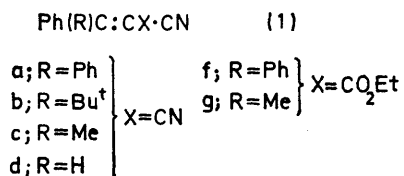# Electro-organic Reactions. Part IV.[1] Preparative Aspects of the Cathodic Hydrogenation of Activated Carbon–Carbon Double Bonds

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Compounds of the type $Ph(R)C\vdots C(CN)X$ (R = Ph or Bu^t, X = CN or CO_2Et) undergo smooth, efficient, and specific cathodic hydrogenation of the carbon–carbon double bond in aprotic solvents in the presence of added proton donors. For $R = Bu^t$ and X = CN, cathodic reduction in the presence of chiral proton donors gives a racemic product which implies that, for established cases of asymmetric electrochemical reduction, protonation is not the stereochemistry-determining step.

Mixtures of stereoisomeric cyclic hydro-dimers are the only products of similar reductions of compounds with R = Me or H and X = CN.

PART III[1] of this series dealt with the elucidation of the mechanisms of cathodic reduction of compounds (1a—g). For aprotic solutions cyclic voltammetry enabled the

$$Ph(R)C\vdots CX\cdot CN \qquad (1)$$

$$\begin{array}{l} a; R=Ph \\ b; R=Bu^t \\ c; R=Me \\ d; R=H \end{array} \Bigg\} X=CN \qquad \begin{array}{l} f; R=Ph \\ g; R=Me \end{array} \Bigg\} X=CO_2Et$$
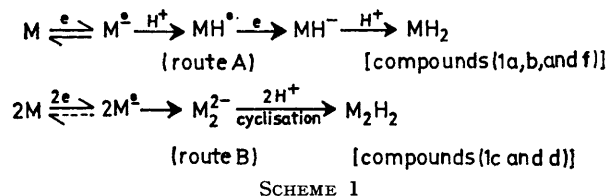
identification of two mechanisms which could be characterised according to the essentially reversible or irreversible nature of the first electron transfer. The alternative pathways determined by compound type are summarised in Scheme 1.

We now report the structures of the products and the development of the cathodic reduction as a preparative method. In comparison chemical reductions of compounds of type (1) give poor results. Reduction of the carbon–carbon double bond with hydride reagents competes poorly with the simultaneous reduction of the cyano and ester groups.[2,3] Catalytic hydrogenation

works well for compound (1b) but, apparently, compound (1a) is not easily reduced by this method and use of sodium borohydride gives but a moderate yield.[2] Moreover, treatment of (1f) with borohydride results largely in reduction of the ester group and gives less than 10% reduction of the carbon–carbon double bond.[3] A convenient electrochemical method is described herein,

$$M \rightleftharpoons M^{\bullet-} \xrightarrow{H^+} MH^\bullet \xrightarrow{e} MH^- \xrightarrow{H^+} MH_2$$
$$\text{(route A)} \qquad \text{[compounds (1a,b, and f)]}$$

$$2M \rightleftharpoons 2M^{\bullet-} \longrightarrow M_2^{2-} \xrightarrow[\text{cyclisation}]{2H^+} M_2H_2$$
$$\text{(route B)} \qquad \text{[compounds (1c and d)]}$$

SCHEME 1

which, when dimerisation is precluded, specifically reduces the carbon–carbon double bond. It is likely therefore to be a useful method for the hydrogenation of activated carbon–carbon double bonds in the presence of ester or cyano-groups.

An additional purpose of this investigation was to test

[1] Part III, L. A. Avaca and J. H. P. Utley, J.C.S. Perkin II, 1975, 161.

[2] E. Campaigne and W. L. Roelofs, J. Org. Chem., 1965, 30, 396.

[3] J. A. Meschino and C. H. Bond, J. Org. Chem., 1963, 28, 3129.

the hypothesis that optically active reduction products may result from induction of asymmetry by protonation with a chiral proton donor. Compound (1b) is particularly suitable for such a study because it can be reduced at potentials at which alkaloid salt proton donors are not discharged and the expected product [Ph(Bu^t)-CH·CH(CN)$_2$] can exist as enantiomers. Optically active products have been produced by the reduction of coumarins [4] and acetophenone [5,6] in the presence of chiral electrolytes but in each case the reduction potential is close to that at which the electrolyte is discharged and the mechanism of asymmetric induction is not clear. We report therefore on the results of macro-scale reduction of (1b) in the presence of optically active proton donors.

