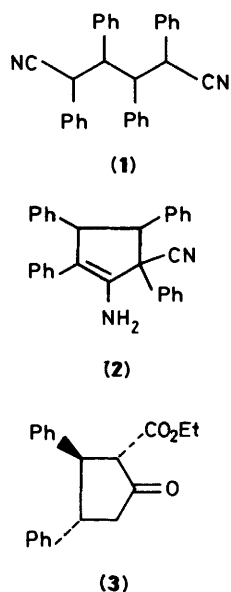


Electro-organic Reactions. Part 26.† The Cathodic Reduction of Dicyanoethylene Derivatives; Competition between Hydrogenation and Hydrodimerisation

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Dicyanoethylene derivatives, and related compounds, undergo smooth cathodic reduction to give the products of hydrogenation ($2 F \text{ mol}^{-1}$), hydrodimerisation ($1 F \text{ mol}^{-1}$), or a mixture of both. The product distribution depends crucially upon steric factors and upon the stability–basicity of the intermediate radical-anions. The latter factor is reflected in the significant influence exerted by electrolyte acidity. Twelve activated ethylene compounds of considerable structural diversity have been included in the study and by consideration of substituent effects and the results of cyclic voltammetric experiments a detailed mechanistic rationalisation of their reduction is presented. In particular, the hydrodimerisation reactions are shown to be under kinetic control (giving cyclic hydrodimers through subsequent intramolecular reaction); one highly strained cyclic hydrodimer (**20**) rearranges thermally to the more stable linear isomer (**19**).

The competition between hydrodimerisation and hydrogenation has been much studied for acrylonitrile and related compounds; the suppression of hydrogenation to propionitrile and the encouragement of hydrodimerisation to adiponitrile was crucial to the development of the Baizer–Monsanto process.¹ The competition was found to be very sensitive to the nature of the solvent and electrolyte cation. Similar influences were found for the cathodic reduction of phenylcinnamionitrile² which, in addition to the linear hydrodimer (**1**), also gave in the presence of tetraethylammonium ion the cyclic hydrodimer (**2**). The efficient cathodic formation of the cyclic hydrodimer (**3**) from



cinnamate esters has been reported³ and the stereochemistry of the product elucidated.^{3b} Both hydrodimerisation and hydrogenation of the carbon–carbon double bond were shown⁴ to be a function of structure in a number of dicyanoethylene

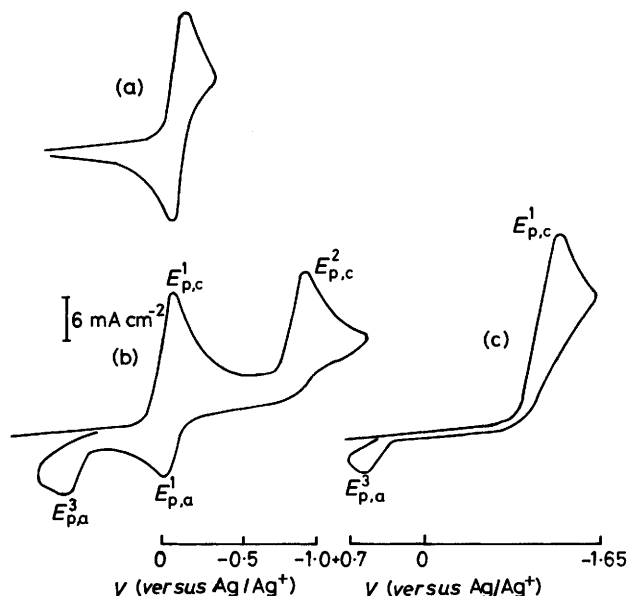


Figure. Cyclic voltammograms: Type A behaviour; (a) and (b) compound (**4**) (4 mM), acetonitrile, Et_4NBF_4 (0.1M), vitreous carbon cathode, 0.3 V s^{-1} . Type B behaviour; (c) compound (**9**) (7 mM), conditions as for (a) and (b)

compounds of the type $\text{Ph(R)C}=\text{C}(\text{CN})_2$ where $\text{R} = \text{H, Me, Bu}^t$, or Ph . For $\text{R} = \text{Ph, Bu}^t$, and also for the corresponding fluorenylidene compound, cathodically generated radical-anions and dianions are, in aprotic solvent, long lived and have been used as electrogenerated bases.⁵

For media of a given proton-donating ability it was shown that the competition between hydrogenation and hydrodimerisation was guided mainly by steric factors.⁴ In this paper the operation of such factors is examined further using dicyanoethylene derivatives of considerable structural diversity.

