

Electrochemical Reductive Ring Cleavage of 1-Cyclopropylethylidenemalononitriles

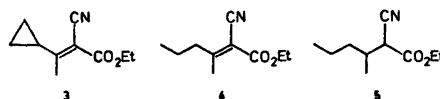
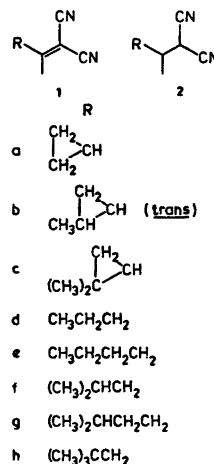
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The electrochemical reduction of 1-cyclopropylethylidenemalononitriles, *1a–c*, in acetonitrile involves ring cleavage after the addition of one electron, giving a product distribution in the case of *1b* and *1c* which reflects the radical nature of the cleavage. Linear sweep voltammetry indicates that the reduction mechanism involves the sequence: electron transfer at the electrode, ring cleavage, electron transfer in solution (disproportionation) and protonation, with the rate determining step being the ring cleavage for *1a* and *1b*, and the electron transfer in solution for *1c*.

Although a study¹ of the effect of alkyl substituents upon the direction of ring cleavage in the lithium-ammonia reduction of acetylcyclopropanes indicated that the species undergoing cleavage was carbanionic, it was not possible to decide whether this species was formed by the addition of one or two electrons to the carbonyl group. An attempt to resolve this by an electrochemical study of the reduction of acetylcyclopropanes in liquid ammonia revealed that these compounds were not electroactive within the cathodic range. We, therefore, reduced these compounds using electro-generated solvated electrons with butyltrimethylammonium fluoroborate as the supporting electrolyte. Under these conditions the same product distributions were obtained as with the lithium-ammonia system, indicating that the same intermediates were involved.² In the presence of tetraethylammonium fluoroborate as the supporting electrolyte, tertiary alcohols were formed by reductive ethylation

of the ring cleaved ketones.³ We now report that the direct electrochemical reduction in acetonitrile of the related alkylidenemalononitriles, *1a–c*, formed by condensing the acetylcyclopropanes with malononitrile, involves ring cleavage by a radical species after the addition of one electron.³



The electrochemical reduction of a related system, **3**, had previously been studied.⁴ This exhibited a 1-electron reduction wave on polarography in anhydrous DMF, and completely irreversible behaviour on cyclic voltammetry. The addition of phenol caused the polarographic wave height to double. Preparative electrolysis

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of **3** in DMF containing both water and acetic acid, gave ring cleavage products **4** and **5**, together with ethyl cyanoacetate, acetylcyclopropane and pentan-2-one formed by hydrolysis of **3** and **4**; no hydrodimers were detected. Thus this type of system was known to undergo reductive ring cleavage, with the electroanalytical data indicating that the cleavage occurred at the radical-anion stage.

The voltammetric behaviour of the 1-cyclopropylethylidenemalononitriles **1a–c** in acetonitrile was similar to that reported⁴ for **3**, and also similar to that of an acyclic analogue **1d** (see Table 1). Thus, as observed previously,⁴ the cyclopropyl group is not involved to any significant extent in the initial reduction process. Some of the voltammetric measurements were complicated by the presence of adsorption maxima, particularly with **1a** and **1b**, and also with **1c** at higher concentrations (see Experimental). The results of a linear sweep voltammetric study of the variation of E_P as a function of (i) the sweep rate (v), (ii) the substrate concentration (C°), and (iii) the concentration of added phenol (Z°) for **1a–c** are also given in Table 1. The variation with the sweep rate could only be measured approximately for **1a** and **1b** due to the adsorption phenomenon, and for the same reason the variation with the concentration of **1c**, while being definitely anodic, could not be determined accurately.

The preparative electrolysis of **1a–c** at -2.4 V *vs.* Ag|0.1 M Ag⁺ in anhydrous acetonitrile gave products similar to those reported⁴ for **3**, although there was no hydrolysis to malononitrile and the corresponding ketones under our conditions. The reduction of **1a** gave the

ring cleaved product **1d**, and in the presence of phenol the latter was further reduced to the saturated malononitrile derivative **2d**. The reduction of **1b** and **1c** both gave mixtures of the ring cleaved products formed by the two alternative modes of cleavage, *viz.* C¹–C² and C¹–C³, **1e** and **1f** from **1b**, and **1g** and **1h** from **1c**, together with the further reduction products **2e** and **2f**, and **2g** and **2h**, respectively. Cleavage of the C¹–C² bond was preferred in both cases, the ratio C¹–C² *vs.* C¹–C³ being between 2 and 9 for **1b** and >30 for **1c**. These results are typical for a radical type cleavage, with the formation of a secondary radical in the case of **1b**, or a tertiary radical in the case of **1c**, being preferred to the formation of a primary radical. Authentic radical cleavage of *trans*-1-acetyl-2-methylcyclopropane and 1-acetyl-2,2-dimethylcyclopropane, using di-*t*-butyl peroxide and butan-2-ol, gave C¹–C² *vs.* C¹–C³ cleavage ratios of 4.4–4.7 and 36–45 respectively.^{1a}