RESULTS AND DISCUSSION

Compounds undergoing Reversible One-electron Reduction in Aprotic Solution (1a, b, *and* f).—These compounds are reduced according to route A (Scheme 1) at cyclic voltammetric peak potentials in the range —0·45 to —0·85 V (in DMF vs. Ag–AgI).[1] Details of macro-scale electrolyses are given in Table 1. Efficient preparative

TABLE 1

Cathodic hydrogenation

$$\text{Ph(R)C:CX·CN} \xrightarrow{\text{2e, 2H}^+} \text{Ph(R)CH·CHX·CN}$$

R	X	Cathode	Cathode potential (V)	Current yield (%) [a]
Ph	CN	Vit. C [b]	—2·4 (vs. Ag–Ag$^+$)	≥80 [c]
		Pb [d]	—1·8 (vs. Ag–Ag$^+$)	≥80 [c]
		Hg [e]	—1·0 (vs. Ag–AgI)	≥90 [f]
Ph	CO$_2$Et	Vit. C [e]	—0·76 (vs. Ag–AgI)	85 [g] (n = 2·3; cf. Table 2)
Bu^t	CN	Vit. C [e]	—1·0 (vs. Ag–AgI)	≥90 [g]
		Hg [e]	—1·0 (vs. Ag–AgI)	87 [f]

[a] Calculated for 2 F mol^{-1}. [b] 4-Methyl-1,3-dioxolan-2-one, Et$_4$NBF$_4$ (0·25M), AcOH (0·25M). [c] From g.l.c. analysis. [d] 4-Methyl-1,3-dioxolan-2-one, LiClO$_4$ (1·0M), AcOH (0·25M). [e] DMF, Bu$_4$NI (0·1M), AcOH (ca. 1—2M). [f] Isolated yield. [g] N.m.r. analysis of crude product.

scale reductions were carried out at mercury, vitreous carbon, or lead cathodes at potentials in the region of —1·0 V (vs. Ag–AgI). For substrate solutions of concentration ca. 0·1—0·15M initial current densities were ca. 5 mA cm^{-2}, falling to a low background value (ca 0·1 mA cm^{-2}) after the passage of 2 F mol^{-1}. Acetic acid was used as proton donor, the solvents being either 4-methyl-1,3-dioxolan-2-one or dimethylformamide (DMF).

Reduction in the Presence of Chiral Proton Donors.—It has been established [1] that amine salts such as triethylamine hydrochloride, (—)-ephedrine hydrochloride, (—)-quinine sulphate, and (+)-quinidine sulphate may be used as proton donors in reductions of compound (1b): indeed in dimethylformamide solution all except the quinine salt are more effective than acetic acid.

Controlled potential preparative scale reduction of (1b), in DMF and in the presence of (—)-ephedrine

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

[5] L. Horner, *Chem. Ing. Tech.*, 1972, **44**, 209; *Tetrahedron Letters*, 1971, 2141, 1245; 1970, 1103, 2803, 3679; 1968, 5889.

hydrochloride or (+)-quinidine sulphate, gave Ph(Bu^t)-CH·CH(CN)$_2$ with high current efficiency (Table 2).

TABLE 2

Reduction of (1b) in the presence of chiral proton donors [a]

H$^+$ Donor	[H$^+$ donor]/ M	Initial current density (mA cm^{-2})	Current yield (%)	n [b]
(—)-Ephedrine, HCl	0·1	7	>90	1·6
(+)-Quinidine, H$_2$SO$_4$	0·2	8	ca. 100	

[a] Substrate (0·03M) in DMF solution, Bu$_4$NI (0·1M), vitreous carbon cathode at —1·0 V (vs. Ag–AgI); work-up as for example in the Experimental section. [b] See Experimental section.

Polarimetric examination at 589 nm of solutions (0·2 g cm^{-3}) of the crude products in chloroform gave a rotation of 0 ± 0·01°. Application of Brewster's rules, by using the method and parameters described by Eliel,[7] gives a value of about 1° for the expected molecular rotation, M_D, for Ph(Bu^t)CH·CH(CN)$_2$. This is likely to be a low estimate because the method demands the equal weighting of contributions from rotational conformers. The low value is the result of the cancelling of relatively large contributions (M_A, M_B, M_C) from three staggered conformations (Figure) and for steric reasons it is likely that

M_A 342 M_B —210 M_C —128
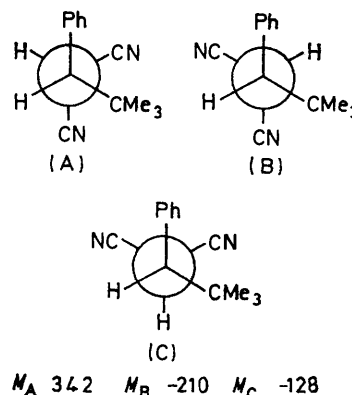
Conformations for application of Brewsters' rules

the contribution from conformer (B) is greater than from conformer (A). The value of 1° can therefore be used to predict with some confidence the degree of asymmetric induction which would have been detectable from the electrolyses described above.

