Electro-organic Reactions. Part III.† Mechanistic Aspects of the Cathodic Hydrogenation of Activated Carbon–Carbon Double Bonds

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Mechanisms have been elucidated for the cathodic reduction of compounds of the type Ph(R)C:C(CN)X (R = H, Me, Bu^t, or Ph; X = CN or CO_2Et), methyl phenanthrene-9-carboxylate, and methyl 10-methylphenanthrene-9-carboxylate. Cyclic voltammetry in aprotic solvents and e.s.r. spectroscopy have been used to show that, except for R = H or Me, reversible one-electron reduction to a radical-anion is followed at more cathodic potentials by further irreversible reduction to a dianion. In the presence of an added proton donor two-electron cathodic hydrogenation of the carbon–carbon double bond is observed in the region of the first reduction peak potential. The relative effectiveness of a variety of proton donors is discussed on the basis of cyclic voltammetric results. For compounds with R = H or Me irreversible one-electron reduction with dimerisation is observed even with an added proton source. Rapid dimerisation of the radical-anions is proposed.

THERE has been much empirical study of the cathodic reduction of multiple bonds and recently stereoselective reduction of such functions has been realised.[1-3] A useful understanding of key factors governing such stereoselectivity required the study of model compounds that are in principle reducible to stereoisomeric products and that are suitable for detailed mechanistic investigation.

Stereoselectivity in reduction could in principle result from the following pathways: (i) by an adsorption process which could include (*a*) reaction of an intermediate adsorbed in a preferred conformation, (*b*) electron transfer at an asymmetric electrode environment, and (*c*) electron transfer to or from diastereoisomeric complexes formed in bulk solution (*e.g.* between an asymmetrical electrolyte and the substrate); (ii) by the formation at the electrode of an intermediate (*e.g.* carbanions, organometallic compounds) in a preferred conformation which is preserved in bulk solution; or (iii) by the formation of an intermediate ($M^{\cdot}$, M^-, $M^{\dot{-}}$) with subsequent stereoselective reaction with an asymmetric proton donor or radical transfer reagent.

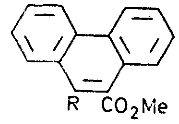
Horner and his co-workers[1] have achieved moderate optical yields of reduction products in the cathodic reduction of carbon–oxygen and carbon–nitrogen double bonds in the presence of chiral alkaloids, tertiary amines, and quaternary ammonium salts. The results have been rationalised in terms of pathway (i)(*b*). Similarly Gileadi and his co-workers[2] have achieved a relatively high (17%) optical yield of 1-phenylethanol from the reduction of acetophenone in the presence of pre-reduced quinidine sulphate. In this case independent electrochemical evidence is given for the adsorption of quinidine (but not for the unknown products of the essential pre-reduction). In addition the low concentrations of quinidine (*ca.* 10^{-3}M) which lead to asymmetric induction are taken as evidence that the key interaction is near to the electrode surface where the effective concentration of chiral species is high. Such studies leave unresolved the question of which of the pathways (i)(*b*), (i)(*c*), or (iii) are involved. Grimshaw and his co-workers,[3] for the cathodic asymmetric reduction of substituted coumarins to optically active dihydrocoumarins, have invoked pathway (iii) in which it is proposed that reduction of a chiral trialkylammonium ion (*e.g.* an alkaloid salt) leads to a chiral hydrogen transfer agent ($R^1R^2R^3N^{\cdot}H$).

We have chosen to study the cathodic hydrogenation of the series of compounds (1) and (2). Such compounds might be expected to be good models for a mechanistic study because (*a*) reduction is likely to be smooth and efficient at potentials that are low and well clear of competing electrode processes, (*b*) it follows that the effectiveness of proton donors, including optically active ones, could be defined [thus commenting on pathway (iii)], and (*c*) the mechanism is likely to be amenable to study by voltammetric methods.

