Cyanomethylation *versus* Reductive Saturation and Hydrodimerisation during the Electroreduction of αβ-Unsaturated Nitriles in Acetonitrile

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Results for the electroduction of cinnamonitrile, 3-methylcinnamonitrile, and acrylonitrile in acetonitrile under a variety of conditions are reported in detail, and the factors which favour the formation of glutaronitrile derivatives (cyanomethylation) *versus* reductive saturation and hydrodimerisation have been identified. Cyanomethylation of acrylonitrile has also been studied using (i) azobenzene–acetonitrile, and (ii) phenylsulphonylacetonitrile–dimethylformamide, as the source of electrogenerated $^{-}CH_2CN$.

We have previously reported [1] that the electroreduction of aromatic carbonyl compounds, PhCOR (R = Me, Ph, H), in acetonitrile gives significant amounts of nitrile products formed by reaction of the electrogenerated cyanomethyl anion ($^{-}CH_2CN$) with the carbonyl compound and with the subsequently formed αβ-unsaturated nitrile, PhCR=CHCN. In order to gain a better understanding of the factors which influence the distribution of the nitrile products *viz.* PhCHR·CH_2CN, PhCR-$(CH_2CN)_2$, $(PhCRCH_2CN)_2$, and to find the electrolysis conditions which give the highest selectivity for the formation of glutaronitrile derivatives, *e.g.* PhCR-$(CH_2CN)_2$, we have now studied the electroreduction of cinnamonitrile (PhCH=CHCN), 3-methylcinnamonitrile (PhCMe=CHCN), and acrylonitrile (CH_2=CHCN) in acetonitrile.

trans-*Cinnamonitrile.*—Since *trans*-cinnamonitrile had been detected as an intermediate in the formation of nitrile products during the electroreduction of benzaldehyde in acetonitrile [1a,2] a study of the reduction of the unsaturated nitrile was undertaken. The cyclic voltammogram of *trans*-cinnamonitrile (2mM in 0.1M-Et_4NBF_4–acetonitrile) at *v* 230 mV s^{-1} exhibits a one-electron, irreversible reduction peak at E_p −2.19 V (*versus* Ag–0.1M-$AgNO_3$–CH_3CN), and the fast following reaction has been shown [for dimethylformamide (DMF) solutions] [3] to involve dimerisation of the radical anion. Preparative electrolysis in wet DMF gives 2-phenylpropiononitrile (20%) and a mixture of ββ-, αα-, and αβ-coupled hydrodimers (80%) in an overall yield of 92%.[4] It seems likely that in acetonitrile the initial reductive processes are similar to those occurring in DMF, except that the solvent may also function as a proton donor, thereby generating $^{-}CH_2CN$. Thus electroreduction of cinnamonitrile in acetonitrile should promote cyanomethylation of the αβ-unsaturated nitrile. By suitable selection of experimental conditions, particularly concentration and temperature, it has been shown (Table 1) that the conversion of PhCH=CHCN to $PhCH(CH_2CN)_2$ can become the major cinnamonitrile consuming process.

All the experiments described in Table 1 were performed under controlled current conditions, and were terminated when the $PhCH(CH_2CN)_2$ concentration had reached its maximum value. Electrolysis beyond this point caused a slight decrease in the $PhCH(CH_2CN)_2$ concentration. Analysis of the samples removed during the electrolyses was by g.l.c., and gave data for PhCH=CHCN, $PhCH_2CH_2CN$, and $PhCH(CH_2CN)_2$, but not for hydrodimers. It was assumed that any PhCH=CHCN not accounted for was converted to hydrodimers or oligomers of PhCH=CHCN. In most experiments no $PhCH_2CH_2CN$ was detected.

An analysis of the results in Table 1 led to the following conclusions concerning the affect of various factors on the yield of $PhCH(CH_2CN)_2$: (a) decreasing the concentration of PhCH=CHCN (exps. 1—4) increases the yield of $PhCH(CH_2CN)_2$, (b) varying the current density (exps. 5, 3, and 6) has no significant effect on the yield of $PhCH(CH_2CN)_2$ or on the amount of PhCH=CHCN not accounted for, (c) increasing the temperature (exps. 6, 9, and 10) favours the chemical reaction over the electrochemical reactions, (d) varying the concentration of the supporting electrolyte (exps. 6—8) has no effect on the yield of $PhCH(CH_2CN)_2$, (e) adding small amounts of water (exps. 12—14) has no effect, but larger amounts of water (exps. 15 and 16) decreases the yield of PhCH-$(CH_2CN)_2$, (f) varying the nature of the supporting electrolyte has very little effect if tetra-alkylammonium salts are used (exps. 6, 17—20), but the formation of $PhCH(CH_2CN)_2$ is completely suppressed if alkali metal salts are used (exps. 21 and 22).

The highest conversion into $PhCH(CH_2CN)_2$, 80% (exp. 11), was achieved by combining the most beneficial factors, *viz.* low concentration of PhCH=CHCN and high temperature (reflux). These conditions however most certainly do not represent the optimum for the formation of $PhCH(CH_2CN)_2$.