The direction of ring cleavage in the preparative electrolysis of **1b** and **1c** suggests that the cleavage occurs after the initial electron transfer, *i.e.* at the radical-anion stage. This is supported by the cyclic voltammetric behaviour which shows an irreversible 1-electron transfer even at the highest sweep rates (500 Vs⁻¹). In interpreting the E_P behaviour as the sweep rate, concentration of substrate, and concentration of added phenol, are varied, a number of other factors have to be borne in mind, in particular that the formation of the primary reduction products, *e.g.* **1d**, is overall a 2-electron process, and although the n value during an electrolysis without phenol is around one, large amounts of starting material are recovered even though the current has decreased to the background level. This is most probably due to the substrate also functioning as a proton donor to the reduced species, the conjugate base of the substrate being non-reducible.

The absence of any shift in E_P on addition of phenol indicates that protonation of the reduced species occurs after the rate controlling step, and that the initial radical-anion is not protonated. Furthermore, if the initial radical-anion is not protonated, it is even less likely that the cleaved radical-anion will be protonated since the anion will be more stabilised. The increase in wave height in the presence of phenol supports the conclusion that in the

Table 1. Voltammetric behaviour of 1-cyclopropylethylidenemalononitriles (**1a–d**) in CH₃CN/0.4 M Et₄NBF₄.

Com- pound	$E_{1/2}/V^a$	$E_P/V^{a,b}$	$-\frac{\partial E_P}{\partial \log v}$	$\frac{\partial E_P}{\partial \log C^\circ}$	$\frac{\partial E_P}{\partial \log Z^\circ}$
			mV per decade at 25 °C		
1a	-2.01	-2.08	ca. 30	0	0
1b	-2.03	-2.10	ca. 30	0	0
1c	-1.93	-2.00	20.3, 22.0	$\neq 0$	0
1d	-2.08	-2.13	—	—	—

^a *vs.* Ag|0.1 M AgNO₃. ^b 0.20 V s⁻¹.

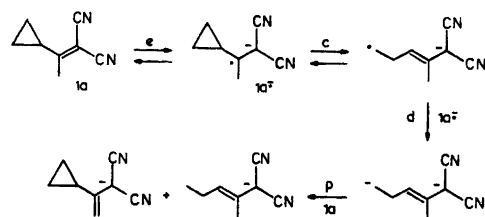
absence of phenol some substrate molecules become deprotonated. The remaining data on the E_P behaviour, although not accurately measured in some cases, fit the criteria presented by Nadjo and Saveant⁵ for the DISP 1 and DISP 2 mechanisms, with *1a* and *1b* following the former and *1c* the latter. Both DISP 1 and DISP 2 have the following reaction sequence:

- (i) $A + e \rightleftharpoons A^{\cdot-}$ (electron transfer at electrode)
 (ii) $A^{\cdot-} \rightleftharpoons B^{\cdot-}$ (ring cleavage)
 (iii) $B^{\cdot-} + A^{\cdot-} \rightarrow B^{2-} + A$ (electron transfer in solution)

with the rate determining step being (ii) for DISP 1 and (iii) for DISP 2. DISP 1 specifically requires $-(\partial E_P/\partial \log v)_{25^\circ\text{C}} = 29.6/n$ mV per decade with no E_P variation with C° or Z° , and DISP 2 requires $-(\partial E_P/\partial \log v)_{25^\circ\text{C}} = 19.7/n$ and $(\partial E_P/\partial \log C^\circ)_{25^\circ\text{C}} = 19.7/n$ mV per decade with no E_P variation with Z° (cf. Table 1). The data for *1a* and *1b* also fit the criteria for an e.c.e. reaction scheme, the latter being very similar to those for DISP 1,⁵ with the second electron transfer occurring at the electrode rather than in solution. We feel, however, that if *1c* follows the DISP 2 mechanism, then *1a* and *1b* are more likely to follow the DISP 1 mechanism than the e.c.e. mechanism. The full mechanism for the formation of the primary reduction products is, therefore, most probably $e-c-d-p-p$ [electron transfer at electrode, chemical reaction (ring cleavage), disproportionation (electron transfer in solution, the initial radical-anion being the most likely electron donor although the cleaved radical-anion could also function in this way), protonation (by the substrate),* protonation (during work-up)], with *c* being rate determining for *1a* and *1b*, and *d* for *1c* (see Scheme 1). The second protonation must occur to some extent on the time scale of a preparative electrolysis in order to account for the formation of secondary reduction products, e.g. *2d*.