Results and Discussion

Cyclic Voltammetry.—Two broad classes of behaviour were observed. For several of the derivatives two reduction peaks

† Part 25, D. W. Sopher and J. H. P. Utley, *J. Chem. Soc., Perkin Trans.* 2, 1984, 1361.

Table 1. Cyclic voltammetric^a results: R¹R²C:C(X)CN

Substrate R ¹	R ²	X	Compound	-E _{p,c} ¹ /V	-E _{p,a} ¹ /V	E _{p,c} ¹ - E ₃ /V	E _{p,a} ³ /V	Behaviour type
	9-Fluorenyl	CN	(4)	0.070	0.014			A ^b
Ph	Ph	CN	(5)	0.443	0.390		+0.512	A ^c
Ph	Bu ¹	CN	(6)	0.90	0.845		+0.540	A ^d
Ph	H	CN	(7)	0.48		0.049	+0.47	B
Ph	Me	CN	(8)	0.62		0.049	+0.56	B
Me	Me	CN	(9)	1.25			+0.54	B
Me	Bu ¹	CN	(10)	1.11		0.052	+0.58	B
	Cyclopentyl	CN	(11)	1.11		0.070	+0.60	B
	Cyclohexyl	CN	(12)	1.17		0.070	+0.60	B
	4-t-Butylcyclohexyl	CN	(13)	1.22		0.055	+0.60	B
	3,5,5-Trimethylcyclohexyl	CN	(14)	1.23		0.054	+0.51	B
Me	Me	CO ₂ Et	(15)	1.44		0.059	+0.50	B
Me	Bu ¹	CO ₂ Et	(16)	1.16		0.049	+0.80	B

^a Vitreous carbon cathode, DMF-Et₄NBF₄ (0.1M), substrate ca. 5 mM, 0.3 V s⁻¹, Ag-AgI(s) reference electrode. ^b E_{p,c}² -0.96 V; E_{p,a}² -0.90 V. ^c E_{p,c}² -1.11 V. ^d E_{p,c}² -1.29 V.

were found with the first peak being reversible at modest sweep speeds; this will be referred to as type A behaviour. In some cases [dicyano(fluoren-9-ylidene)methane (4), and 7,7,8,8-tetracyanoquinodimethane⁶] the reversible formation of dianions may also be observed. The second type of voltammetric behaviour (type B) was irreversible reduction at the first reduction potential which persisted at relatively high sweep speeds. The Figure displays typical cyclic voltammograms and also serves to identify the peaks referred to in Table 1, in which the detailed results of voltammetry are given.

