=Br, R₁=R₂=H
 (20) X=Y=Br, R₁=H, R₂=CO₂Me
 (21) X=H, Y=Cl, R₁=R₂=OMe
 (22) X=Y=Br, R₁=H, R₂=OMe
 (23) X=Y=Br, R₁=R₂=OMe
 (24) X=Cl, Y=Br, R₁=R₂=OMe



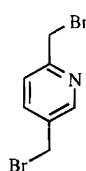
(25)



(27)



(26)



(28)

Table 4. Electrogeneration^a of polyxylylene (PPX) and poly(*p*-phenylenevinylene) (PPV) polymers (see Fig. 10).

Precursor	$-E_{\text{red}}$	Yield of PPX or PPV (%)	Soluble fraction (%)
16	1.50	78 (PPX)	—
17	1.03	95 (PPV)	42
18	1.30	90 (PPX)	—
19	1.25	80 (PPV)	37
20	1.03	37 (PPV)	0
21	1.70	60 (PPX)	—
22	1.60	89 (PPV)	37
23	1.70	82 (PPV)	56
24	1.80	82 (PPV)	38
25	0.70	92 (PPV)	10
26	1.30	62 (PPV)	0
27	0.85	80 (PPX)	—
28	1.50	76 (PPX)	—

^aDivided cell, Hg pool cathode, DMF-Et₄NBr (0.1 M), electrolysis to ca. 2 or 4 F as appropriate, V vs. Ag/AgBr.

of two different starting materials, e.g. 1,4-bis(bromomethyl)benzene (**18**) and 2,5-bis(bromomethyl)pyridine (**28**), gave a true co-polymer in which the units were combined statistically. This implies radical-like reactivity which was confirmed by cathodic polymerisation from 2-acetoxy-1,4-bis(bromomethyl)benzene (**16**). The key experiment is described in Fig. 12; the polymer product

was soluble in organic solvents, and examination by ¹H NMR spectroscopy showed that the C–C bond formation was entirely statistical, rather reminiscent of the cross-coupling found for Kolbe electrolyses. One application of this reactivity is that co-electrolysis of different bis(halomethyl)arenes gives random co-polymers derived from cross-coupling of the different quinodimethanes formed.

2.4.3 Mediated generation of quinodimethanes. *ortho*-Quinodimethanes are much used in organic synthesis as dienes in cycloaddition reactions, notably the Diels–Alder reaction. There is a considerable driving force for this reaction because aromaticity is restored by cycloaddition. One of the early examples, which was intended to be a straightforward trapping of an electrogenerated *o*-quinodimethane, is given in Fig. 13. The Diels–Alder adduct was indeed produced in excellent yield from co-electrolysis^{31,32} of the precursor compound **29** and maleic anhydride. But the reduction potential of the maleic anhydride was higher (less cathodic) by several hundreds of millivolts than that required for direct reduction of 1,2-bis(bromomethyl)benzene, **29**. Furthermore, it was shown³² by cyclic voltammetry that the dienophile 2,3-dimethylmaleic anhydride was reversibly reduced at relatively low scan rates and that addition of the less easily reduced **29** caused reduction to become irreversible with a considerable rise in cathodic peak current (much more than a doubling). This behaviour is characteristic of redox catalysis and is compelling evidence that the dienophile plays the dual role of mediator for the formation of *o*-quinodimethane and reactant with it.

The scope of this reaction has been explored³³ and the dienophile/mediator role is not confined to maleic anhydride derivatives. Quinones also may be used providing that their reduction potentials are sufficiently close to those of the 1,2-bis(bromomethyl)benzene. Table 5 lists some relevant potentials and these data are linked to details of the preparative-scale reductions and associated Diels–Alder reactions displayed in Fig. 14. In most cases the yields are high (48–98%) and the procedure is more convenient (and cleaner) than the competing method of zinc-induced reduction. The products and their stereochemistry are as expected and, where comparison is possible, identical with those obtained by zinc-induced formation of the *o*-quinodimethane, for instance a single stereoisomer of the adduct **38** was obtained by both the electrochemical and zinc-dust method in the reaction depicted in Fig. 15.

It is conceivable that these reactions proceed in a manner analogous to the cathodic reduction of vinylpyridines and vinylquinolines, which involved cycloaddition between radical-anions and neutral starting materials. This suggests that the dienophile radical-anions (SOMO) react with the quinodimethanes (LUMO) in the propagating step. But with the evidence to hand, especially the parallels with the known reactivity in thermal cycloadditions of *o*-quinodimethanes and the dienophiles con-

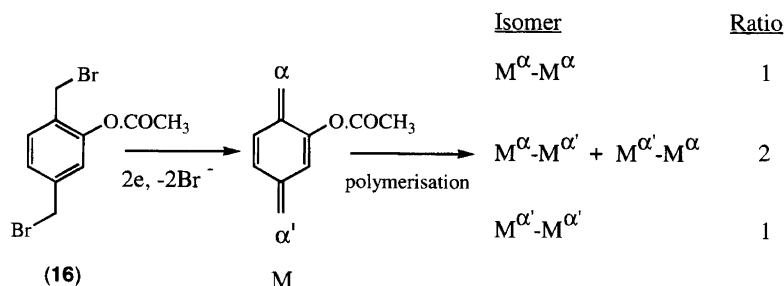


Fig. 12. Statistical combination of electrogenerated quinodimethanes.