The observation that the presence of water up to concentrations of *ca.* 2 500 p.p.m. (exp. 15) has only a small effect on the cyanomethylation of cinnamonitrile is significant in the context of the electroreduction of benzaldehyde in acetonitrile.[2] The formation of cinnamonitrile from benzaldehyde under these conditions would be accompanied by the generation of water (up to 300 p.p.m. for 0.013M-benzaldehyde), and although water should be capable of protonating $^{-}CH_2CN$, it does not appear to seriously interfere with the cyanomethylation process. The presence of water does however affect the current efficiency, the current yield of PhCH-$(CH_2CN)_2$ being 2.3 mol F^{-1} for exp. 6 (dry acetonitrile),

TABLE 1

Reduction of *trans*-cinnamonitrile

Exp.	Conditions [a]	Initial PhCH=CHCN Conc. (mM)	Current (mA)	PhCH=CHCN Charge consumed t [b]/min	10^4F	mol F^{-1}	$PhCH(CH_2CN)_2$ formed yield (%)	mol F^{-1}	PhCH=CHCN lost [c] mol F^{-1}
1		81	40	41	10.2	3.3	21	0.69	2.6
2		42	40	15	3.73	4.6	30	1.4	3.2
3		20	40	5.5	1.37	5.9	46	2.7	3.2
4		10	20	6.5	0.81	5.1	61	3.1	2.0
5		21	80	3.3	1.64	4.9	43	2.1	2.8
6		20	20	12.8	1.59	5.0	46	2.3	2.7
7	0.2M-Et_4NBF_4	20	20				49		
8	0.023M-Et_4NBF_4	23	20				47		
9	40—46 °C	20	20	11	1.37	5.8	57	3.3	2.5
10	72—76 °C	20	20	7.5	0.93	8.7	74	6.4	2.3
11	79—81 °C	10	10	10	0.62	6.6	80	5.3	1.3
12	*d*	23	20				46		
13	2.5 × 10^{-4} vol% H_2O	24	20				44		
14	2.5 × 10^{-2} vol% H_2O	23	20				47		
15	2.0 × 10^{-1} vol% H_2O	23	20	29	3.61	2.6	36	0.94	1.7
16	2.5 × 10^{-1} vol% H_2O	23	20	17 [e]	2.11 [e]		20 [e]		
17	0.1M-Et_4NI	21	20				46		
18	0.1M-Et_4NOTs	22	20	20	2.49	3.3	42	1.4	2.3 [f]
19	0.1M-Bu_4NBF_4	22	20				45		
20	Saturated Me_4NBF_4	21	20				38 [g]		
21	0.1M-NaI	21	20	20 [h]	2.49	0.80	0	0.0	0.8 [h]
22	0.1M-$LiClO_4$	21	20	16 [i]	1.99	0.75	0	0.0	0.9 [j]

[a] Except where stated otherwise the conditions were: 0.1M-Et_4NBF_4-dry acetonitrile (38 ml); 22—24 °C. [b] Time required for $[PhCH(CH_2CN)_2]$ to reach maximum value. [c] Unaccounted for by cyanomethylation or by reduction to $PhCH_2CH_2CN$. [d] Acetonitrile passed through a column of freshly activated alumina before use. [e] For 53% conversion of PhCH=CHCN in 17 min. [f] 3% $PhCH_2CH_2CN$. [g] For 80% conversion of PhCH=CHCN. [h] For 19% conversion of PhCH=CHCN. [i] For 14% conversion of PhCH=CHCN. [j] 5% $PhCH_2CH_2CN$.

but only 0.94 mol F^{-1} for exp. 15 (2 500 p.p.m. H_2O), for electrolyses at the same current density.

Since almost all of the electrolyses which were examined in detail had current yields of $PhCH(CH_2CN)_2$ of >1 mol F^{-1} (exceptions, exps. 1 and 15), the cyanomethylation process is catalytic, with a chain length of >5 under favourable conditions (exps. 10 and 11). Each electron transferred from the cathode to a molecule of PhCH=CHCN should result in the subsequent generation of one molecule of $^-CH_2CN$, which can add to a further molecule of PhCH=CHCN. The initial adduct, the conjugate base of $PhCH(CH_2CN)_2$, can then abstract a proton from the solvent regenerating $^-CH_2CN$. Clearly the highest current yields will be achieved when the Michael addition and proton abstraction are faster than the consumption of PhCH=CHCN by reduction at the electrode.

3-*Methylcinnamonitrile*.—3-Methylcinnamonitrile had already been shown [1a,2] to be an intermediate in the formation of nitrile products during the electroreduction of acetophenone in acetonitrile. The cyclic voltammogram of 3-methylcinnamonitrile (1mM in 0.1M-Et_4NBF_4–acetonitrile) at *v* 200 mV s^{-1} exhibits an almost totally reversible, one-electron reduction at −2.30 V ($i_{p,a}/i_{p,c}$ 0.93), and a somewhat smaller, irreversible peak at −2.71 V [$i_{p,c}$ (2)/$i_{p,c}$ (1) 0.72, i_d (2)/i_d (1) 0.94].

The results of some controlled potential reductions of 3-methylcinnamonitrile in acetonitrile are given in Table 2. In this case the products were analysed for PhCMe=CHCN, $PhCHMeCH_2CN$, $PhCMe(CH_2CN)_2$, and the hydrodimer, 1-amino-2-cyano-3,4-dimethyl-3,4-diphenylcyclopent-1-ene, formed by base catalysed cyclisation of 3,4-dimethyl-3,4-diphenyladiponitrile. The latter can exist in two diastereoisomeric forms, DL and *meso*, which on cyclisation would give two DL forms of 1-amino-2-cyano-3,4-dimethyl-3,4-diphenylcyclopent-1-ene, DL and D'L', respectively. Although a definite assignment was not made, it is felt that those factors which (i) favour the formation of the DL-hydrodimer in the reduction of acetophenone,[5,6] and (ii) favour the faster elution of the *meso*-hydrodimer of acetophenone on h.p.l.c. analysis, will have corresponding effects on the formation and properties of the hydrodimers of 3-methylcinnamonitrile. Thus we tentatively assign the more rapidly eluted isomer on h.p.l.c. analysis as the D'L' form, and the major isomer as the DL form (see column 10, Table 2).