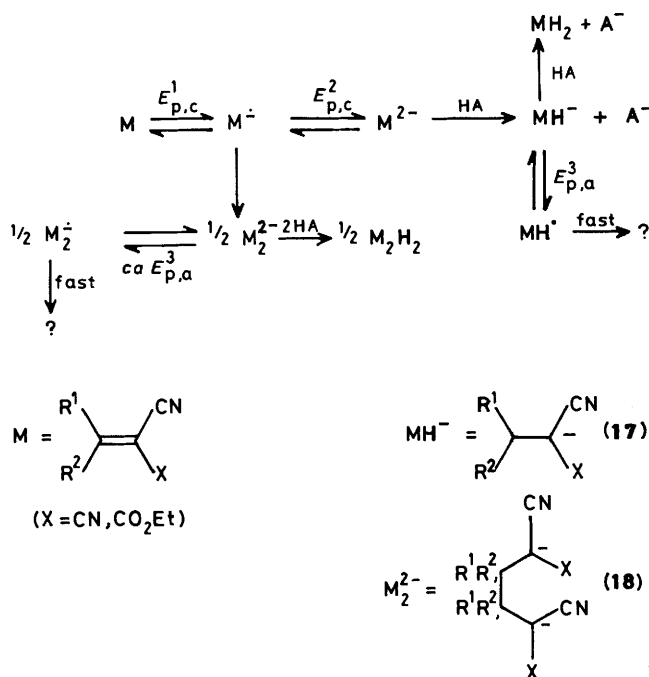
Table 1 refers to experiments in *NN*-dimethylformamide (DMF) solution with Et₄NBF₄ as electrolyte; several of the substrates were examined in other solvent-electrolyte systems, e.g. DMF-Bu₄NI, MeCN-Et₄NBF₄, but essentially similar results were obtained. These results extend those previously obtained⁴ which were used to support the assignment of the various reduction peaks according to Scheme 1. The oxidation peaks at E_{p,a}³ require separate comment. For those derivatives

giving a second reduction peak it is necessary to sweep past that potential in order to observe the peak at E_{p,a}³; on the other hand for those derivatives giving irreversible reduction, oxidation peaks are observed following a cathodic sweep to the first reduction potential. Furthermore, despite the considerable variation of substrate structure the oxidation potentials span only the range 0.47–0.80 V. In terms of Scheme 1 this implies that MH⁻ and M₂²⁻ have similar oxidation potentials which is reasonable if they correspond to the partial structures (17) and (18). The anionic nature of the oxidisable intermediates is also suggested by the disappearance of the oxidation peak upon the addition of proton donor (e.g. acetic acid).

Preparative-scale Electrolyses.—Products from the preparative-scale cathodic reduction of compounds (4)–(16) depend partly on the structure of the starting material and partly on the electrolyte composition. Three distinct types of behaviour were observed: 2 F mol⁻¹ hydrogenation; 1 F mol⁻¹ hydrodimerisation; and the intermediate case in which both types of product were formed. The preparative results, given in Table 2, are organised according to the above divisions.

Amine-Imine Tautomerism in the Hydrodimers.—The structures of the cyclic hydrodimers derived from compounds (7) and (8) have been thoroughly established⁴ by ¹H n.m.r. and i.r. spectroscopy; in these cases *cis*- and *trans*-isomers were obtained in roughly equal amounts. For those cyclic hydrodimers, and for the dimers described herein (Table 3), the strong i.r. absorption at ca. 1660 cm⁻¹ is indicative of imine-amine tautomerism. The cyclic hydrodimer (24) appears, however, to undergo very slow interconversion on the n.m.r. time scale (in [²H₆]DMSO-CDCl₃). The 400 MHz ¹H n.m.r. spectrum contains singlet signals at δ 3.14 (CHCN) and at 7.58 (C=CNH₂); the =NH proton signal is apparently obscured by those from aromatic protons. Irradiation at δ 7.58 causes the signal at δ 3.14 to disappear. This is the result of saturation transfer which confirms the interconversion of discrete chemical species, tautomers in this case. In contrast, and in CDCl₃ solution, the cyclic hydrodimers (20)–(23) are either predominantly in the amine form or, more probably, are involved in rapid tautomerisation. No n.m.r. signal is observed corresponding to CHCN and the NH₂ signal is in the region of δ 5.2, i.e. possibly a time-averaged signal.

Effect of Structure.—The results of the preparative experiments confirm the earlier conclusion⁴ that the hydrodimerisation reaction could be inhibited sterically, in which case



Scheme 1.

hydrogenation became the preferred reaction: compounds (5), (6), (10), (15), and (16) hydrogenate exclusively even in the least acidic electrolyte ($\text{Et}_4\text{NBF}_4\text{-DMF}$) although the current yield is low in this medium. These compounds, with the important exception of (15), contain bulky substituents. For (4)–(6) type A cyclic voltammetric behaviour is found, *i.e.* in aprotic conditions the radical-anions are relatively long-lived and those of (5) and (6) do not rapidly dimerise.