The linear sweep voltammetric results may also be compared with predictions for similar

* The data do not exclude the possibility of the disproportionation step and the first protonation step being replaced by a hydrogen atom transfer between the ring opened radical-anion and the substrate radical-anion.



Scheme 1. Reduction mechanism for 1-cyclopropylethyldenemalononitrile (*1a*).

reactions of radical-anions in which the chemical step is a cyclisation instead of a cleavage, and protonation of the cyclised di-anion occurs.⁶ (No predictions specifically concerned with cleavage reactions have been published). We believe that these predictions should also be applicable to a ring cleavage reaction, and indeed, for the specific mechanisms dealt with above, $e-C-d-p-p$ (and $e-C-e-p-p$) and $e-c-D-p-p$, the predicted E_P behaviour⁶ is identical to that from the generalised DISP 1 and DISP 2 cases, respectively.

The kinetic differences which are observed between *1c*, and *1a* and *1b* are consistent with the stabilities of the various intermediates involved in the reactions as follows. (i) The initial cleavage of the radical-anion generates a radical which will be more stable, and therefore more easily formed, when it is tertiary than when it is primary or secondary. Thus this step should be faster for *1c* than for *1a* or *1b*. The ring cleavage in *1c* may also be assisted by the *cis*-methyl group exerting a steric influence on the conformation of the radical-anion (cf. Ref. 1). (ii) In the following disproportionation step a carbanion is generated and this will be more stable, and therefore more easily formed, when it is primary or secondary than when it is tertiary. Thus this step should be faster for *1a* and *1b* than for *1c*.* Then by combining these two factors the observed kinetic behaviour of *1a-c* would be produced. This of course is an oversimplification because for *1b* and *1c* there is an internal competition between primary and secondary or tertiary

* If the third step is a hydrogen atom transfer between the ring-opened radical-anion and the substrate radical-anion, this should also be slower for *1c* than for *1a* and *1b*, again due to the greater stability of the tertiary radical.

sites respectively and this will affect the overall picture. However, there appears to be a delicate balance of electronic effects in these systems which has already been encountered in the lithiumammonia reduction of the corresponding acetylcyclopropanes.^{1a}

EXPERIMENTAL

Substituted acetylcyclopropanes. These were prepared by reacting the corresponding $\alpha\beta$ -unsaturated ketone with dimethyl sulfoxonium methylide.^{7,8} *trans*-Pent-3-en-2-one (21.3 g; from oxidation of *trans*-pent-3-en-2-ol using pyridinium chlorochromate⁹) gave *trans*-1-acetyl-2-methylcyclopropane in two fractions (i) b.p. 87–94°C/20 mmHg (3.2 g), 95% pure, (ii) b.p. 94°C/20 mmHg (5.6 g), 99% pure. 4-Methylpent-3-en-2-one (21.0 g) gave 1-acetyl-2,2-dimethylcyclopropane (9.5 g), b.p. 120°C/80 mmHg, 99% pure.

Alkylidenemalonitriles. Malononitrile (0.05 mol), the ketone (0.05 mol), ammonium acetate (0.005 mol) and glacial acetic acid (0.001 mol) in benzene (50 ml) were heated under reflux until water no longer separated in the Dean–Stark trap (4–5 h). Ether (50 ml) was added to the cooled mixture and the solution was then washed with a saturated, aqueous solution of sodium bicarbonate (100 ml), water (100 ml), and brine (100 ml). After drying (MgSO₄), the ether was removed by rotary evaporation and the residue was purified to give the alkylidene-malononitrile.