The most obvious conclusion to be drawn from the results in Table 2 is that direct reduction to $PhCHMeCH_2CN$ is much more important in this case, compared to that of PhCH=CHCN, and that cyanomethylation is less important. Both probably result from a slower cyanomethylation step. With the exception of exp. 1, there is an inverse correlation between the yield of $PhCMe(CH_2CN)_2$, as a percentage of the total products detected, and the (initial) current density, the lowest current density (exp. 3) giving the highest yield (22%) and the highest current density (exp. 5) giving the lowest yield (7%), irrespective of other experimental differences, *cf.* PhCH=CHCN. Surprisingly the addition of water does not have a dramatic effect upon either the yield of $PhCHMeCH_2CN$ (compare exps. 4 and 5 with 1 and 2), or

on the ratio of $PhCHMeCH_2CN$ to hydrodimer. However, in view of the irreproducibility of the results (compare exps. 1 and 2), we feel it would be unwise to pursue the analysis further.

Acrylonitrile.—The cyanomethylation of acrylonitrile by electroreduction in acetonitrile had already been remainder (exps. 12—21) were allowed to continue until all the acrylonitrile had been consumed. Since the objective was to achieve a high selectivity for cyanomethylation with a minimum amount of electroreduction, all experiments were run at a low current density (*ca.* 1 mA cm^{-2}), *cf.* the current densities used in ref. 7 were

TABLE 2

Reduction of 3-methylcinnamonitrile

Exp.	Conditions [a]	Potential (V) [b]	Initial current (mA)	n/F mol^{-1}	Total yield of identified products (%)	Distribution of products (%)		
						$PhCHMeCH_2CN$	$PhCMe(CH_2CN)_2$	Hydrodimers [c] (DL : D'L') [d]
1		−2.6	480	1.38	77	23	30	47 (5.2 : 1)
2		−2.6	140	3.37	42	31	14	55 (5.7 : 1)
3		−3.0	62	0.70	77	13	22	65 (6.6 : 1)
4	0.05 vol% H_2O–0.1M-Bu_4NBF_4	−2.6	260	2.26	85	25	8	67 (8.0 : 1)
5	0.3 vol% H_2O–0.1M-Bu_4NBF_4	−2.6	450	1.73	74	42	7	51 (6.3 : 1)
6	0.1M-Bu_4NBF_4–0.01M-$LiClO_4$	−2.5	140	1.33	92	32	14	54 (10.0 : 1)
7	DMF solvent	−2.6	134	1.00	70	21		79 (13.1 : 1)

[a] Except where stated otherwise the conditions were: 0.1M-3-methylcinnamonitrile, 0.1M-Et_4NBF_4–dry acetonitrile (50 ml), 16 °C. [b] *versus* Ag–0.1M-$AgNO_3$ in acetonitrile. [c] 1-Amino-2-cyano-3,4-dimethyl-3,4-diphenylcyclopent-1-ene. [d] Ratio of diastereoisomers of hydrodimer (see text).

reported in a Japanese patent.[7] The major products were glutaronitrile and adiponitrile, the selectivity for the formation of these products being 34—16 and 42—37%, respectively, for 77—93% conversion of acrylonitrile.

The molar ratio of glutaronitrile to adiponitrile was 1.7—0.87. Our objective was to find electrolysis conditions which give a high molar ratio of glutaronitrile to adiponitrile together with high selectivities. While the former has been achieved, the selectivities were not high with most of the acrylonitrile consumed being converted into oligomers.

The cyclic voltammogram of acrylonitrile (2mM in 0.1M-Et_4NBF_4–acetonitrile) at v 250 mV s^{-1} exhibits a totally irreversible reduction at −2.52 V, which is still irreversible at v 25 V s^{-1}. The reduction products in completely aprotic conditions are adiponitrile and oligomers of acrylonitrile,[8] but under less aprotic conditions the hydrodimer predominates.[8,9] The oligomerisation which occurs in the absence of a proton donor most probably involves reaction of the primary dimerisation product, adiponitrile dianion, with acrylonitrile. In acetonitrile as the solvent, adiponitrile dianion could abstract protons from the solvent and thus generate the $^-CH_2CN$ required for cyanomethylation.

The results of a series of controlled current electrolyses in acetonitrile are given in Table 3. A preliminary investigation indicated that the highest selectivity for the formation of glutaronitrile occurred at *ca.* 10 min electrolysis time, when *ca.* 30% of the acrylonitrile had been consumed. The first series of experiments (exp. 1—11) were therefore terminated at 10 min; the 20—50 mA cm^{-2}. No evidence for the formation of propiononitrile (>7mM), 2-methylglutaronitrile (the αβ-coupled hydrodimer), or 1-amino-2-cyanocyclopent-1-ene (the cyclised hydrodimer) was obtained for any of the electrolyses. An unidentified unsaturated C_6-dinitrile was detected in most of the electrolyses (see Experimental section and Table 3), its concentration increased and then decreased during the course of an electrolysis with a maximum yield of >5%. This product was not formed when *NN*-dimethyl-*p*-nitroaniline, a radical inhibitor, was present (exps. 17 and 18).

An analysis of the results in Table 3 led to the following conclusions concerning the affect of various factors on the yield of glutaronitrile: (a) decreasing the concentration of acrylonitrile (exps. 12—16) increases the yield of glutaronitrile while the yield of adiponitrile decreases slightly, leading to an increase in the molar ratio of these products, (b) increasing the temperature (exps. 7—9, and 10 and 11) favours cyanomethylation *versus* hydrodimerisation, (c) increasing the concentration of the supporting electrolyte (exps. 1 and 2 *versus* 11) has little effect on cyanomethylation *versus* hydrodimerisation, (d) the addition of water (exp. 5) or acetic acid (exp. 4) totally suppresses cyanomethylation, significantly reduces both the overall conversion and the formation of the unsaturated C_6-dinitrile, but leaves the formation of adiponitrile largely unchanged.

