Cyanomethylation during the Electroreduction of Aromatic Carbonyl Compounds in Acetonitrile

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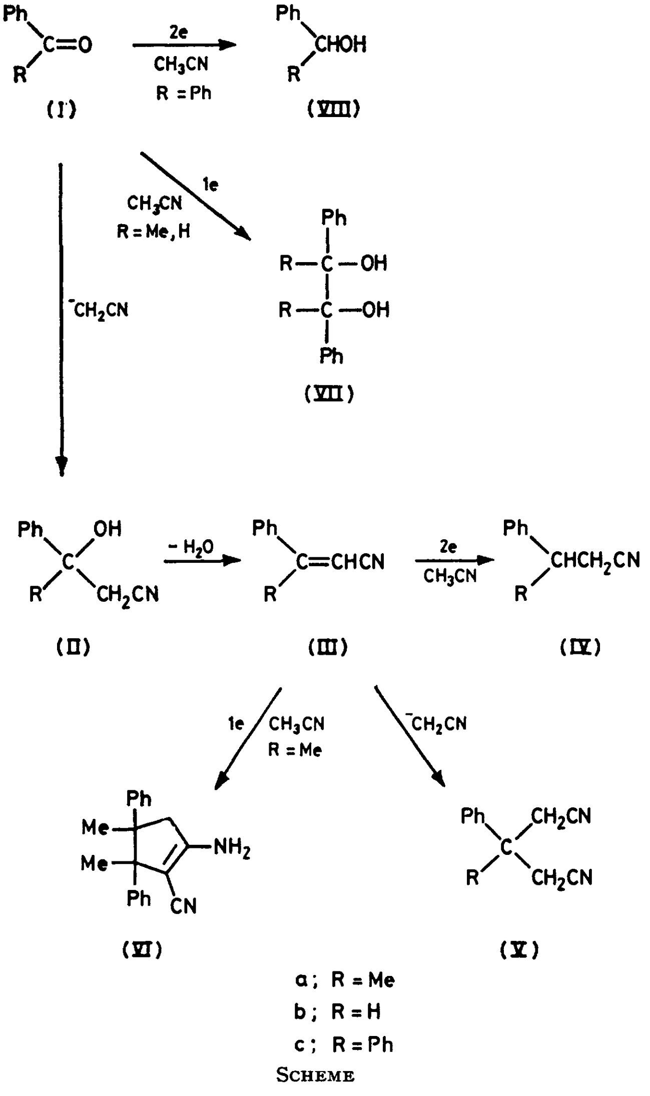
The formation of substituted 3-hydroxy-3-phenylpropiononitriles (II), cinnamonitriles (III), 3-phenylpropiononitriles (IV), and 3-phenylglutaronitriles (V) during the electroreduction of acetophenone, benzaldehyde, and benzophenone in acetonitrile has been studied. The factors which influence the distribution of these products and their importance relative to the 'normal' reduction products, pinacols (VII) and carbinols (VIII), have been identified; current density, temperature, and water concentration are the most important. The distribution of acetonitrile-derived products is compared with that found when the corresponding cinnamonitriles (III) are electroreduced.

In a preliminary communication [1] we reported that the electroreduction of aromatic carbonyl compounds in dry acetonitrile gives significant yields of cyanomethylation products *via* reaction of electrogenerated $^{-}CH_2CN$ with the carbonyl compound (see Scheme). Subsequently, other examples of cyanomethylation occurring during electroreductions in acetonitrile have been reported.[2] We have also described a linear potential sweep method for studying the rate of addition of electrogenerated $^{-}CH_2CN$ to aromatic carbonyl compounds (I) and αβ-unsaturated nitriles (III).[3] In the present paper we describe in more detail our study of the reduction of aromatic carbonyl compounds in dry acetonitrile.