Ph(R)C:C(X)CN

(1)

a; R = Ph, X = CN
b; R = Bu^t, X = CN
c; R = Me, X = CN
d; R = H, X = CN
e; R = Ph, X = CO_2Et
f; R = Me, X = CO_2Et



(2)

a; R = H
b; R = Me

Much previous work on the cathodic reduction of other activated olefins related to (1) has been concerned with hydrodimerisation and cathodic hydrogenation is usually regarded as an undesirable competing reaction.[4] The complications resulting from the reduction, by catalytic hydrogenation or chemical reagents, of alkenes which are hindered or substituted with other reducible groups highlight the preparative implications of the study herein reported.

RESULTS AND DISCUSSION

The cyclic voltammetric behaviour typical of the compounds under study is exemplified in Figure 1.

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† Part II, J. P. Coleman, R. Lines, J. H. P. Utley, and B. C. L. Weedon, *J.C.S. Perkin II*, 1974, 1064.

[1] L. Horner, *et al.*, *Chem. Eng. Tech.*, 1972, **44**, 209; *Tetrahedron Letters*, 1971, 1241, 1245; 1970, 1103, 2803, 2679; 1968, 5889.

[2] E. Kariv, H. A. Terni, and E. Gileadi, *Electrochim. Acta*, 1973, **18**, 433.

[3] R. N. Gourley, J. Grimshaw, and P. G. Millar, *J. Chem. Soc.* (*C*), 1970, 2318.

[4] 'Organic Electrochemistry,' ed. M. M. Baizer, Marcel Dekker, New York, 1973, pp. 679 *et seq.*

It is convenient to discuss the results according to the reversible (A) or essentially irreversible (B) nature of the one-electron reduction observed in the absence of added proton donor. As a qualification of this division it should be noted that at high sweep speeds (30—100 V s^{-1}) some degree of reversibility is observed even for compounds in category B.

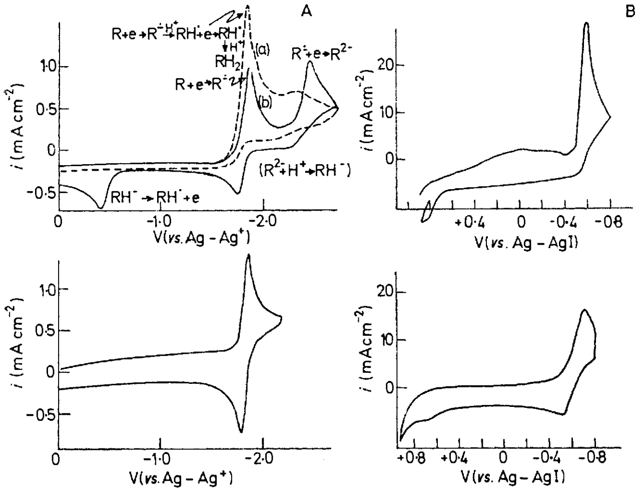

FIGURE 1 Cyclic voltammograms: A, $Ph_2C{:}C(CN)_2$ (5 mM), propylene carbonate, Et_4NBF_4 (0·25M), vitreous carbon cathode, 0·3 V s^{-1}; B, $Ph(Me)C{:}C(CN)_2$ (6 mM), DMF, Bu_4NI (0·1M), vitreous carbon cathode, 0·1 V s^{-1} (top), 100 V s^{-1} (bottom)

For each compound studied the type of behaviour and relevant electrochemical parameters are summarised in Table 1.