As with cinnamonitrile, the most important factors affecting the yield of the cyanomethylation product are concentration and temperature, and although under certain conditions high molar ratios of glutaronitrile to adiponitrile can be obtained, a high proportion of the

acrylonitrile consumed is not being accounted for. We assume that this acrylonitrile is being consumed by polymerisation reactions with adiponitrile mono- or di-anion,* and with glutaronitrile mono-anion.

all the acrylonitrile had been consumed when only 3% of the azobenzene had been reduced, the major reaction pathway most probably involves anionic polymerisation of acrylonitrile.

TABLE 3

Reduction of acrylonitrile

Exp.	Conditions [a]	Initial CH_2=CHCN conc. (mM)	Conversion of CH_2=CHCN (%)	Yield (%) (Selectivity [b] [%]) Glutaronitrile	Adiponitrile	Unsaturated C_6-dinitrile	Molar ratio glutaronitrile / adiponitrile
1			32	2.4 (7.5)	0.32 (1.0)	0.74 (2.3)	15
2			33	3.5 (10.6)	0.38 (1.2)	1.7 (5.2)	18
3	20 min electrolysis		45	5.0 (11.1)	0.84 (1.9)	2.7 (6.0)	12
4	+0.15 mmol HOAc		17	0.0 (0.0)	0.44 (2.6)	0.02 (0.1)	0.0
5	+0.67 vol% H_2O		21	0.0 (0.0)	0.50 (2.4)	0.02 (0.1)	0.0
6	+0.045 mmol *p*-HOC_6H_4OH		31	1.6 (5.2)	0.36 (1.2)	0.92 (3.0)	8.8
7	13 °C		25	2.1 (8.4)	0.52 (2.1)	2.0 (8.0)	8.1
8	19 °C		26	4.3 (16.5)	0.58 (2.2)	1.3 (5.0)	15
9	26 °C		26	5.7 (21.9)	0.87 (3.3)	1.4 (5.4)	13
10	13 °C–0.3M-Et_4NBF_4		23	2.1 (9.1)	0.61 (2.7)	0.96 (4.2)	6.9
11	20 °C–0.3M-Et_4NBF_4		21	5.3 (25.2)	0.65 (3.1)	0.82 (3.9)	16
12		90	*c*	18	6	*d*	6.0
13		45	*c*	26	5	*d*	10
14		46	*c*	23	3	*d*	15
15		24	*c*	46	3	*d*	31
16		12	*c*	45	4	*d*	22.5
17	+0.035 mol% *p*-$Me_2NC_6H_4NO$	12	*c*	47	3	*e*	31
18	+0.45 mol% *p*-$Me_2NC_6H_4NO$	12	*c*	51	3	*e*	34
19	0.3M-Et_4NBF_4	46	*c*	32	6	*d*	11
20	0.3M-Et_4NOTs	46	*c*	17	10	*d*	3.4
21	34—37 °C	45	*c*	32	6	*d*	11

[a] Except where stated otherwise the conditions were: 10 mmol acrylonitrile in 0.1M-Et_4NBF_4–dry acetonitrile (150 ml), 21—24 °C. Current 10 mA for 10 min. [b] Based on CH_2=CHCN consumed. [c] Electrolysis continued until all acrylonitrile consumed ∴ yield = selectivity. [d] Generated and then destroyed. [e] Not detected throughout electrolysis.

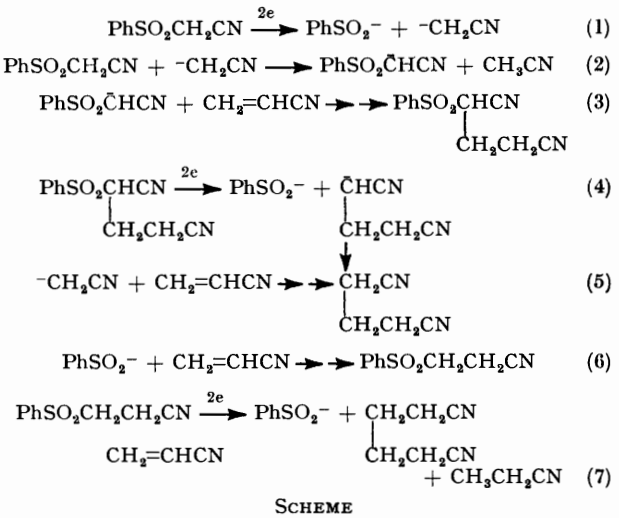
As an alternative to the electrogeneration of $^-CH_2CN$ by the reduction of acrylonitrile in acetonitrile, we have explored the use of other probases *viz.* azobenzene in acetonitrile [11] and phenylsulphonylacetonitrile in DMF.[12] We had previously used azobenzene in acetonitrile,[1b,c] and phenylsulphonylacetonitrile in DMF [1d] to generate $^-CH_2CN$ in an electroanalytical method [1b,c] for studying the rate of addition of $^-CH_2CN$ to aromatic carbonyl compounds and αβ-unsaturated nitriles. The formation of glutaronitrile (20%) by the electroreduction of cyanomethylsulphonium toluene-*p*-sulphonate in the presence of acrylonitrile has been reported.[13]

A controlled potential reduction of a mixture of azobenzene and acrylonitrile in acetonitrile at −2.0 V, sufficiently cathodic to reduce azobenzene [$E_{p,c}$ (1) −1.80 V (reversible), $E_{p,c}$ (2) −2.18 V (irreversible)], but not acrylonitrile ($E_{p,c}$ −2.55 V), gave glutaronitrile (26.5%) and no adiponitrile. The unsaturated C_6-dinitrile was also formed and consumed during the electrolysis. As in the electrolyses of acrylonitrile, most of the substrate was not accounted for, and since