a; R = Me
b; R = H
c; R = Ph

SCHEME

RESULTS AND DISCUSSION

Reduction of Acetophenone (Ia).—The polarogram and cyclic voltammogram of acetophenone exhibit two reduction waves–peaks when Et_4NBF_4 is used as the supporting electrolyte in acetonitrile *viz.* $E_{\frac{1}{2}}$ (1) —2.41 V, $E_{\frac{1}{2}}$ (2) —2.79 V, i_d (2)/i_d (1) 0.87, $E_{p,c}$ (1) —2.46 V, $E_{p,c}$ (2) —2.90 V, $i_{p,c}$ (2)/$i_{p,c}$ (1) 0.30 (v 200 mV s^{-1}) (all for 0.24 mM-$PhCOCH_3$), but when Bu_4NBF_4 is used as the supporting electrolyte the second wave–peak is essentially obscured by the electrolyte cathodic limit. With both electrolytes, the first reduction peak is only partially reversible at low sweep rates [$i_{p,a}$ (1)/$i_{p,c}$ (1) 0.52 for v 200 mV s^{-1}, due to dimerisation of the resulting anion-radicals, the rate constant for which decreases with decreasing concentration of water.[4] Reversibility was observed at v 1—4 V s^{-1}. The small value for $i_{p,c}$ (2) relative to $i_{p,c}$ (1) (in 0.1M-Et_4NBF_4) can be attributed to deactivation of a portion of the substrate molecules arriving at the electrode by electrogenerated bases–nucleophiles, *e.g.* $PhCOCH_3^{2-}$ or $^{-}CH_2CN$, being produced at the potential of the second wave–peak.[5]

A previous report [6] of the preparative reduction of acetophenone in acetonitrile (containing only 0.2% H_2O) at a controlled potential of —1.74 to —1.79 V *versus* s.c.e. (*ca.* —2.1 V *versus* Ag–0.1M-$AgNO_3$–CH_3CN) [7] indicated that the corresponding pinacol was the only product (95%). However, our own exploratory reductions of acetophenone in acetonitrile (< 100 p.p.m. H_2O) (Table 1) at both high (—3.0 V) and low (—2.5 V) potentials gave only small amounts of the pinacol, the majority of the products being formed by reaction with the solvent, *viz.* 3-phenylbutyronitrile (IVa), 3-methyl-3-phenylglutaronitrile (Va), and 1-amino-2-cyano-3,4-dimethyl-3,4-diphenylcyclopent-1-ene (VI). The distribution of products was not affected either by doubling the substrate

TABLE 1

Exploratory electrolysis of acetophenone (Ia)

Experiment [a]	Potential (V) [b]	Initial current (mA)	n/F mol^{-1}	Product yield (isolated) (%) (IVa)	Product yield (isolated) (%) (Va) + (VI)
1	−3.0 [c]	90	1.14	34	45
2	−3.0 [c]	90	>2	51	37
3	−3.0	24	1.64	11	35
4 [d]	−3.0	40	1.3	14	34
5	−2.5	17	1.6	14	42
6 [e]	−3.0	24	1.25	12	40

[a] Unless otherwise specified, $PhCOCH_3$ (0.01 mol) in 0.1M-Et_4NBF_4–dry acetonitrile (200—300 ml), mercury electrode area 10—15 cm^2 (experiments 1 and 2), *ca.* 3 cm^2 (experiments 3—6), in an H-type cell. [b] *versus* Ag–0.1M-$AgNO_3$–CH_3CN. [c] Reference electrode *ca.* 2 cm from working electrode surface. [d] $PhCOCH_3$ (0.02 mol). [e] Electrolysis of PhMeC=CHCN (IIIa) (0.01 mol).

concentration (experiment 4 *versus* 3), or lowering the reduction potential (experiment 5 *versus* 3), and the same product distribution was also obtained when 3-methylcinnamonitrile was used as the substrate (experiment 6). In experiments 1 and 2, the reference electrode was positioned badly and the potential of the working electrode was probably much less than —3.0 V, but in the remaining experiments the reference electrode was more ideally positioned. For reasons we do not understand, this difference produced a higher yield of (IVa) in experiments 1 and 2 than in the other experiments, but the combined yield of (Va) and (VI) was not affected.