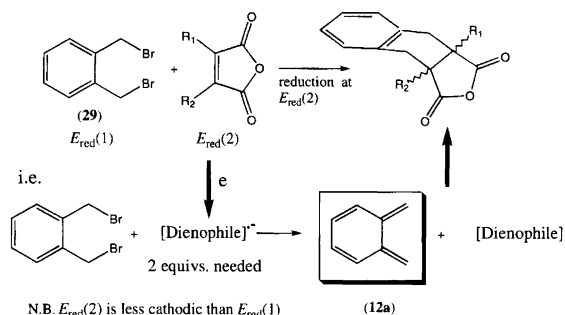


Fig. 13. Redox-catalysed electrogeneration of *o*-quinodimethanes combined with cycloaddition.

Table 5. Reduction potentials:^a dienophiles cf. precursor **29** and reaction yields.

Dienophile (see Fig. 14)	$-E^\circ$ (V vs. SCE)	Diels-Adduct (% yield)
29	1.38 ^b	—
30	1.01	78
31	1.04	98
32	0.86 ^b	83
33	2.00 ^c	48
34	0.84	58
35	0.99	78
36	1.13	87
37	0.54	43

^aBy cyclic voltammetry at 1–500 V s⁻¹, Hg/Pt electrode, DMF–Bu₄NPF₆ (0.1 M). ^bIrreversible reduction, therefore the peak potential measured. ^cDienophile reduction potential more negative than that of precursor **29** therefore quinodimethane presumably formed by direct reduction.

cerned, Occam's Razor must prevail. The simplest explanation accounting for the facts is that given in Fig. 13.

3. Further aspects of mediated electrogeneration of quinodimethanes

Most of the useful examples of electrogeneration of quinodimethanes discussed so far involve 1,2- or 1,4-reductive elimination of dibromides. In several cases the benzylic bromides concerned are labile and lachrymatory. Also, bromo-compounds are more expensive than the corresponding chloro-compounds. The use of chloro-derivatives in direct reduction is problematical because

they reduce at potentials negative of the reduction potentials of the quinodimethanes produced. Consequently the quinodimethanes are rapidly further reduced before they can undergo other useful reactions. Mediated electrolysis offers a solution to this difficulty. A systematic examination³⁴ of conventional redox mediators, i.e. compounds which form relatively persistent radical-anions known to engage in electron transfer, allowed the selection of mediators capable of catalysing the formation of PPX polymers from 1,4- and 1,2-bis(dichloromethyl)arenes. High yields (>70%) of polymers have been obtained using as redox mediators compounds such as benzophenone, fluorenone, polycyclic aromatic hydrocarbons, the radical-anions of which engage in outer-sphere electron transfer. Transition metal co-ordination complexes of Cr, Ni or Co can also be used³⁴ as mediators but in these cases both outer-sphere and inner-sphere electron transfer is possible. Poly-*p*-phenylene (PPP) is produced³⁵ by nickel complex-catalysed cathodic reduction of 1,4-dibromobenzene and there are many examples of the use of nickel complexes to effect coupling of aryl halides.³⁶

Mechanistically, however, there is an ambiguity concerning the use of metal complexes. In some cases they act, in a reduced form, as electron transfer agents and in cyclic voltammetry the characteristic behaviour, with the production of a catalytic wave, is observed. However, it is well established³⁷ that some electroreductive couplings catalysed by metal complexes, e.g. of bromobenzene to give biphenyl in the presence of L₂Ni^{II}Cl₂, take place with the crucial intermediacy of a species [Ar₂Ni^{III}BrL₂] formed by oxidative addition. Oxidative addition of benzyl halides to nickel complexes has also been well demonstrated³⁸ with, in one case,^{38b} formation of bibenzyl.

There is very strong evidence³⁹ that a similar mechanism is responsible for the efficient formation (98%) of poly-*p*-xylylene (PPX) and, with lower yield, of its *ortho*-analogue by co-electrolysis of the relevant bis(dichloromethyl)benzenes in the presence of L₂Ni^{II}Cl₂, [L₂ = Ph₂P(CH₂)_nPPh₂, dppe, *n* = 2; or dppp, *n* = 3]. The proposed mechanism is given in Fig. 16. Key evidence in its favour comes from a detailed comparison of the above route to PPX with the conversion, by the same method, of benzyl chloride (which cannot form a quinodimethane) into bibenzyl. A complete reaction profile has been

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