The preparative behaviour of compound (4) is noteworthy in that a significant amount of hydrodimerisation occurs despite the longevity of its radical anion in aprotic conditions and on the cyclic voltammetric time scale. It may be that in this case the rate of protonation is also relatively low; exclusive hydrogenation was only achieved by reduction in acetonitrile solution containing dissolved hydrogen chloride. This process was inefficient because of competing hydrogen evolution.

Compounds (10) and (16) show type B voltammetric behaviour (irreversible) and in these cases it is probable that the 2 F mol^{-1} hydrogenation arises because the radical ions are sufficiently basic to be rapidly protonated on the preparative electrolysis time scale, even in nominally aprotic conditions.

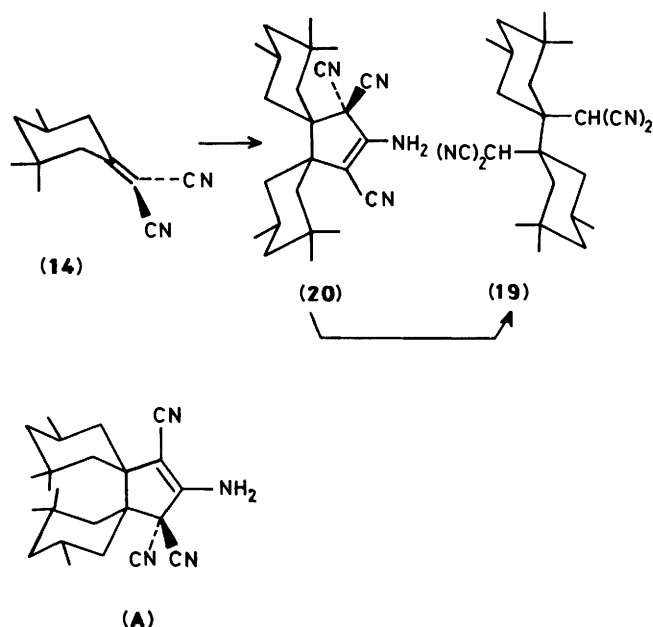
In support of this it is noteworthy that, in contrast with (4)–(6), anion-stabilising phenyl substituents are absent and the first reduction potentials for (10) and (16) are *ca.* 0.25 V cathodic of that for (6) which implies the formation of more reactive (basic?) radical-anions.

That $\text{Me}_2\text{C}:\text{C}(\text{CN})\text{CO}_2\text{Et}$ (15) gives hydrogenation only cannot be explained by steric constraint; by comparison $\text{Me}_2\text{C}:\text{C}(\text{CN})_2$ (9) undergoes hydrodimerisation only. The reason for the difference is probably that the radical-anion of (15), formed at -1.44 V , is more reactive than that of (9), formed at -1.25 V . This indicates that CO_2Et is less effective at delocalising spin or charge than CN; consequently the radical-anion of (15) will be more quickly quenched than that of (9), either by hydrogen-atom abstraction or by protonation. In the use of similar compounds for the generation of bases at cathodes a relationship between apparent basicity and reduction potential was observed⁶ and this is being quantified.⁷ For (9) therefore, dimerisation of radical-anions will be more rapid than protonation whereas the reverse is true for (15).

The concept of encouragement of the hydrodimerisation route by structural features which stabilise the radical-anion is supported by consideration of the results for compounds (7) and (8) which are efficiently reduced to hydrodimers. These are reduced at relatively low potentials and the radical-anions are likely to be highly stabilised by delocalisation over the benzylic system and both nitrile groups. The radical-anions will be poor bases but, as they are not highly hindered, will be capable of rapid combination.