TABLE 2

Electrolysis of acetophenone (Ia)

Expt.	Conditions [a]	Initial current (mA)	n/F mol^{-1}	Yield (by g.l.c. analysis) (%) (Ia)	(IIa)	(IIIa)	(IVa)	(Va)	(VIIIa)	Yield (by h.p.l.c. analysis) (%) (VI)	(DL/D′L′ [b])	(VIIa)	(DL/*meso*)
1		500	2.90	6	0	0	32	9	0	2.5	(12.0)	74	(2.0)
2		95	2.14	0	0	0	21	8	0	7	(12.7)	62	(2.2)
3	−3.2 V	450	1.17	4	0	0	20	11	0	7.5	(8.5)	78	(3.5)
4	−2.6 V	280	2.21	7	0	0	20	18	0	5	(11.1)	63	(1.7)
5	−2.25 V	25	1.93	0	0	0	18	35	0	8	(6.5)	25	(—)
6	+0.1% v/v H_2O	450	1.93	7	0	0	8	10	0	trace	(10.6)	70	(2.5)
7	Pt electrode [c]	43	1.46	2.5	1.5	12.5	15	3.5	trace	5	(10.9)	82	(3.6)
8	C electrode [c]	39	2.35	2.5	0	0	8.5	7.5	trace	2.5	(7.3)	62	(2.6)
9	10 mA constant current	(10)	(1.00)	9	0	0	24	3	0	6	(10.8)	55	(2.0)
10	0.1M-Bu_4NBF_4	470	2.03	4	0	0	26	14	0	9	(14.1)	47	(2.5)
11	*d*	62	0.70			0	10	17		50	(6.6)	—	

[a] Unless otherwise specified, $PhCOCH_3$ (0.1M) in 0.1M-Et_4NBF_4–dry acetonitrile, *T* 15—20 °C, mercury electrode (*ca.* 3 cm^2) at −2.95 V *versus* Ag–0.1M-$AgNO_3$–CH_3CN. [b] For the stereochemical assignment see ref. 8. [c] 1—2M-Acrylonitrile present in solvent; pre-reduced before adding $PhCOCH_3$. [d] Electrolysis of PhMeC=CHCN (IIIa).

Table 2 gives the results of a more detailed study of the electroreduction of acetophenone, in which the experimental conditions *e.g.* temperature, potential, solution composition, were more closely controlled. In most of these experiments the corresponding pinacol was found to be the major product, but the products (IVa), (Va), and (VI) were still formed in significant quantities, and in similar relative yields. The DL : *meso* ratio of the pinacol was somewhat lower (1.7—3.5) than had been observed by Stocker and Jenevein (6.9—9.2).[6] The yield of (VI) obtained when acetophenone was the substrate was consistently much lower than when 3-methylcinnamonitrile (IIIa) was the substrate (experiment 11), indicating that a lower concentration of (IIIa) was present during the course of the former electrolyses. In most cases (IIIa) was detected at low concentrations at intermediate stages in the electrolyses. The ratio of the diastereoisomers of (VI) (DL : D′L′) was in most cases higher than when (IIIa) was used as the substrate (experiment 11).[8] The yields of (IVa) and (VI) were not greatly affected by changes in the cathode potential (experiments 1—5), but using a less negative potential, and hence lower current density, increased the yield of (Va) and decreased that of (VIIa). While water must be liberated during the electrolyses (up to 0.1M; inversely proportional to the yield of pinacol), the addition of further water [*ca.* 0.056M (*i.e. ca.* 0.5 times the water concentration in the acetonitrile used by Stocker and Jenevein [6]), experiment 6] reduced the yields of (IVa) and (VI), but did not affect the yields of (Va) and (VIIa). Other changes in the experimental conditions, *viz.* platinum or graphite as the working electrode, Bu_4NBF_4 as the electrolyte, did not significantly affect either the yields or the product distribution.

Reduction of Benzaldehyde (Ib).—The cyclic voltammogram of benzaldehyde (2mM) in 0.1M-Et_4NBF_4–dry acetonitrile exhibits an irreversible reduction peak at —2.20 V (v 250 mV s^{-1}), indicating that the radical-anion rapidly dimerises. However, on the longer time scale of a preparative electrolysis significant yields of nitrile-containing products were obtained *viz.* (IIb) and (IIIb) as intermediates, and (IVb) and (Vb) as final products. Table 3 gives analytical data at various stages in a controlled current electrolysis. The samples were not analysed for the corresponding pinacol (VIIb) or the hydrodimer of (IIIb). No benzyl alcohol was detected. The data clearly show the initial conversion of (Ib) into (IIb), and the slower dehydration of (IIb) to *trans*- and *cis*-(IIIb). The rate of conversion of (IIIb) into (IVb) and (Vb) initially favours (IVb), but (Vb) ultimately predominates. We have previously reported[8] that cyanomethylation during the reduction of *trans*-(IIIb) is only seriously affected when >0.1M-water is present; in the present experiment water is liberated during the formation of (IIIb), but its maximum bulk concentration, even if no pinacol formation occurs, is only 0.013M.