A similar reduction of a mixture of phenylsulphonylacetonitrile and acrylonitrile in DMF at −1.8 V resulted in the formation of glutaronitrile and adiponitrile, together with acetonitrile and propiononitrile. The formation of adiponitrile and propiononitrile, direct reduction products of acrylonitrile, is surprising considering the electrolysis potential ($E_{p,c}$ for acrylonitrile in DMF −2.55 V). A further unexpected observation was that glutaronitrile continued to be formed long after all the acrylonitrile had been consumed. However the latter can be rationalised by the pathway shown in the Scheme. Phenylsulphonylacetonitrile undergoes a two-electron reduction to give $PhSO_2^-$ and $^-CH_2CN$ [step (1)], but in the absence of competing reactants $^-CH_2CN$ deprotonates a molecule of $PhSO_2CH_2CN$ [step (2)]. The polarographic and linear sweep voltammetric behaviour of $PhSO_2CH_2CN$ therefore involves a 1-electron reduction wave/peak.[1d] For reduction of $PhSO_2CH_2CN$ in the presence of acrylonitrile, $^-CH_2CN$ can react by two routes, deprotonation of $PhSO_2CH_2CN$ as before [step (2)] and Michael addition to acrylonitrile to give glutaronitrile [step (5), the direct route]. The anion $PhSO_2\bar{C}HCN$ can also react with acrylonitrile in a Michael addition to give $PhSO_2CH(CN)CH_2CH_2CN$ [step (3), see below] which can be reduced in a similar manner to $PhSO_2CH_2CN$ to give $PhSO_2^-$ and $NC\bar{C}H$-CH_2CH_2CN, and hence glutaronitrile [step (4); the indirect route]. From the yield of acetonitrile (50%), it

* Baizer and Anderson have reported [10] that electroreduction of acrylonitrile in dry acetonitrile gives polyacrylonitrile (*ca.* 50%) with an average molecular weight of 982. A hydrotrimer, 1,3,6-tricyanohexane, and two hydrotetramers, 1,3,5,8- and 1,3,6,8-tetracyano-octane, were characterised. In the presence of water, no polyacrylonitrile was formed; *e.g.* the absence of glutaronitrile in exp. 5 is presumably due to protonation by the water preventing the formation and reaction of $^-CH_2CN$.

appears that almost all $^{-}CH_2CN$ is consumed by reaction (2) and that the major route to glutaronitrile is *via* reactions (3) and (4). It is possible that adiponitrile and propiononitrile are formed by reduction of the Michael adduct of $PhSO_2^-$ and acrylonitrile,[14] reactions (6) and (7). In contrast to the previous electrolyses involving acrylonitrile, most of the acrylonitrile (70%) was accounted for in the products glutaronitrile, adiponitrile, and propiononitrile, and the formation of glutaronitrile, instead of being a catalytic process involving regeneration of $^{-}CH_2CN$ (*cf.* azobenzene–acrylonitrile in acetonitrile electrolysis), is more directly related to the charge passed.



SCHEME

In order to obtain further support for the Scheme, $PhSO_2CH(CN)CH_2CH_2CN$ was prepared and its electrochemical behaviour was studied. The preparation involved treating the conjugate base of $PhSO_2CH_2CN$ with acrylonitrile (see Experimental section). The occurrence of reaction (3) is thus established. The electroanalytical behaviour of $PhSO_2CH(CN)CH_2CH_2CN$ (2mM in 0.1M-Et_4NBF_4–DMF) is very similar to that of $PhSO_2CH_2CN$,[1d] exhibiting a one-electron polarographic wave at $E_{\frac{1}{2}}$ −2.14 V, and an irreversible one-electron peak at $E_{p,c}$ −2.20 V on cyclic voltammetry (*v* 200 mV s^{-1}), slightly less cathodic than the corresponding wave/peak for $PhSO_2CH_2CN$. Preparative electroreduction of $PhSO_2CH(CN)CH_2CH_2CN$ in DMF, without an added proton donor, at −2.4 V gave glutaronitrile (44%) as the only nitrile-containing product, with an *n* value of 1.09. Combining the electroanalytical and preparative results, we conclude that $PhSO_2CH(CN)CH_2CH_2CN$ undergoes a two-electron, reductive cleavage to give benzenesulphinate anion and the conjugate base of glutaronitrile [reaction (4)]. In the absence of an added proton donor, the latter deprotonates a further molecule of the substrate, leading to an *n* value of 1 and a maximum yield of glutaronitrile of 50%. The proposal that the major route to glutaronitrile in the co-electrolysis of $PhSO_2CH_2CN$ and acrylonitrile is *via* reactions (3) and (4) is thus demonstrated to be sound. The further proposal that adiponitrile and propiononitrile are formed *via* reactions (6) and (7) is less sound. Although reaction (6) has been shown [14] to occur, $PhSO_2CH_2CH_2CN$ is much less readily reduced than either $PhSO_2CH_2CN$ or $PhSO_2CH(CN)CH_2CH_2CN$ *viz.* $E_{\frac{1}{2}}$ −2.53 V (*n* 1.20) and $E_{p,c}$ −2.59 V (*v* 200 mV s^{-1}, irreversible) (both for 2mM solutions in 0.1M-Et_4NBF_4–DMF), and if formed during the coelectrolysis of $PhSO_2CH_2CN$ and acrylonitrile it is unlikely to be reduced at the potential used (−1.8 V).