The importance of steric factors is highlighted by a comparison of the results for (9) and (14). Stabilisation of the radical-anions of these compounds by polar factors must be similar, yet compound (14) is highly hindered. Both are reduced to give hydrodimers as the only detected product. However, reduction of the more highly hindered (14) is less efficient and both a linear (19) and cyclic hydrodimer (20) result. Furthermore the thermal interconversion shown in Scheme 2 indicates that production of the strained cyclic hydrodimer is kinetically controlled whereas that of the linear hydrodimer is thermodynamically controlled.

Effect of Electrolyte.—The solvent–electrolyte systems described in the footnote to Table 2 may be qualitatively ordered according to their proton-donating ability. It has been established, by measuring the amounts of proton donor needed to suppress reversible reduction, that a given proton donor is much less effective in DMF solution than in acetonitrile.⁴ For instance, in DMF solution, concentrations of acetic acid in



Scheme 2. i. Distillation at $100\text{ }^\circ\text{C}$ and 0.1 mmHg or refluxing dioxane for 6 h. An alternative isomer (A) would be even more strained

excess of 2M were required to render the first reduction peak of compound (5) irreversible. The reactions of other activated alkenes are known to be profoundly influenced by the electrolyte cation, different products predominating in the presence of Li^+ and quaternary ammonium ions.² For the electrolytes used in the present study it is reasonable to suppose that DMF solution without added proton donor will be the least acidic and MeCN solution with added proton donor will be the most acidic. The most acidic electrolyte system will be that introduced by Breslow and his co-workers,⁸ *i.e.* guanidinium perchlorate in acetonitrile. In this case the salt acts both as proton donor and electrolyte.

For those compounds which hydrogenate only the effect of acidity of electrolyte is on the current efficiency; not surprisingly hydrogenation is less efficient in media of relatively poor proton-donating ability.

Those compounds undergoing rapid hydrodimerisation do so efficiently both in DMF and MeCN solution although marginally better in the latter system. Acidity of the electrolyte does, however, determine whether the linear or cyclic hydrodimer is formed from compound (14), *cf.* Scheme 2. The more stable product (linear) is formed by electrolysis in the less acidic solvents whereas kinetically controlled formation of the cyclic isomer is associated with the more acidic solution. The mechanistic implications of this will be discussed later.

The most profound effect of electrolyte acidity is found for those reductions which produce both hydrogenated and hydrodimerised products. In media of lower acidity (DMF electrolytes) hydrodimerisation predominates and in media of higher acidity hydrogenation is the only detected reaction.

Summary and Mechanistic Rationalisation.—The results of both cyclic voltammetric and preparative-scale experiments confirm the mechanism outlined in Scheme 1. The distinction between cyclic and linear hydrodimers (M_2H_2) is not made in Scheme 1. The results of electrolysis of compound (14) suggest strongly that the linear hydrodimer is the more stable product; the cyclic hydrodimer, the product of kinetic control, requires an acidic electrolyte for its formation and this is powerful evidence in support of the contention (embodied in Scheme 1)

Table 2. Preparative-scale cathodic reduction^a

$$R^1R^2C:C(X)CN \longrightarrow R^1R^2CHCH(X)CN + \begin{array}{c} X \\ | \\ R^1R^2 \\ | \\ R^1R^2 \\ | \\ CN \end{array} + \begin{array}{c} X \\ | \\ R^1R^2 \\ | \\ R^1R^2 \\ | \\ NH_2 \\ | \\ CN \end{array}$$

(X = CN or CO₂Et) (X = CN)

(Hydrogenation, 2 F mol⁻¹) (Hydrodimerisation, 1 F mol⁻¹)