TABLE 3

Electrolysis of benzaldehyde (Ib)[a]

	Yield (by g.l.c. analysis) (%)					
t/min	(Ib)	(IIb)	*trans*-(IIIb)	*cis*-(IIIb)	(IVb)	(Vb)
0	100	0	0	0	0	0
3.3	52	28	0.5	0	0	0
6.5	18	86	1.0	0.3	0	0
10.0	4	68	2.3	0.4	0	0
13.2	3	46	9.9	1.8	2.0	0
16.3	3	43	11.2	1.0	5.6	0.8
18.7	0	38	8.8	0.6	7.0	5.6
21.2	0	26	2.2	trace	9.4	17.4
25.1	0	—	0.7	trace	11.4	24

[a] Conditions: benzaldehyde (0.47 mmol) in 0.1M-Et_4NBF_4–dry acetonitrile (35 ml), 23 °C, mercury cathode, 20 mA constant current.

Reduction of Benzophenone (Ic).—The polarogram and cyclic voltammogram of benzophenone exhibit two reduction waves–peaks *viz.* $E_{\frac{1}{2}}$ (1) -2.20 V, $E_{\frac{1}{2}}$ (2) -2.48 V, i_d (2)/i_d (1) 0.60 (for 0.23mM-substrate), $E_{p,c}$ (1) -2.21 V, $i_{p,a}/i_{p,c}$ 0.93, $E_{p,c}$ (2) -2.59 V (irreversible), $i_{p,c}$ (2)/$i_{p,c}$ (1) 0.53 (for 1.0mM-substrate, v 200 mV s^{-1}), all in 0.1M-Et_4NBF_4–dry CH_3CN.

Preparative electrolysis of benzophenone in dry acetonitrile was carried out under both controlled potential and controlled current conditions. In both cases the major product was (IVc), 34 and 47%, respectively. At low current density (controlled current 20 mA), (Vc) was also formed in significant yield (17%), together with the carbinol (VIIIc) (13%), but at high current density (controlled potential) the yield of (Vc) was very low (1%) and the yield of (VIIIc) was higher (26%). The yields of (IIc) and (IIIc) were low in both electrolyses. The full analytical data are given in the Experimental section.

Reaction Scheme.—An analysis of the data for the three systems studied here, and for the reduction of the related αβ-unsaturated nitriles,[8] suggests that the most likely route to the nitrile-derived products is as shown in the Scheme.

Cyanomethylation of carbonyl compounds by $^-CH_2CN$ is a well established reaction,[9-13] and further dehydration of the hydroxy-nitrile (II) to the αβ-unsaturated nitrile (III) has been observed to occur under the same experimental conditions in some cases *e.g.* R = Me, H, or Ph.[11-13] The Michael addition of $^-CH_2CN$ to αβ-unsaturated nitriles is also a known reaction.[9a] Many of the authentic samples of (II)—(IV) which were required for this study were prepared by these reactions (see Experimental section and ref. 8).

The initiation of cyanomethylation of the substrate during the electroreduction of aromatic carbonyl compounds (Ia—c) arises, we believe, by the 'normal' reduction to the pinacol (VII) and the carbinol (VIII); each reaction would generate two $^-CH_2CN$ ions per molecule of product. Further quantities of $^-CH_2CN$ would be generated during the reduction of the intermediate (III) to give (IV) and hydrodimers of (III).[*] For our electrolysis conditions the generation of $^-CH_2CN$ by direct [2c] or indirect [11] reduction of the solvent does not seem likely. Once $^-CH_2CN$ has been formed, the subsequent cyanomethylation processes *viz.* (I) ⟶ (II), (III) ⟶ (V), continue to regenerate the ion by proton abstraction from the solvent *i.e.* the process becomes catalytic. This has been demonstrated for the electroreduction of benzaldehyde (Table 3), where the rate of conversion of (Ib) into (IIb) exceeds the rate of electrolysis by a factor of 4—5, for the electroreduction of cinnamonitrile,[8] where the yield of (Vb) is >1 mol F^{-1}, and for the electroanalytical cyanomethylation of indan-1-one.[3b]

The other steps in the Scheme, involving reduction of the intermediate αβ-unsaturated nitrile for the cases of (IIIa and b) have been studied separately,[8] the unsaturated nitrile being used as the substrate. Although higher yields of hydrodimer are obtained when higher concentrations of (III) are present, the results do support the Scheme. Other control reactions have eliminated both the direct reduction of (II) to (IV), and the displacement of the OH group in (II) by $^-CH_2CN$ to give (V), as alternative routes to these products.