The following compounds were prepared: 2-Cyano-3-cyclopropylbut-2-enitrile (*1a*; 57%), m.p. 64–65°C (from ethanol–water below 60°C) from acetylcyclopropane; 2-cyano-3-(*trans*-2-methylcyclopropyl)but-2-enitrile (*1b*; 14%), b.p. 120°C/5.5 mmHg, ¹H NMR [100 MHz, CDCl₃]: δ 1.14 (m, 3H, cyclopropyl protons at C2 and C3), 1.22 (d, *J* 5.0 Hz, CH₂–CH), 1.89 (s, CH₃C=C), and 2.05 (m, cyclopropyl proton at C1), MS[IP 70 eV; *m/e*]: 146, 145, 131, 104 (the accurate mass of *m/e* 146 corresponded to C₉H₁₀N₂). Found: C 72.2, 74.14; H 7.09, 7.21; N 18.3, 18.85. Calc. for C₉H₁₀N₂: C 73.9; H 6.89; N 19.19, from *trans*-1-acetyl-2-methylcyclopropane; 2-cyano-3-(2,2-dimethylcyclopropyl)but-2-enitrile (*1c*; 38%), b.p. 100–101°C/2.5 mmHg, ¹H NMR[100 MHz, CDCl₃]: δ 1.1 (s, *cis*-CH₃), 1.15 (m, *trans*-CH), 1.3 (s, *trans*-CH₃), 1.9 (m, *cis*-CH and CH at C1) and 2.16 (s, CH₃C=C), MS[IP 70 eV; *m/e*]: 160, 159, 145, 118 (the accurate mass of *m/e* 160 corresponded to C₁₀H₁₂N₂). Found: C 65.98, 71.78; H 6.63, 7.04; N 18.01, 20.75. Calc. for C₁₀H₁₂N₂: C 75.0; H 7.54; N 17.5, from 1-acetyl-2,2-dimethylcyclopropane, which although pure by GC and ¹H NMR spectroscopy when freshly prepared, decomposed on standing in air; 2-cyano-3-methylhex-2-enitrile (*1d*; 84%),

b.p. 96–97°C/4 mmHg, from pentan-2-one; 2-cyano-3-methylhept-2-enitrile (*1e*; 86%), b.p. 140–141°C/20 mmHg, from hexan-2-one; 2-cyano-3,5-dimethylhex-2-enitrile (*1f*; 46%), b.p. 119°C/9 mmHg, from 4-methylpentan-2-one; 2-cyano-3,6-dimethylhept-2-enitrile (*1g*; 71%), b.p. 159°C/30 mmHg, from 5-methylhexan-2-one; 2-cyano-3,5,5-trimethylhex-2-enitrile (*1h*; 41%), b.p. 100°C/3.5 mmHg from 4,4-dimethylpentan-2-one. In most cases the ¹H NMR spectrum was almost the same as that of the starting ketone. All compounds exhibited two characteristic strong absorptions in the IR at 2210–2250 and 1569–1610 cm⁻¹. They were colourless when purified, but in the case of liquids became dark coloured on standing.

Alkylmalononitriles. These were prepared by reducing the corresponding alkylidenemalononitriles with triethylamine–formic acid.¹⁰

Triethylamine was added to ice–cold formic acid (98–100%) until the solution became basic. Rotary evaporation of the solution followed by distillation of the residue gave the azeotrope triethylamine–formic acid, b.p. 80°C/3.5 mmHg. The alkylidenemalononitrile (0.02 mol) was added to a solution of the azeotrope (5.4 g) in CH₃CN (40 ml) and the solution was refluxed until no alkylidenemalononitrile remained. Ether (100 ml) and water (100 ml) were added, and the organic layer was separated and washed with water (3 × 100 ml). After drying (MgSO₄) the solvent was evaporated and the residue was distilled to give the alkylmalononitrile. The following compounds were prepared: 2-Cyano-3-methylhexanenitrile (*2d*; 55%), b.p. 97–99°C/5.5 mmHg; 2-cyano-3-methylheptanenitrile (*2e*; 74%), b.p. 99°C/3 mmHg; 2-cyano-3,5-dimethylhexanenitrile (*2f*; 70%), b.p. 90–91°C/2.7 mmHg; 2-cyano-3,6-dimethylheptanenitrile (*2g*; 55%), b.p. 101–103°C/2 mmHg; 2-cyano-3,5,5-trimethylhexanenitrile (*2h*; 42%), b.p. 98–100°C/1.5 mmHg. All of these compounds were pure by GC analysis, and exhibited a nitrile absorption at ν_{\max}^{film} 2250 cm⁻¹, and the expected ¹H NMR spectrum.