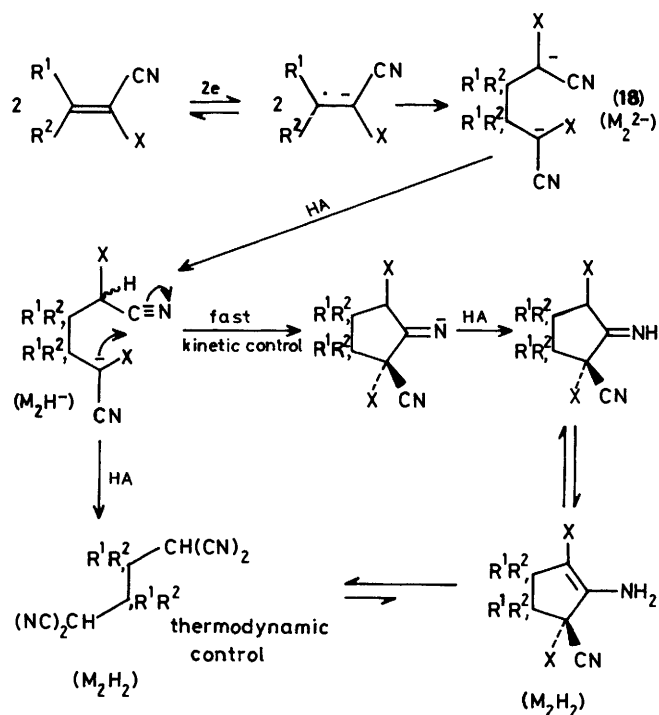
Substrate			Electrolyte ^b			
R ¹	R ²	X	A	B	C	D
Ph	Ph	CN (5)	90	95	52	67
Ph	Bu ^t	CN (6)	88	90	50	63
Me	Bu ^t	CN (10)	90	90	56	72
Me	Me	CO ₂ Et (15)	87	90		
Me	Bu ^t	CO ₂ Et (16)	90	92	54	

Electrolyte^b

Substrate			E	F	G	H	I
Ph	H	CN (7)	80		85		89
Ph	Me	CN (8)	90		93		92
Me	Me	CN (9)	80		87		89
3,5,5-Trimethyl-cyclohexyl		CN (14)	60 ^d	52 ^d	75	67	
9-Fluorenyl		CN (4)		Hydrodimerisation only			
4-t-Butylcyclohexyl		CN (13)		44 (HD); 38 (H ₂)			
Cyclohexyl		CN (12)		70 (HD); 15 (H ₂)	70 (H ₂)		73 (H ₂)
Cyclopentyl		CN (11)		70 (HD); 20 (H ₂)	70 (H ₂)		75 (H ₂)
				64 (HD); 15 (H ₂)	70 (H ₂)		70 (H ₂)

Electrolyte^b

^a Controlled-potential electrolysis, Hg cathode, divided cell. ^b A, Et₄NBF₄ (0.1M)-DMF-HOAc (1M); B, Et₄NBF₄ (0.1M)-MeCN-HOAc (1M); C, Et₄NBF₄ (0.1M)-DMF; D, Et₄NBF₄ (0.1M)-MeCN; E, LiClO₄ (0.1M)-DMF-HOAc (1M); F, Bu₄NI (0.1M)-DMF-HOAc (1M); G, LiClO₄ (0.1M)-MeCN-HOAc (1M); H, Bu₄NI (0.1M)-MeCN-HOAc (1M); I, (NH₂)₂C:NH₂ClO₄ (0.4M)-MeCN. ^c Based on isolated yield after 1 or 2 F mol⁻¹ as appropriate. ^d Linear hydrodimer, see text for structure and conditions.



Scheme 3.

that a key intermediate is M_2H^- . Scheme 3 shows in detail how this can explain the formation of both cyclic and linear hydrodimers and the dependence on acidity of the electrolyte. At first sight it is surprising that acidic conditions do not favour complete protonation of the dianion to give the linear product. However, it is reasonable to suppose that the first protonation is rapid but, thereafter, rapid cyclisation of M_2H^- would compete with the (slower) second protonation; M_2H^- must be considerably less basic than M_2^{2-} .

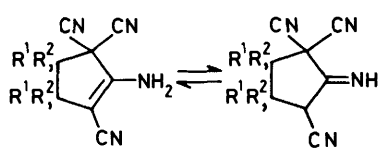
Experimental

Starting Materials.—The dicyanoethylene and cyano(ethoxycarbonyl)ethylene derivatives used in this study are all known compounds which were prepared by Knoevenagel condensation.⁹ Solvents and electrolytes were as for earlier papers in this series.