TABLE 1

Cyclic voltammetric parameters

Compound	Type of behaviour	Peak potentials (V) $(R_1)E_c^2$	$(R_2)E_c^2$	$(O_1)E_a^1$	$(O_2)E_a^2$	$E - E_{\frac{1}{2}}$
(1a)	A [a]	−1·81	−2·38	−1·75	−0·39	0·058
(1a)	A [b]	−0·45	−1·19	−0·39	*c*	0·060
(1e)	A [a]	−1·91	−2·33	−1·85	−0·41	0·059
(1e)	A [b]	−0·56	−1·16	−0·49	*c*	0·060
(1f)	B [a]	−2·13			−0·53	0·048
(Same for *E*- and *Z*-isomers)						
(1f)	B [b,d]	−0·82	−1·40		+0·73	0·060
(1b)	A [b]	−0·85	−1·28	−0·79	+0·84	0·058
(1c)	B [b]	−0·59			+0·84	0·045
(1d)	B [b]	−0·48			+0·64	0·052
(2a)	A [b]	−1·26	−1·88	−1·20	0	0·056
(2b)	A [b]	−1·55	−1·89	−1·45	+0·07	0·070

[a] Vitreous carbon cathode, propylene carbonate, Et_4NBF_4 (0·25M), 0·3 V s^{-1}, ref. electrode Ag–Ag$^+$. [b] Vitreous carbon cathode, dimethylformamide, Bu_4NI (0·1M), 0·1 V s^{-1}, ref. electrode Ag–AgI. [c] Buried under I$^-$ oxidation peak. [d] Dropwise addition of acetic acid caused the suppression of the second cathodic peak (E_c^2) and the second anodic peak (E_a^2) and a consequent increase (*ca.* 50%) in the peak current associated with E_c^1.

Reversible Reduction (Type A): Electrochemical Reversibility.—For the first process (R_1–O_1) the ΔE_p and $E_p - E_{\frac{1}{2}}$ values of *ca.* 60 mV compare well with the theoretical value of 58 mV for a perfectly reversible one-electron process.[5] Furthermore plots of peak current (i_p) against $\nu^{\frac{1}{2}}$ (ν = sweep speed) are linear over a wide range of sweep speeds (typically 0·01—1·0 V s^{-1}) and the peak potentials were constant throughout this range.

The radical-anions. The formation at the microelectrode (Hg or vitreous C) of an intensely red-coloured intermediate was observed as the first reduction peak potential (R_1) was approached and the colour persisted until the onset of the second electron transfer. This observation, together with the general form of the voltammetric results, suggests the initial formation of a radical-anion by one-electron transfer. Confirmation of this comes from the measurement and analysis of the e.s.r. spectrum of the radical-anion of compound (1a) (Figure 2). The spectrum was obtained by *in situ* electrochemical generation at constant current under conditions which correspond to electrolysis at the first wave. Analysis of the spectrum * led to a value of a_N of 3·8 G, which corresponds to a spin density at nitrogen, ρ_N, of *ca.* 0·14 (assuming that $\rho_N = a_N/Q$ with Q 27 G).[6]

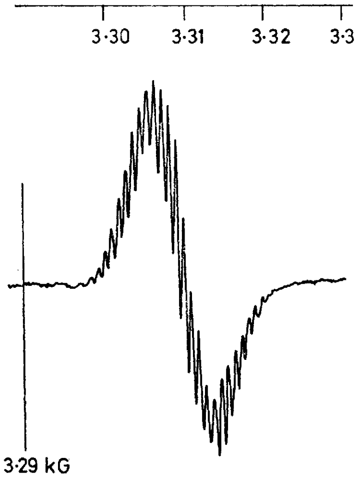

FIGURE 2 E.s.r. spectrum of $Ph_2C{:}C(CN)_2$ radical-anion: compound (1a) (13 mM), propylene carbonate, Et_4NBF_4 (0·25M), Hg cathode

Mechanism of reduction. With the gradual addition of a proton donor (*e.g.* acetic acid) several changes in voltammograms of type A (Figure 1) are observed. At very low concentrations of proton donor the oxidation peak O_2 is completely suppressed. As the amount of proton donor is gradually increased the peak R_1 grows as the peak R_2 diminishes. Also with the gradual addition of proton donor the peak current for process R_1 increases until eventually it reaches twice its initial value whereas the peak current for process O_1 decreases

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* We are grateful to Dr. K. D. Sales, Queen Mary College, for assistance in the analysis of the e.s.r. spectra. The number and relative intensities of the lines were accounted for using the relationships $\alpha_p = \alpha_N/2$, $\alpha_0 = \alpha_p/2$.