For 100% optical yield the observed rotation of the solutions of Ph(Bu^t)CH·CH(CN)$_2$ would have been ≥0·2°. Thus an optical yield of ca. 10% would easily have been detected. Induced asymmetry in electrochemical reductions sometimes gives <10% optical yield [4-6] so the experiments described herein could profitably be repeated with an easily reduced substrate which gives a product of much higher specific rotation. Our results are, nevertheless, a strong indication that asymmetry is not likely to be introduced during the protonation step. This, in turn, reinforces the hypothesis involving asym-

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

[7] E. L. Eliel, 'Stereochemistry of Carbon Compounds,' McGraw-Hill, New York, 1962, p. 398 et seq.

metric complex formation between the electrolyte and an intermediate, possibly at the cathode surface.[5,6]

Compounds undergoing Irreversible One-electron Reduction in Aprotic Solution (1c and d).—Cyclic voltammetric experiments showed that under aprotic conditions one-electron irreversible reduction occurred [1] for compounds (1c and d). We now report that macro-scale reduction proceeds smoothly, in aprotic solvent with added acetic acid, with the consumption of 1 F mol^{-1}. The reaction conditions and results of the electrolyses are given in Table 3.

TABLE 3
Cathodic hydrodimerisation [a]

$$2Ph(R)C\!:\!C(CN)_2 \xrightarrow[2H^+]{2e} (2a \text{ and } b)$$

R	Cathode potential (V vs. Ag–AgI)	Current yield (%) [b]	n [c]
H	−0·64	82	1·06
	−1·00 [d]	95	1·03
Me	−0·80	>90	0·91

[a] DMF, Bu$_4$NI (0·1M), AcOH (ca. 1M), vitreous carbon cathode, initial current density ca. 7 mA cm^{-2}. [b] Calculated for 1 F mol^{-1}; yields from n.m.r. analysis of isolated product. [c] See Experimental section for method. [d] LiClO$_4$ (0·1M) electrolyte; V vs. Ag wire.

Even though a proton donor was present, none of the 2 F mol^{-1} cathodic hydrogenation product was found.

ca. 1660 cm^{-1} is evidence for the C=C–NH$_2$ ⇌ C–C=NH entity. Characteristic N–H stretching bands are also present and, in the n.m.r. experiments, NH protons were exchanged in D$_2$O. The deuteriation was confirmed by accurate mass measurements on the molecular ions of samples previously shaken with D$_2$O. Molecular formulae were derived from accurate mass measurements on molecular ions. Information about isomer ratios comes from the n.m.r. spectra. For (2a) an isomer ratio of 1 : 1 was deduced from the relative peak areas of the signals assigned to the benzylic ring protons. For (2b) a ratio of 3 : 2 was given by similar comparison of the signals corresponding to the ring methyl groups. It is not possible to assign the individual isomers from the available information and, in our hands, the isomers could not be separated by t.l.c.

There is good precedent for the electrochemical formation of such cyclic hydro-dimers. The cathodic reduction of α-phenylcinnamonitrile in wet DMF gives a mixture of cyclic and linear hydro-dimers [8,9] (3a and b). In this case the ratio of cyclic to linear compound varies according to the supporting electrolyte cation: Et$_4$N$^+$ promotes cyclisation whereas Li$^+$ promotes formation of the linear dimer.[9] In our case cyclic hydro-dimers were the only detected products and they were formed efficiently in the presence of both Bu$_4$N$^+$ and Li$^+$ salts (Table 2).
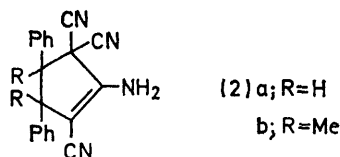
TABLE 4
Spectroscopic identification of the 2-amino-4,5-diphenylcyclopent-2-ene-1,1,3-tricarbonitriles (2a and b)