The relative importance of the various steps in the Scheme appears to depend upon both the substituent R and the electrolysis conditions. We have shown by an electroanalytical method [3b] that both cyanomethylation steps, (I) ⟶ (II) and (III) ⟶ (V), are relatively fast for R = Me and Ph.[3b,c] The data in Table 3 suggest that this is so for R = H also. The slowest step in the sequence is most probably (II) ⟶ (III). For dehydration to occur at a reasonable rate under basic conditions heating is normally required.[11-13] For example, solutions of the sodium salt of acetonitrile in acetonitrile at room temperature only converts (Ia) into (IIa), but under reflux conditions (IIIa) is the product; for (Ib), some (IIIb) is formed even at room temperature.[12] Since it is known [10] that the formation of (II) is reversible, higher electrolysis temperatures and hence more rapid dehydration should favour the formation of nitrile products, and this could be why higher yields of these products were obtained in the exploratory electrolyses of the acetophenone (Table 1) when the temperature was allowed to increase, compared to those electrolyses in which the temperature was controlled (*e.g.* Table 2).

The competition between the formation of (IV) and (V) from (III) depends upon both R and the current density. Since the αβ-unsaturated nitriles are slightly more easily

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[*] For those experiments in which acetonitrile containing 1—2mM-acrylonitrile as an impurity was used as the solvent, the pre-reduction procedure to remove acrylonitrile would also generate some $^-CH_2CN$.

reduced than the corresponding carbonyl compounds *viz.* +0.01 V for R = H, +0.16 V for R = Me, a potential sufficient to reduce the carbonyl compound will also be sufficient to reduce the derived αβ-unsaturated nitrile. For (IIIa) the balance between (IVa) and (Va) is affected by the electrolysis potential and hence current density, but both products are usually obtained with (IVa) > (Va) in most cases. For (IIIb) also, both (IVb) and (Vb) are formed with (IVb) < (Vb), but for (IIIc) the formation of (Vc) only competes effectively with the formation of (IVc) at low current densities; very little (Vc) is formed at high current densities. Thus (IIIc) appears to be cyanomethylated somewhat more slowly than (IIIa) and (IIIb), the rates for Michael addition of $^-CH_2CN$ following the order: (IIIb) > (IIIa) > (IIIc). The partition of (III) between (IV) and hydrodimer is dependent upon current density and also on the concentration of (III). Higher yields of hydrodimer are obtained when (III) is the substrate for the electrolysis[8] than when (III) is an intermediate in the electrolysis of (I).

The balance between nitrile products and the 'normal' reduction products of (I), *e.g.* (VII) and (VIII), is also dependent upon the current density, as well as upon the water concentration in the solution. If the electrolysis is performed at a low current density less carbonyl compound is reduced since more time is available for cyanomethylation, while at a high current density the converse obtains. The formation of (VIII) is only important for (Ic); for (Ia) and (Ib) the formation of (VII) is the only important direct reduction route. The level of water in the medium is known to affect both the rate of formation and the stability of pinacols, the rate of dimerisation of the radical-anion of the carbonyl compound, and hence the rate of formation of (VII), decreasing with decreasing water concentration in the range 0—5%,[4] and the absence of water favouring decomposition of pinacols under basic conditions.[14] In addition we have found that the presence of water in the electrolysis medium decreases the yield of nitrile products. These three factors probably explain why these products were not observed previously.[6] Furthermore they suggest that the yield of nitrile products might be increased further if the water liberated during the dehydration of (II) to (III) could be continuously removed from the medium.

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 (<10 p.p.m. H_2O) was stored over freshly activated molecular sieve (Linde type 4Å). The exploratory electrolyses of acetophenone were performed using a divided H-type cell; all other electrolyses were performed using a cell consisting of 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.