[5] P. Delahay, 'New Instrumental Methods in Electrochemistry,' Wiley–Interscience, New York, 1954.

[6] 'Radical Ions', eds. E. T. Kaiser and L. Kevan, Wiley–Interscience, New York, 1968.

to zero. The relative effectiveness of different proton donors in various solvents is discussed below in a separate section.

The mechanism suggested by these results is given in Figure 1 and is closely analogous to that which is now generally accepted for the cathodic reduction of polynuclear aromatic hydrocarbons.[7]

The products (RH_2) of two-electron reduction in the presence of added proton donor have been isolated and characterised and where type A voltammetric behaviour is found the products correspond to hydrogenation of the carbon–carbon double bond. The detailed results of such preparative scale experiments are the subject of an ensuing paper.

The relative effectiveness of proton donors. The role of added proton donors has been assessed according to the experiments and results described in Table 2. The relative amount of donor required to suppress the oxidation corresponding to O_1 (*i.e.* $M \longrightarrow M^{\cdot-} + e$) is an indication of the relative effectiveness of the donors in protonating the radical-anion in a particular solvent. Alkaloid salts and ephedrine hydrochloride were included as examples of chiral electrolytes which might induce asymmetry in reduction products during the protonation step.

The absolute effectiveness of a given donor depends on the solvent, *e.g.* acetic acid is much more effective in propylene carbonate than in dimethylformamide. This is indicated by the irreversibility of reduction of (1a) in propylene carbonate at an [HA]/[S] ratio of 0·5 whereas the same reduction is still reversible in dimethylformamide at an [HA]/[S] value of 570. Furthermore, in a given solvent, the donors differ greatly in their effectiveness. An example of this is the reduction of (1a and b) in, respectively, propylene carbonate and dimethylformamide, in each case acetic acid causes the cyclic voltammetric behaviour to become irreversible whereas with butan-2-ol at much higher [HA]/[S] ratios, the systems behave reversibly. It is particularly interesting that although of similar structure quinidine sulphate is in these reactions a significantly better proton donor than quinine sulphate. Such results lend credence to the view that even for solutions of low bulk concentration induction of asymmetry during the protonation step should be considered when rationalising pathways for stereoselective reduction.

TABLE 2

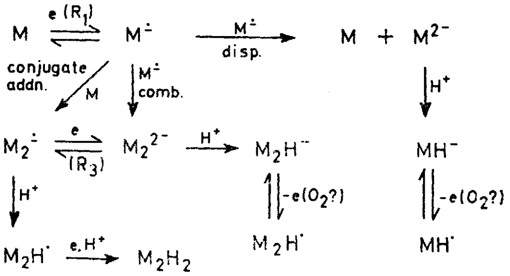
Effect of proton donors on reversibility of first reduction peak

Compound, S, (mM)	H^+ donor, HA, (mM)	[HA]/[S]	$R^1 \rightleftharpoons O^1$ behaviour (solvent)
(1a) (38)	Bu^sOH (3800)	100	Rev.,[a] 1e (propylene carbonate)
(1a) (40)	AcOH (20)	0·5	Irrev.,[a] 2e (propylene carbonate)
(1a) (2·5)	AcOH (1400)	570	Rev.,[b] 1e (DMF)
(1a) (2·5)	AcOH (2200)	894	Irrev.,[b] 2e (DMF)
(1b) (4·3)	Ephedrine, HCl (13·2)	3·1	Irrev.,[b] 2e (DMF)
(1b) (7·0)	Ephedrine, HCl (26·6)	3·6	Irrev.,[b] 2e (DMF)
(1b) (5·0)	Quinine sulphate (15·0)	3·0	Rev.,[b] 1e (DMF)
(1b) (3·2)	Quinidine sulphate (10·3)	3·2	Irrev.,[b] 2e (DMF)
(1b) (2·4)	Quinidine sulphate (5·9)	2·5	Irrev.,[b] 2e (DMF)
(1b) (8·1)	Et_3NHCl (13·4)	1·7	Irrev.,[c] 2e (DMF)
(1b) (1·5)	AcOH (256)	170	Irrev.,[c] 2e (DMF)
(1b) (6·4)	Bu^sOH (3100)	480	Rev.,[c] 1e (DMF)
(2a) (2·7)	AcOH (40)	14·7	Irrev.,[b] 2e (DMF)
(2a) (9·2)	AcOH (58)	6·4	Irrev.,[b] 2e (DMF)