Method	Compound	Major features	Interpretation
Mass measurement on M$^+$	(2a)	m/e 310·121	C$_{20}$H$_{14}$N$_4$ (calc. 310·122)
	(2a) *	310·134	C$_{20}$H$_{12}$D$_2$N$_4$ (calc. 312·134)
	(2b)	338·153	C$_{22}$H$_{18}$N$_4$ (calc. 338·153)
	(2b) *	340·165	C$_{22}$H$_{16}$D$_2$N$_4$ (calc. 340·166)
^{1}H N.m.r.†	(2a)	δ(CDCl$_3$) 3·81 (d), 4·57 (d); J 9·2 Hz} 4·23 (d), 4·52 (d); J 7·0 Hz} 2H	Benzylic H's in 1 : 1 mixture of 2 isomers
		5·43br (s), 5·56br (s); 2H 6·75—7·40 (m); 10H	N–H of 2 isomers Ph
	(2b)	1·20 (s), 1·46 (s), 1·84 (s), 2·03 (s); 6H	Me groups in 3 : 2 mixture of 2 isomers
		5·48br (s); 2H 6·89 (m), 7·32 (m); 10H	N–H Ph
I.r.	(2a)	ν$_{max.}$(Nujol)/cm^{-1} 1660 2210 3210, 3345, 3420	C:C·NH$_2$ ⇌ C·C:NH C:N NH
	(2b)	1665 2195 3200, 3320, 3420	C:C·NH$_2$ ⇌ C·C:NH C:N NH

* Sample recovered after shaking with CDCl$_3$–D$_2$O. † Measured at 100 and at 60 MHz to distinguish coupling from chemical shift differences.

The only products, obtained with high current efficiency, were mixtures of stereoisomeric cyclic hydro-dimers (2a and b). The assignments of structure are based on

(2) a; R=H
b; R=Me

the spectroscopic evidence summarised in Table 4. For both compounds (2a and b) the strong i.r. absorption at

The cyclic voltammetric study [1] led to the conclusion that, following electron transfer, rapid combination of

(3a)   (3b)
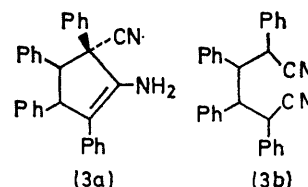
the radical ions took place. This conclusion is consistent with the mechanism established for the hydrodimerisation

[8] S. Wawzonek, A. R. Zigman, and G. R. Hansen, *J. Electrochem. Soc.*, 1970, **117**, 1351.

[9] J. P. Petrovich and M. M. Baizer, *J. Electrochem. Soc.*, 1971, **118**, 447.

of other activated olefins at low concentration [10] and the probable route to compounds (2a and b) is given in Scheme 2. In addition to the voltammetric results the formation of, in each case, similar amounts of diastereo-isomers suggests the rapid and random combination of radical ions. An alternative route, conjugate addition of a radical ion or carbanion to starting material, would have a higher energy of activation with a more product-like transition state which would result in preferred formation of the least strained diastereoisomers. The competition between dimerisation and further electron transfer is, however, susceptible to steric influence because under comparable conditions compounds (1a, b, and f) are exclusively hydrogenated in the 2 F mol^{-1} process. It is tempting to speculate that this may be a consequence of twisting of the phenyl group, *i.e.* steric interference with the spin and charge distribution in the radical ion.

and isomer
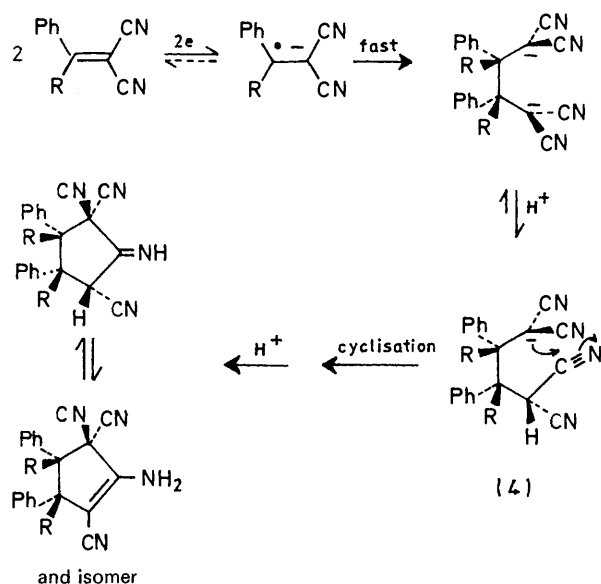
SCHEME 2

The sequence of protonation and cyclisation, following the formation of the dianion, cannot be determined from the information available. However, according to the earlier voltammetric results, irreversible one-electron reduction is observed with and without added proton donor which suggests either rapid intramolecular cyclisation of the dianion or, more likely, and as suggested in Scheme 2, rapid protonation to give the carbanion (4), which cyclises to the tautomeric species.