Exploratory Electrolyses of Acetophenone (*Table* 1, *Experiment* 1).—Acetophenone (0.01 mol) in 0.1M-tetraethylammonium fluoroborate–dry acetonitrile was reduced under nitrogen using a stirred mercury pool cathode (10—15 cm^2) and a graphite anode, at a controlled potential of −3.0 V (*versus* Ag–0.1M-$AgNO_3$–CH_3CN). The acetonitrile used in these experiments still contained 1—2mM-acrylonitrile as an impurity. This was removed by electroreduction before adding the substrate. No attempt was made to control the temperature. The initial current was 90 mA; the current rose to 125 mA during 1 h and then decreased to *ca.* 20 mA (4 h). Continued electrolysis produced no further decrease in the current. The electrolysis was terminated at 1.14 F mol^{-1} of acetophenone.

The catholyte was quenched with ammonium chloride (if this was not done, 4-amino-2,6-dimethylpyrimidine and 3-aminocrotononitrile were formed), the acetonitrile was removed by rotary evaporation, water (25 ml) was added to the residue, and the products were isolated by extraction with ether (3 × 100 ml). Analysis of the final product mixture (1.66 g) by t.l.c. and g.l.c. showed that besides unchanged acetophenone, there were many components present; one of the minor components was isolated by preparative g.l.c. (10% SE30, 200 °C) and identified as 3-methylcinnamonitrile.

The crude reaction mixture was separated by wet column chromatography (Al_2O_3; light petroleum–ether–ethanol). The major component was eluted first and was identified as 3-phenylbutyronitrile (0.48 g, 34%; 61% current yield); $\nu_{\max.}^{\text{film}}$ 2 225 cm^{-1} (CN); δ_H (CCl_4) 1.39 (d, *J* 7 Hz, CH_3), 2.43 (d, *J* 7 Hz, CH_2), 3.07 (sextet, *J* 7 Hz, CH), and 7.15 (m, Ph); δ_C 20.593 (CH_3), 26.191 (CH_2), 36.415 (CH), 126.362 [Ph, C(2) and C(6)], 127.099 [Ph, C(4)], 128.644 [Ph, C(3) and C(5)], and 142.982 p.p.m. [Ph, C(1)]; *m/e* 145 (*P*), 130 ($P-CH_3$), and 105 ($P-CH_2CN$).

A more polar fraction (0.83 g, *ca.* 45%) was shown by n.m.r., i.r., and mass spectroscopy to be largely 3-methyl-3-phenylglutaronitrile (*m/e* 184), contaminated with a mixture of the diastereoisomers of 1-amino-2-cyano-3,4-dimethyl-3,4-diphenylcyclopent-1-ene (*m/e* 288; $\nu_{\max.}^{\text{film}}$ 2 180 cm^{-1}; $\lambda_{\max.}^{\text{EtOH}}$ 260 nm). This mixture could not be separated by distillation (b.p. 90—130 °C at 0.2 mmHg) or chromatography. In addition there were small amounts of 2,3-diphenylbutane-2,3-diol and 1-phenylethanol. When the products from a similar electrolysis were separated by dry column chromatography (deactivated alumina; ether), four main fractions were obtained: (i) largely 3-phenylbutyronitrile (0.49 g), (ii) 3-methyl-3-phenylglutaronitrile (0.1 g), (iii) 2,3-diphenylbutane-2,3-diol (0.04 g), and (iv) 3-hydroxy-3-phenylbutyronitrile + 2,3-diphenylbutane-2,3-diol (0.05 g).

In experiments 1 and 2, the reference electrode was *ca.* 2 cm from the surface of the working electrode, but in experiments 3—5 it was much closer. The same reduction products were obtained when the electrolysis conditions were changed as follows: (a) concentration of $PhCOCH_3$ increased, (b) electrolysis potential −2.5 V, (c) platinum working electrode used, and (d) 1% v/v water present. When 10% v/v water was present, no cyanomethylation products were obtained, the major product (82%) was the pinacol.