Preparative-scale Electrolyses.—Details of experimental conditions (solvent, electrolyte, etc.) are included in Table 2. A typical electrolysis and work-up procedure is the following.

A conventional H-cell with a sintered glass separator was used; the catholyte volume was 40 cm³, and the cell was equipped with a mercury pool cathode (area 12.6 cm²), a graphite rod anode, and an Ag-AgI reference electrode. The substrate (ca. 2 g) was added to the cathode compartment together with 40 cm³ of the appropriate solvent-electrolyte system. The catholyte was stirred magnetically and continuously flushed with a slow stream of nitrogen. Potentiostatic

Table 3. Characterisation of new compounds

Formula	
$(\text{NC})_2\text{CHC}(\text{R}^1\text{R}^2)\text{C}(\text{R}^1\text{R}^2)\text{CH}(\text{CN})_2$	
$\text{R}^1\text{R}^2 = 3,5,5\text{-trimethylcyclohexyl}$ (19)	B.p. 160 °C at 0.1 mmHg; $\delta(\text{CDCl}_3)$ 0.98, 1.02 (s, 12 H), 1.12 (s, 6 H), 1.50 (m, 14 H), 3.70 (s, 1 H), and 3.77 (s, 1 H); $\nu_{\text{max.}}(\text{film})$ 2 200 and 2 100 cm^{-1} (Found: <i>M</i> , 378.270. $\text{C}_{24}\text{H}_{34}\text{N}_4$ requires <i>M</i> , 378.278)
	