In view of the occurrence of reactions (3) and (6), the reported [1d] decrease in $i_{p,c}$ of acrylonitrile on addition of $PhSO_2CH_2CN$ is probably not due solely to the removal of acrylonitrile by the addition of the electrogenerated $^{-}CH_2CN$ [step (5)]. These other addition reactions no doubt make some contribution towards decreasing the concentration of acrylonitrile at the electrode surface. The situation is further complicated by the fact that the product of reaction (6) is reduced at about the same potential as acrylonitrile.

EXPERIMENTAL

Acetonitrile (Fisons SLR grade) was purified by the method of Forcier and Olver,[15] which involved removal of acrylonitrile by treatment with sodium hydride as the first stage. The purified solvent (<100 p.p.m. H_2O) was stored over freshly activated molecular sieve (Linde type 4Å).

DMF was dried by storing over freshly activated molecular sieve (Linde type 3Å or 4Å, 225 g l^{-1}) for at least 3 days before use.

Preparative electrolyses were performed in a divided cell (two concentric glass cylinders, the inner cylinder being the anodic compartment and separated by a sintered glass disc at its base from the outer cathodic compartment), under nitrogen, with a stirred mercury pool (area *ca.* 11 cm^2) as the working electrode and a carbon rod as the secondary electrode.

Electrolyses of trans-*Cinnamonitrile*.—The standard conditions involved controlled current electrolysis at 20 mA (c.d. *ca.* 2 mA cm^{-2}) of 20mM-cinnamonitrile in 0.1M-tetraethylammonium fluoroborate in dry acetonitrile (50 ml) at 22—24 °C. Samples (0.5 ml) were removed during the course of the electrolysis, and after adding the g.l.c. standard (*o*-nitroaniline) these were analysed (10% ApL at 195 °C) for (in order of elution): 3-aminocrotononitrile, 4-amino-2,6-dimethylpyrimidine (dimer and trimer of acetonitrile respectively), 3-phenylpropiononitrile, *cis*-cinnamonitrile, *trans*-cinnamonitrile, *o*-nitroaniline, and 3-phenylglutaronitrile. The product assignments were confirmed by g.l.c.–m.s. The results are given in Table 1.

3-*Phenylglutaronitrile*.—This was prepared by the method of Schiemenz and Engelhard.[16] The product (88%), b.p. 150—154 °C at 0.3 mmHg, had δ ($CDCl_3$) 2.85 (4 H, d, *J* 6 Hz, CH_2CN), 3.2—3.7 (1 H, m, CH), and 7.38 (5 H, s, Ph). G.l.c.–m.s. showed the presence of trace amounts (<1%) of *cis*- and *trans*-cinnamonitrile.

3-*Phenylpropiononitrile*.—Hydrogenation of cinnamonitrile (10 mmol) in ethyl acetate (75 ml) and acetic acid (10 ml) over 10% palladium on charcoal (12 mg) at atmospheric pressure during 16 h gave 3-phenylpropiononitrile,

b.p. 120—123 °C at 30 mmHg. It had δ ($CDCl_3$) 2.4—3.1 (4 H, m, CH_2CH_2) and 7.27 (5 H, s, Ph).

Electrolyses of 3-Methylcinnamonitrile.—0.1M-3-Methylcinnamonitrile [17] in 0.1M-tetraethylammonium fluoroborate in dry acetonitrile (50 ml) was reduced under controlled potential conditions. When no attempt was made to control the temperature of the cell, the temperature increased during the first few minutes and this was accompanied by an increase in current. Thereafter the current decreased exponentially. There was no initial increase in the current when the temperature was controlled. The electrolyses were terminated when the current had decreased to a constant level (sometimes as high as 40 mA). An excess of aqueous ammonium chloride solution was added to the catholyte, followed by the standards for g.l.c. (benzonitrile) and h.p.l.c. (*m*-nitroacetanilide) analysis. The mixture was extracted with either ether or methylene chloride (2 × 100 ml), the extracts were combined, washed with water (2×), dried ($MgSO_4$), and concentrated by rotary evaporation at <50 °C.

Ether was unsuitable as the extraction solvent when the sample was to be analysed by h.p.l.c. due to preferential loss of the standard; methylene chloride however was found to be satisfactory.

G.l.c. analyses were performed on a 10% ApL column with temperature programming (165 °C for 12 min, then increasing at 8 °C min^{-1} to 230 °C). H.p.l.c. analyses were performed using Spherisorb Alumina (7 μm) (10 cm × 0.5 cm) with 20% ethyl acetate (0.5% H_2O w/w) in n-hexane. The results, given in Table 2, are accurate to ±5% for 3-phenylbutyronitrile, to ±10% for 3-methyl-3-phenylglutaronitrile (both by g.l.c.), and to ±5% for 1-amino-2-cyano-3,4-dimethyl-3,4-diphenylcyclopent-1-ene (h.p.l.c.).

3-Methyl-3-phenylglutaronitrile.—Sodium hydride (0.58 g, 24 mmol) was treated, with dry acetonitrile (300 ml) under nitrogen. Tetraethylammonium chloride (4.05 g, 25 mmol) was added to the solution, and after the sodium chloride has separated (30 min) 3-methylcinnamonitrile (3.00 g, 21 mmol) was added. The solution was refluxed under nitrogen during 14 h. An excess of aqueous ammonium chloride was added and the product was extracted into ether (3 × 100 ml). Column chromatography and distillation gave the glutaronitrile (33%), b.p. 190 °C at 5 mmHg, which had $\nu_{max.}$ (film) 2 245 cm^{-1}; δ ($CDCl_3$) 1.67 (3 H, s, CH_3), 2.80 (4 H, s, CH_2), and 7.32 (5 H, s, Ph); *m/e* 184, 144, 118, 103, 91, and 77.