Electrolysis of 3-*Methylcinnamonitrile* (*Table* 1, *Experiment* 6).—3-Methylcinnamonitrile (0.01 mol) in 0.1M-tetraethylammonium fluoroborate–dry acetonitrile was reduced at −3.0 V using a stirred mercury pool cathode (*ca.* 3 cm^2). The initial current was 24 mA; this increased and then decreased to 7 mA. The electrolysis was terminated at 1.25 F mol^{-1} of 3-methylcinnamonitrile. The catholyte was worked up as before to give a mixture of products (1.56 g) which was partially separated by dry column chromatography (alumina; ether). Two fractions were isolated, (i) 3-phenylbutyronitrile (0.17 g, 12%) and (ii) a mixture (0.80 g) of 3-methyl-3-phenylglutaronitrile (*ca.* 30%) and 1-amino-2-cyano-3,4-dimethyl-3,4-diphenylcyclopent-1-ene (*ca.* 10%).

Electrolysis in the presence of 20% v/v water gave only 3-phenylbutyronitrile.

Detailed Analysis of the Electrolysis Products from Acetophenone.—The electrolyses were performed under nitrogen, with a stirred mercury pool (area *ca.* 3 cm^2) as the working electrode. The reference electrode was Ag–0.1M-AgNO$_3$–CH$_3$CN. In general a 0.1M solution of acetophenone in 0.1M-tetraethylammonium fluoroborate in dry acetonitrile (*ca.* 40 ml) was used. The acetonitrile used in experiments 7 and 8 still contained 1—2mM-acrylonitrile as an impurity. This was removed by electrolysis at -2.95 V before adding the substrate. As in the exploratory electrolyses, the current increased initially, and then decreased. The initial increase appears to be associated with an increase in temperature since when the electrolyses were conducted at -28 °C and 81 °C (constant temperature) no such increase in current occurred. The electrolyses were discontinued when the current had decreased to a constant value, sometimes as high as 40 mA. An excess of aqueous ammonium chloride solution was added to the catholyte, followed by the g.l.c. (benzonitrile or benzophenone) and h.p.l.c. (*m*-nitroacetanilide) standards. The mixture was extracted with either ether (not for h.p.l.c. analysis) or methylene dichloride (2 × 100 ml), the extracts were combined, washed with water (2 × 100 ml), dried (MgSO$_4$), and concentrated by rotary evaporation below 50 °C. The results are given in Table 2.

The accuracy of the g.l.c. yields (10% ApL; 165 °C for 12 min, then 8 °C min^{-1} to 230 °C) is estimated to be $\pm 10\%$ for (Va) and $\pm 5\%$ for (Ia)—(IVa) and (VIII). The accuracy of the h.p.l.c. yields [7μm Spherisorb Alumina; 20% ethyl acetate (0.5% w/w H$_2$O) in hexane] is estimated to be $\pm 5\%$ for (VI) and $\pm 20\%$ for (VII). No attempt was made to normalise the yields.

Since the pre-electrolysis to remove acrylonitrile was probably generating $^-$CH$_2$CN, a control experiment was performed in which acetophenone was added to (i) an electrolyte solution which had been pre-reduced, and (ii) an electrolyte solution which had not been pre-reduced. Both solutions were worked up and analysed (g.l.c.) without further electrolysis. The pre-reduced sample gave the following analysis: (Ia) (2%), (IIa) (4%), (IIIa) (0.5%), and (IVa) (0.5%), while the other sample contained only (Ia) (28%).

Electrolysis of Benzaldehyde.—Benzaldehyde (50 mg, 0.47 mmol; purified by washing with aqueous sodium carbonate solution, drying over anhydrous sodium carbonate, and distilling from zinc dust under reduced pressure) in 0.1M-tetraethylammonium fluoroborate in dry acetonitrile (35 ml) was reduced under controlled current conditions (20 mA) at 23 °C using a stirred mercury pool cathode (3 cm^2). Samples (0.5 ml) were withdrawn periodically and known quantities of diethyl phthalate (g.l.c. standard) were added before g.l.c. analysis (10% ApL; 196 °C). The samples were analysed for (in order of elution): 3-aminocrotononitrile, benzaldehyde, benzyl alcohol, 4-amino-2,6-dimethylpyrimidine, 3-phenylpropiononitrile, *cis*-cinnamonitrile, *trans*-cinnamonitrile, 3-hydroxy-3-phenylpropiononitrile, diethyl phthalate, and 3-phenylglutaronitrile. At the end of the electrolysis, the catholyte was worked up and analysed by g.l.c.–m.s. (10% ApL) to confirm the peak assignment. The results are presented in Table 3.