EXPERIMENTAL

Starting materials, solvents, and electrolytes have been described in a previous paper.[1]

Cells, Electrodes, and Electronic Equipment.—Conventional H-cells were used, equipped with sintered glass separators

* In early experiments this product, although apparently pure, failed to crystallise.

and either a vitreous carbon rod or a mercury pool electrode. Reference electrodes were, for electrolysis in 4-methyl-1,3-dioxolan-2-one, a silver wire immersed in a 4-methyl-1,3-dioxolan-2-one solution of silver perchlorate (20mM) and lithium perchlorate (1·0M) or, for electrolysis in DMF, a silver wire in a DMF solution of tetrabutylammonium iodide (0·1M). Chemical Electronics Ltd. potentiostats (TR2A) and an electronic current integrator were used.

Coulometry.—Assuming a negligible background current and the constancy throughout the reaction of n (which has its usual significance), the following expressions may be derived. Initially, $i_0 = AN_0$, and $i_t = AN_t$ where A is a constant and N the amount of substrate (mol). Hence, $i_0 - i_t = A(N_0 - N_t)$, and the amount of substrate consumed, $(N_0 - N_t)$, is Q_t/nF, where Q_t is the number of coulombs passed. It follows that $i_0 - i_t = (AN_0/n)(Q_t/FN_0)$, which may be converted into $i_t/i_0 = 1 - (Q_t/$F$N_0)/n$. For the electrolyses described herein plots of i_t/i_0 versus $Q_t/$FN_0 were linear and the n values so derived are quoted in Tables 1—3.

Electrolyses.—The procedure is typified by the following experiment.

Reduction of Ethyl 2-Cyano-3,3-diphenylacrylate (1f).—The substrate (1 g, 0·0036 mol) and acetic acid (5 cm^3) were added to the cathode compartment of an H-cell equipped with a mercury pool cathode (area 12·6 cm^2) a graphite rod anode, and a Ag–AgI reference electrode. The cell was filled with a DMF solution of tetrabutylammonium iodide (0·1M) (catholyte volume 40 cm^3). The catholyte was stirred magnetically and flushed continuously with a slow stream of nitrogen. The cathode potential was set at −1·0 V and after the passage of 720 C (2·05 F mol^{-1}) the current had fallen from an initial value of 60 to 0·8 mA.

The catholyte was mixed with benzene (50 cm^3) and the solution washed successively with water (300 cm^3), aqueous sodium thiosulphate (*ca.* 0·5%; 300 cm^3), and water (300 cm^3). The benzene layer was dried (MgSO$_4$) and removed, and the solid residue (0·94 g) was crystallised from ethanol to yield a solid, m.p. 75—77°.

Products.—The characterisation of the cyclic hydro-dimers is discussed above. The products of the cathodic hydrogenation reactions were (diphenylmethyl)malononitrile, m.p. 80—81° * (lit.,[2] 81—82°), δ (CDCl$_3$) 4·40 (1H, d), 4·60 (1H, d), and 7·30 (10H, s) [lit.,[2] 4·40 (1H, d) and 4·58 (1H, d)]; ethyl 2-cyano-3,3-diphenylpropionate, m.p. 75—77° (lit.,[11] 78°), δ (CDCl$_3$) 1·05 (3H, 1 : 2 : 1 t), 4·06 (2H, 1 : 3 : 3 : 1 q), 4·18 (1H, d, J 8·5 Hz), and 4·69 (1H, d, J 8·5 Hz); (2,2-dimethyl-1-phenylpropyl)malononitrile, m.p. 50—52° (lit.,[2] 54°), δ (CDCl$_3$) 1·08 (9H, s), 2·99 (1H, d, J 6·0 Hz), and 4·20 (1H, d, J 6·0 Hz).

Polarimetry.—Products from the experiments described in Table 2 were examined with a Bellingham and Stanley Pepol 60 polarimeter.

[10] V. J. Puglisi and A. J. Bard, *J. Electrochem. Soc.,* 1972, **119**, 829.
[11] E. P. Kohler and M. Reimer, *Amer. Chem. J.,* 1905, **33**, 333.