Electroanalytical measurements. Polarographic *E*_{1/2} potentials and linear sweep voltammetric peak potentials (*E*_p) were measured relative to the Ag|0.1M AgNO₃ in CH₃CN reference electrode (Luggin capillary), using 1 mM solutions of the substrate in 0.4 M Et₄NBF₄ in acetonitrile. The working electrode for the linear sweep voltammetric experiments was a long drop time capillary electrode; the peak current was maintained approximately constant as the sweep rate (0.1–100 Vs⁻¹) and substrate concentration (0.1–5.0 mM) were varied by varying the delay period after the formation of a new drop. The deviations from reversible behaviour exhibited by a known reversible system *viz.* benzophenone, were used to correct the observed response for an unknown system for the effects of uncompensated cell resist-

ance.¹¹ The measurement of the variation of E_P , with sweep rate for a previously studied system,¹² *N*-prop-2-ylidenepyrrolidinium perchlorate, using this method gave 22.1 and 18.1 mV/decade at 1.0 and 0.135 mM concentrations respectively, compared with the reported¹² value of 18.1 mV/decade at 1.0 mM concentration.

The results are given in Table 1. The polarograms and cyclic voltammograms of *1a* and *1b* are unusual in that they exhibit maxima beyond the first wave or peak and *1c* exhibited similar behaviour at higher concentrations; *1d* behaved normally.

The height of the polarographic wave for *1c* and *1d* corresponds to a 1-electron reduction, by comparison with the wave height of the first electron transfer of benzophenone under the same conditions at various concentrations. For *1a* and *1b* the wave is slightly larger than that expected for a 1-electron reduction, but it is not known how the maxima would affect this value. In all cases, the addition of phenol caused the heights of the waves to double, but no change in $E_{1/2}$ or E_P was observed.

Compounds *1a-c* exhibited totally irreversible behaviour on cyclic voltammetry (0.1 → 500 Vs⁻¹). For *1a* and *1b*, the cathodic E_P did not vary with concentration, but *1c* did show a definite anodic shift with increasing concentration. However, this could not be measured accurately due to the interference of the maximum at higher concentrations. The measurement of the E_P variation with sweep rate was also difficult for *1a* and *1b* due to the same problem. At concentrations > 1 mM, the E_P values were irreproducible, but at lower concentrations (0.1–0.5 mM) a cathodic shift of about 30 mV/decade was observed. The measurement of the E_P with sweep rate for *1c* was straightforward and two determinations (0.1 → 100 Vs⁻¹) gave 20.3 and 22.0 mV/decade, with correlation coefficients greater than 0.99.

Electrolysis procedure. A 0.01 M solution of the alkylidenemalononitrile in 0.1 M Et₄NBF₄ in acetonitrile (50 ml) under nitrogen was electrolysed in a divided cell using a mercury pool cathode at -2.4 V (*vs.* Ag|0.1 M AgNO₃). In general the initial current was *ca.* 200 mA, but it decreased within 10 min to *ca.* 10 mA. Strong agitation of the mercury surface was required to maintain the current at this level. Coulometric measurements¹³ gave an *n* value of *ca.* 1 F mol⁻¹. The electrolysis was terminated after 1 h when the current was 1–2 mA and *ca.* 1.5 F mol⁻¹ had passed. An excess of aqueous ammonium chloride solution was added to the catholyte, together with the GC standard, benzonitrile. The mixture was extracted with ether (2 × 100 ml) and after drying, the organic phase was concentrated and analysed by GC (10 % Carbowax 20 M; 170 °C). In the absence of phenol, a large quantity of starting material was recovered in every case, even though the current had decreased to the background level.

In the presence of phenol, the *n* value was greater than 1 F mol⁻¹ and the electrolysis, as judged by the amount of starting material remaining, was more complete.

Electrolysis of *1a* gave *1d* (24 %) with *1a* (36 %). Examination of the product mixture by mass spectrometry indicated that no dimers had been formed, the highest *m/e* being 134. In the presence of phenol (0.1 M) the products were *1a* (6 %), *1d* (7 %) and *2d* (40 %).

Electrolysis of *1b* gave typically *1e* (29 %), *2e* (3 %), *1f* (15 %), and *2f* (1 %), with *1b* (24 %). The ratio of (*1e* + *2e*)/(*1f* + *2f*) was 2–9.

Electrolysis of *1c* gave typically *1g* (32 %), *2g* (8 %), *1h* (0 %) and *2h* (trace), with *1c* (20 %). The ratio (*1g* + *2g*)/(*1h* + *2h*) was greater than 30. In the presence of phenol (0.1 M), the yield of *2g* increased at the expense of *1g*. Electrolysis of *1g* without added phenol gave *2g* (40 %), with *1g* (38 %).

For both *1b* and *1c*, no dimeric products were detected by mass spectrometry.

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