[a] Propylene carbonate, Et_4NBF_4 (0·25M), vitreous carbon cathode, 0·3 V s^{-1}. [b] Dimethylformamide, Bu_4NI (0·1M), vitreous carbon cathode, 0·1 V s^{-1}. [c] Dimethylformamide, Bu_4NI (0·1M), hanging Hg drop, 0·065 V s^{-1}.

Irreversible Reduction (*Type B*).—Of the compounds which display type B voltammetric behaviour (1c and d) were chosen for further study.

The height of peak R_1 was unaffected by the addition of acetic acid and, although some reverse oxidation is seen at high sweep speeds (30—100 V s^{-1}), it is clear that the intermediate formed by initial electron transfer is involved in a rapid chemical reaction which does not involve protonation. After allowance for concentration and assuming similar diffusion coefficients for the species involved, comparable R_1 peak currents are found for the irreversible reduction of (1c and d) and the one-electron reversible reduction of (1b). For the compounds under study the one-electron irreversible reduction could be a consequence of the pathways summarised in Scheme 1.



SCHEME 1

The pathway involving conjugate addition is unlikely because to fit the cyclic votammetric results the potential for the second electron transfer (R_3) to the dimeric dianion is required to be less cathodic than for transfer to the neutral starting material. This result is found in aprotic conditions where protonation of $M_2^{\cdot-}$ is unlikely to precede electron transfer. The disproportionation mechanism is attractive because the similarity of the O_2 peak potentials in both type A and B voltammograms argues for a common process (*cf.* Scheme 1

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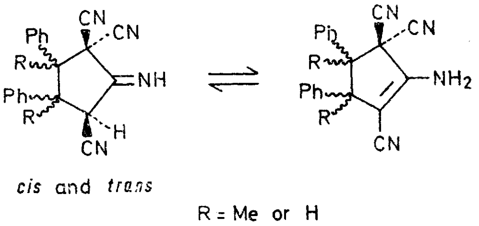
[7] Ref. 4, pp. 253 *et seq.*

and Table 1). However, preparative scale electrolyses in the presence of added proton donor of compounds (1c and d) give products (Scheme 2) which are isomeric and derived from dimerisation and intramolecular cyclisation. Full details of such experiments and the characterisation of the products form part of a following publication. The present discussion of mechanism requires only the knowledge that hydrodimerisation has occurred and this is gained from mass spectrometry. Mass measurement on the molecular ions of the products gave for R = CH_3, *m/e* 338 ($C_{22}H_{18}N_4$) and for R = H high resolution measurement gave *m/e* 310·121 ($C_{20}H_{14}N_4$ requires 310·122).

It seems therefore highly probable that the rapid chemical step following electron transfer is combination of the radical-ions. This result is consistent with recent results concerning the hydrodimerisation of activated olefins.[8] To accommodate the cyclic voltammetric results it must be assumed that (*a*) despite good charge separation the dimeric dianon is sufficiently basic to abstract a proton from the solvent or electrolyte and (*b*) the species M_2H^- is oxidised (O_2) at a potential similar to that required for MH^-.