$\text{R}^1\text{R}^2 = 3,5,5\text{-trimethylcyclohexyl}$ (20)	M.p. 194–198 °C; $\delta(\text{CDCl}_3)$ 1.00, 1.02 (s, 12 H), 1.10 (s, 6 H), 1.60 (m, 14 H), and 5.00 (br s, 2 H); $\nu_{\text{max.}}(\text{film})$ 1 640, 2 210, 3 200, 3 340, and 3 450 cm^{-1} (Found: <i>M</i> , 378.270. $\text{C}_{24}\text{H}_{34}\text{N}_4$ requires <i>M</i> , 378.278)
$\text{R}^1\text{R}^2 = \text{cyclopentyl}$ (21)	M.p. 168–171 °C; $\delta(\text{CDCl}_3)$ 1.80 (m, 16 H), and 5.10, 5.20 (br s, 2 H); $\nu_{\text{max.}}(\text{film})$ 1 645, 2 221, 3 218, 3 340, and 3 450 cm^{-1} (Found: <i>M</i> , 266.150. $\text{C}_{16}\text{H}_{18}\text{N}_4$ requires <i>M</i> , 266.153)
$\text{R}^1\text{R}^2 = \text{cyclohexyl}$ (22)	M.p. 186–190 °C; $\delta(\text{CDCl}_3)$ 1.80 (m, 20 H) and 5.2 (br s, 2 H); $\nu_{\text{max.}}(\text{film})$ 1 660, 2 200, 3 210, 3 300, and 3 430 cm^{-1} (Found: <i>M</i> , 294.170. $\text{C}_{18}\text{H}_{22}\text{N}_4$ requires <i>M</i> , 294.184)
$\text{R}^1\text{R}^2 = 4\text{-}t\text{-butylcyclohexyl}$ (23)	M.p. 252–255 °C; $\delta(\text{CDCl}_3)$ 0.90 (s, 18 H), 1.90 (m, 18 H), and 5.2 (br s, 2 H); $\nu_{\text{max.}}(\text{film})$ 1 659, 2 210, 3 200, 3 324, and 3 420 cm^{-1} (Found: <i>M</i> , 406.300. $\text{C}_{26}\text{H}_{38}\text{N}_4$ requires <i>M</i> , 406.310)
$\text{R}^1\text{R}^2 = 9\text{-fluorenyl}$ (24)	M.p. 278–280 °C; ($[\text{}^2\text{H}_6]$)DMSO- CDCl_3 3.14 (s, 1 H, CHCN), 6.6–7.1 (m, 17 H), and 7.58 (s, 2 H); $\nu_{\text{max.}}(\text{film})$ 1 655, 1 740, 2 200, 3 200, and 3 340 cm^{-1} (Found: <i>M</i> , 458.148. $\text{C}_{32}\text{H}_{18}\text{N}_4$ requires <i>M</i> , 458.154)
$\text{R}^1\text{R}^2\text{CHCH}(\text{X})\text{CN}$	
$\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Bu}^t$, $\text{X} = \text{CN}$ (25)	B.p. 75 °C at 5 mmHg; $\delta(\text{CDCl}_3)$ 1.02 (s, 9 H), 1.35 (d, 3 H), 1.90 (m, 1 H), and 3.95 (d, 1 H) (Found: <i>M</i> , 150.115. $\text{C}_9\text{H}_{14}\text{N}_2$ requires <i>M</i> , 150.116) (Found: C, 72.34; H, 9.0; N, 18.3. $\text{C}_9\text{H}_{14}\text{N}_2$ requires C, 72.0; H, 9.3; N, 18.7%)
$\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Bu}^t$, $\text{X} = \text{CO}_2\text{Et}$ (26)	B.p. 112 °C at 20 mmHg; $\delta(\text{CDCl}_3)$ 1.0 (s, 9 H), 1.25 (t, 3 H), 1.45 (d, 3 H), 3.45 (q, 1 H), 3.65 (d, 1 H), and 4.1 (q, 2 H) (Found: <i>M</i> , 197.146. $\text{C}_{11}\text{H}_{19}\text{N}_2\text{O}_2$ requires <i>M</i> , 197.142) (Found: C, 73.5; H, 10.1; N, 7.4. $\text{C}_{11}\text{H}_{19}\text{N}_2\text{O}_2$ requires C, 73.3; H, 10.5; N, 7.7%)
$\text{R}^1\text{R}^2 = 4\text{-}t\text{-butylcyclohexyl}$, $\text{X} = \text{CN}$ (27)	M.p. 72–74 °C; $\delta(\text{CDCl}_3)$ 0.9 (s, 9 H), 1.67 (m, 10 H), and 3.5 (d, 1 H); $\nu_{\text{max.}}(\text{film})$ 2 250 cm^{-1} (Found: <i>M</i> , 204.159. $\text{C}_{13}\text{H}_{20}\text{N}_2$ requires <i>M</i> , 204.163)

electrolysis, at a potential determined voltammetrically, was continued until the current had fallen to a few milliamps. Typical initial and final currents were 120 mA and 2 mA respectively. The charge passed during such electrolysis was measured using a home-constructed electronic current integrator. The potentiostat was a Chemical Electronics TR70/2A.

The catholyte was added to benzene (100 cm^3) and the solution washed several times with water (200 cm^3 portions). The benzene layer was dried (MgSO_4), the product isolated and recrystallised from ethanol. Mixtures of products were separated and analysed by t.l.c., a suitable solvent system being light petroleum–acetone (10%).

The Reduction of Compound (4).—In this case the crude reduction product was separated into the hydrodimer and hydrogenation products by medium-pressure chromatography [silica gel, Merck 7736 (60H); hydrogenation product eluted with CH_2Cl_2 , the hydrodimer with EtOAc].

New compounds prepared by cathodic reduction are listed in Table 3, together with physical, spectroscopic, and analytical data.

Isomerisation of Compound (20).—The dimeric product obtained from the cathodic reduction of (14) in DMF–HOAc (1M) containing lithium perchlorate (0.1M) was distilled under reduced pressure to give the linear hydrodimer (19), b.p. 160 °C at 0.1 mmHg. This product was also obtained by heating the cyclic hydrodimer (20) in boiling dioxane (100°) for 6 h.

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