3-Phenylbutyronitrile.—Hydrogenation of 3-methylcinnamonitrile as described above for cinnamonitrile, gave 3-phenylbutyronitrile, b.p. 122 °C at 1.3 mmHg, which had $\nu_{max.}$ (film) 2 242 cm^{-1}, δ ($CDCl_3$) 1.40 (3 H, d, *J* 7.0 Hz, CH_3), 2.50 (2 H, d, *J* 7.0 Hz, CH_2), 3.11 (1 H, m, *J* 7.0 Hz, CH), and 7.25 (5 H, m, Ph).

1-Amino-2-cyano-3,4-dimethyl-3,4-diphenylcyclopent-1-ene.—3-Methylcinnamonitrile (5.7 g, 0.04 mol) was added to sodium (0.92 g, 0.04 g atom) in tetrahydrofuran (150 ml), and the mixture was refluxed during 12 h. The unreacted sodium was destroyed with methanol (50 ml) and then water (100 ml) was added. The product was isolated by extraction with ether and was crystallised from hexane, m.p. 165—167 °C, $\nu_{max.}$ (Nujol) 3 420, 3 340 (NH_2), 2 170 (CN), and 1 690 cm^{-1} (C=C); $\lambda_{max.}$ (EtOH) 264 nm, δ ($CDCl_3$) 1.01 (3 H, s, CH_3), 1.1 (3 H, s, CH_3), 2.34 (1 H, d, *J* 16 Hz, C*H*H), 3.31 (1 H, d, *J* 16 Hz, CH*H*), 4.79 (2 H, s, NH_2), and 7.2 (10 H, m, 2Ph); *m/e* 288 (M^+) and 273 ($M - CH_3$).

Electrolyses of Acrylonitrile.—Acrylonitrile (10 mmol) in 0.1M-tetraethylammonium fluoroborate in dry acetonitrile (150 ml) was reduced under controlled current conditions. At the end of the electrolysis, the catholyte solution was distilled under vacuum at room temperature and the distillate was collected in a trap at −80 °C. The volume of the distillate was adjusted by adding purified acetonitrile and the amount of acrylonitrile present was determined by reaction with dodecanethiol [18] as follows. A 10 ml sample of the distillate was added to 0.125M ethanolic dodecanethiol (10 ml), followed by 1M ethanolic potassium hydroxide (10 ml). After 2.0 min, acetic acid (1—2 ml) was added to quench the reaction and the solution was diluted to 75 ml with ethanol. The excess of dodecanethiol was then back titrated with 0.1N-iodine solution. All determinations were performed in duplicate, and control experiments indicated that there was no interference from water, acetonitrile, tetraethylammonium fluoroborate, or propiononitrile.

The residue from the distillation was extracted with chloroform, concentrated, and analysed by g.l.c. using *trans*-cinnamonitrile or diethyl phthalate as the standard [10% ApL at 174 °C, order of elution: 3-aminocrotononitrile, glutaronitrile, 2-methylglutaronitrile (all unresolved), adiponitrile, 4-amino-2,6-dimethylpyrimidine, 1-amino-2-cyanocyclopent-1-ene, and *trans*-cinnamonitrile. 5% Carbowax 20M at 180 °C, order of elution: 2-methylglutaronitrile, glutaronitrile, 3-aminocrotononitrile, then adiponitrile and 4-amino-2,6-dimethylpyrimidine unresolved, diethyl phthalate, and 1-amino-2-cyanocyclopent-1-ene (*trans*-cinnamonitrile was coincident with glutaronitrile)].

Many product mixtures contained an unidentified compound (A) (<2%), which was resolved in 10% ApL but which was not resolved from 2-methylglutaronitrile on 5% Carbowax 20M. G.l.c.–m.s. indicated that this component [*m/e* 106 (36%, M^+), 66 (100, $M - CH_2CN$), 52 (15), and 39 (49)], was not 2-methylglutaronitrile, and was most probably an unsaturated C_6-dinitrile, *e.g. cis-* or *trans*-$NCCH_2CH_2CH{=}CHCN$, *trans*-$NCCH_2CH{=}CHCH_2CN$, or $CH_2{=}C(CN)CH_2CH_2CN$, but not *cis*-$NCCH_2CH{=}CHCH_2CN$ (no *m/e* 39 peak).[19]

Some electrolyses were monitored by periodically removing samples from the catholyte solution. The sample was initially analysed by g.l.c. (15% PEG at 50 °C) to determine the acrylonitrile (eluted before CH_3CN) and the propiononitrile (eluted in the tail of the CH_3CN peak) concentrations. Propiononitrile would have been detected if >7mM, but it was never observed. The sample was subsequently analysed for the higher boiling components using diethyl phthalate as the standard and the same g.l.c. conditions as for a ' worked-up ' sample.

Electrolysis of Azobenzene in the Presence of Acrylonitrile.—Azobenzene (3.78 mmol) and acrylonitrile (1.94 mmol) in 0.1M-tetraethylammonium fluoroborate–acetonitrile (50 ml) was reduced under controlled potential conditions at −2.0 V. The current was initially 70 mA, but this decreased to 10 mA after 1 min. The maximum yield of glutaronitrile (26.5%) coincided with the total consumption of acrylonitrile; only 5.5×10^{-2} F mol^{-1} of azobenzene had passed at this stage. The unsaturated C_6-dinitrile was also formed and consumed during the electrolysis, but adiponitrile was not formed. The electrolysis was terminated after 0.27 F mol^{-1} of azobenzene had passed; 9% of the azobenzene had been consumed.