SCHEME 2

The different reactions of the type A and B compounds can probably best be rationalised in terms of steric hindrance to dimerisation for the radical-anions of the type A compounds (1a, b, and e). Steric hindrance would also in these cases preclude dimerisation by the conjugate addition mechanism should it become important in the higher concentration, preparative scale electrolyses.

EXPERIMENTAL

Organic Substrates.—The Knoevenagel condensation products (1) were prepared in the usual way [9] and the phenanthrene derivatives were prepared by minor modification of literature methods;[10] the physical characteristics of these known compounds were in accord with literature values.

Stereoisomers of $Ph(CH_3)C{:}C(CN)CO_2Et$ (1f). Knoevenagel condensation [9] led to a 1 : 1 mixture of the *E*- and *Z*-isomers of (1f) which were separated and isolated by preparative scale g.l.c. (Perkin-Elmer F21; Silicone grease–Chromosorb P column). The *Z*-isomer had the shorter retention time. Stereochemistry was assigned according to the characteristic chemical shifts established [11] for a series of such isomers, δ (*E*-isomer; 60 MHz; $CDCl_3$) 4·33 (2H, q, *J* 7·5 Hz), 2·68 (3H, s), and 1·37 (3H, t, *J* 7·5 Hz), δ (*Z*-isomer) 4·80 (2H, q, *J* 7·0 Hz), 2·52 (3H, s), and 1·11 (3H, t, *J* 7·0 Hz).

Single Sweep Cyclic Voltammetry.—*Solvents*. Propylene carbonate (B.D.H.) was twice distilled under reduced pressure (*ca*. 1 mmHg) the first distillation being from calcium hydride. The joints of the all-glass apparatus were protected with polytetrafluoroethylene sleeves to obviate the use of grease. Dimethylformamide (B.D.H.; spectroscopic grade) required no further purification.

Supporting electrolytes. Tetra-n-butylammonium perchlorate was prepared by a reported [12] method, recrystallised (× 2) from ethanol, and dried under reduced pressure (*ca*. 5 mmHg) at 100°. Tetramethylammonium tetrafluoroborate (K and K) was recrystallised (×2) from methanol and dried under reduced pressure (*ca*. 5 mmHg) at 100°. Tetra-n-butylammonium iodide (B.D.H.) required no further purification.

Cells, electrodes, and electronic equipment. Conventional H cells, with sintered glass separators, were used. For cyclic voltammetry the cells were equipped with a vitreous carbon microelectrode (area 0·08 cm^2) or a hanging mercury drop electrode. Electrode potentials were measured against reference electrodes composed either of a silver wire immersed in a propylene carbonate solution of silver perchlorate (20mM) and lithium perchlorate (1·0M), or of a silver wire immersed in a dimethylformamide solution of tetra-n-butylammonium iodide (0·1M). Preparative scale electrolyses used vitreous carbon, mercury, or lead cathodes. A Chemical Electronics Ltd. TR2A potentiostat was used in combination with a type RB1 waveform generator, an electronic current integrator, an Electronic Associates Inc. 1100E X-Y recorder, and a Telequipment type D53A oscilloscope with a long persistence screen.

E.s.r. Experiments.—The cell consisted of a Pyrex tube (15 cm × 3 mm o.d.) with a mercury bead cathode at the bottom. Electrical contact was made *via* a sealed platinum wire. The spiral platinum wire anode was in a broader tube, sealed to the 3 mm tube, but clear of the cavity of the spectrometer (Decca X3). The electrolyte was a propylene carbonate solution of tetraethylammonium tetrafluoroborate (0·25M) and substrate (13mM). At these concentrations cyclic voltammetry gave, at a slow scan rate (0·3 V s^{-1}), a peak current density of 2·8 mA cm^{-2}. The *in situ* electrolyses from which e.s.r. spectra were recorded were run at current densities of 0·16 or 0·32 mA cm^{-2}.

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