Electrolysis of Phenylsulphonylacetonitrile in the Presence of Acrylonitrile.—Phenylsulphonylacetonitrile (3.8 mmol)

and acrylonitrile (1.9 mmol) in 0.1M-tetraethylammonium fluoroborate–DMF (50 ml) was reduced under controlled potential conditions at −1.8 V (*versus* Ag–0.1M-$AgNO_3$–DMF). The current was initially only *ca.* 20 mA, but it steadily increased to *ca.* 750 mA and then remained at this level. Both $PhSO_2CH_2CN$ and acrylonitrile had been totally consumed by 1 F mol^{-1} of $PhSO_2CH_2CN$, and acetonitrile (50%, based on $PhSO_2CH_2CN$), glutaronitrile (20%, based on acrylonitrile), adiponitrile (14%, based on acrylonitrile), and propiononitrile (16%, based on acrylonitrile), had been formed. Thereafter adiponitrile and propiononitrile ceased to be formed, but the yield of glutaronitrile continued to increase to 40% at 3.1 F mol^{-1} of $PhSO_2CH_2CN$ when the electrolysis was terminated, while the yield of acetonitrile decreased to 40%.

2-Phenylsulphonylglutaronitrile.—A solution of phenylsulphonylacetonitrile (2.0 g) in acetonitrile (200 ml) was stirred with an excess of sodium hydride for 6 h. The formation of the conjugate base of the substrate was followed by monitoring the absorption maximum at 296 nm.[1d] The excess of sodium hydride was removed and one equivalent of acrylonitrile was added. After stirring for 45 min, the solution was filtered and the filtrate was acidified with acetic acid before the solvent was removed *in vacuo*. The residue was dissolved in ether, washed with water and then concentrated to give a light-brown oil which crystallised on standing. It was recrystallised from ethanol to give pure *2-phenylsulphonylglutaronitrile* (0.68 g, 26%) as crystals, m.p. 72—73 °C (Found: C, 56.6; H, 4.2; N, 12.15. $C_{11}H_{10}N_2O_2S$ requires C, 56.4; H, 4.25; N, 11.95%), $\nu_{max.}$ (Nujol) 2 250 cm^{-1}, δ ($CDCl_3$) 2.1—2.9 (4 H, m, CH_2-CH_2), 4.1—4.3 (1 H, m, CH), and 7.5—8.1 (m, Ph), δ_C ($CDCl_3$) 14.78 ($CHCH_2CH_2$), 23.01 (CH_2CN), 55.36 (*C*H), 112.59 (CH*C*N), 116.78 (CH_2CN), 129.44, 129.76, 134.93, and 135.68 p.p.m. (Ph), *m/e* 234 (M^+), 141, 77, and 51.

An attempt to prepare 2-phenylsulphonylglutaronitrile by an ion-pair extraction procedure, using phenylsulphonylacetonitrile (1.81 g) and acrylonitrile in CH_2Cl_2 (10 ml) and tetrabutylammonium hydroxide (one equiv.) in water (10 ml), gave a mixture of starting material and mono- and dialkylated product when one equiv. of acrylonitrile was used. When two equiv. of acrylonitrile were used, the dialkylated product separated out almost immediately. This was filtered off, washed with dilute hydrochloric acid and water, and recrystallised from ethanol to give pure αα-bis-(*2-cyanoethyl*)*phenylsulphonylacetonitrile* (1.22 g, 43%), m.p. 141—142 °C (Found: C, 58.4; H, 4.65; N, 14.4. $C_{14}H_{13}N_3O_2S$ requires C, 58.55, H, 4.55; N, 14.65%), δ ([$^2H_6$]-DMSO) 2.3—2.95 (8 H, m, CH_2CH_2) and 7.7—8.15 (m, Ph), δ_C ([$^2H_6$]DMSO) 13.0 (CH_2CH_2CN), 26.86 (CH_2CN), 63.9 (*C*CN), 114.56 (*C*CN), 118.76 (CH_2CN), 130.19, 130.69, 132.56, and 136.41 p.p.m. (Ph), *m/e* 287 (M^+), 141, 77, and 51. The electroanalytical behaviour of this compound (2mM in 0.1M-Et_4NBF_4–DMF) exhibited $E_{\frac{1}{2}}$ −1.99 V (*n* 1.14) and $E_{p,c}$ −2.08 V (*v* 200 mV s^{-1}, irreversible.)

3-Phenylsulphonylpropiononitrile.—Acrylonitrile (1.59 g) was added to a solution of sodium benzenesulphinate (3.28 g) in acetate buffer (pH 5, 30 ml) containing a small amount of hydroquinone, and the solution was kept at 50 °C for 1.5 h. After pouring into water (200 ml), the product was extracted with ether (3 × 150 ml) and the combined extracts were washed with aqueous sodium hydrogencarbonate solution and water. On evaporation a solid was obtained which was recrystallised from ethanol to give pure *3-phenylsulphonylpropiononitrile* (0.52 g, 13%), m.p. 93.5—94 °C (lit.,[14] 93—94 °C), $\nu_{max.}$ (Nujol) 2 550 cm^{-1}, δ ($CDCl_3$) 2.6—2.9 (m, CH_2), 3.2—3.6 (m, CH_2), and 7.6—8.2 (m, Ph), *m/e* 195 (M^+), 141, 64, 51, and 28.

Electrolysis of 2-Phenylsulphonylglutaronitrile in DMF.—2-Phenylsulphonylglutaronitrile (0.177 g) in 0.1M-tetraethylammonium fluoroborate–DMF (22 ml) was reduced under controlled potential conditions at −2.4 V (*versus* Ag–0.1M-$AgNO_3$–DMF). The electrolysis was complete after 1 h when 1.09 F mol^{-1} had passed. After addition of the g.l.c. standard (adiponitrile) to the catholyte solution, it was analysed without work-up using 2% Carbowax 20M at 187 °C. Glutaronitrile (31 mg, 44%; maximum yield possible if half of substrate deprotonated 50%) was the only product detected.

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