Electrolysis of Benzophenone.—(i) Benzophenone (1.82 g, 10 mmol) in 0.1M-tetraethylammonium fluoroborate in dry acetonitrile (150 ml; pre-reduced at -2.0 V for 15 min to remove 1—2mM-acrylonitrile before adding benzophenone) was reduced using a stirred mercury pool cathode (3 cm^2) at a controlled current of 20 mA for 24 h. Ammonium chloride (1.07 g) in water (100 ml) was added to the catholyte, the mixture was concentrated and was then extracted with ether, followed by methylene dichloride. The extracts were concentrated separately and analysed by ^{1}H n.m.r spectroscopy and h.p.l.c. [Partisil-10 silica, 20% ethyl acetate (containing 0.3% w/w water) in hexane]. The methylene dichloride extract (0.35 g) contained only benzophenone. The ether extract (2.22 g) had δ 2.81 (d, *J* 7.5 Hz, 18 units, Ph$_2$CHC*H*$_2$CN), 3.10 [s, 6 units, Ph$_2$C(C*H*$_2$-CN)$_2$], 4.23 (t, *J* 7.5 Hz, 8 units, Ph$_2$C*H*CH$_2$CN), and 5.70 (s, 12 units, increased on addition of Ph$_2$C*H*OH). The h.p.l.c. yields were: Ph$_2$CO (22%), Ph$_2$CHOH (13%), Ph$_2$C(OH)-CH$_2$CN (0%), Ph$_2$C=CHCN (trace), Ph$_2$CHCH$_2$CN (47%), and Ph$_2$C(CH$_2$CN)$_2$ (17%) (assumed to be the only products).

(ii) Benzophenone (1.21 g, 7.5 mmol) in 0.1M-tetraethylammonium fluoroborate in dry acetonitrile (10 ml; pre-electrolysed at -3.0 V until current <3 mA) was reduced using a mercury cathode under controlled potential conditions. At -3.0 V the initial current was 700 mA. After 10 min the solution was boiling, therefore the potential was reset at -2.55 V; the current was then <300 mA. After 2.5 h the catholyte was worked up as before. The ether extract (2.38 g) had δ 3.00 (d, *J* 7.5 Hz, 54 units, Ph$_2$CH-C*H*$_2$CN), 4.33 (d, *J* 7.5 Hz, 22 units, Ph$_2$C*H*CH$_2$CN), 5.70 (s, 1 unit, increased on addition of Ph$_2$C=C*H*CN), and 5.77 (s, 18 units, increased on addition of Ph$_2$C*H*OH). The h.p.l.c. yields were Ph$_2$CO (34%), Ph$_2$CHOH (26%), Ph$_2$C(OH)CH$_2$CN (0%), Ph$_2$C=CHCN (5%), Ph$_2$CHCH$_2$CN (34%), and Ph$_2$C(CH$_2$CN)$_2$ (1%) (assumed to be the only products).

Authentic Samples.—3-Methylcinnamonitrile, 3-phenylbutyronitrile, 3-methyl-3-phenylglutaronitrile, 1-amino-2-cyano-3,4-dimethyl-3,4-diphenylcyclopent-1-ene, 3-phenylpropiononitrile, and 3-phenylglutaronitrile were prepared as previously described.[8] Samples of the hydroxy-nitriles (IIa—c) were prepared by the method of Ivanov and Anghelova.[9a] Compound (IIa) had b.p. 157 °C at 4 mmHg, m.p. 55—58 °C (from ethanol) (lit.,[9a] 56—57 °C); δ(CDCl$_3$) 1.78 (s, CH$_3$), 2.84 (s, CH$_2$CN), and 7.45 (m, Ph); $\nu_{max.}$ (Nujol) 3 435 (s, OH) and 2 250 cm^{-1} (s, CN). Compound (IIb) had b.p. 108—116 °C at 0.1 mmHg (lit.,[10] 154—155 °C at 1 mmHg); δ(CDCl$_3$) 2.63 (d, *J* 6 Hz, CH$_2$CN), 3.40br (s, OH), 4.9 (t, *J* 6 Hz, CH), and 7.30 (s, Ph); $\nu_{max.}$ (film) 3 430br (s, OH), and 2 260 cm^{-1} (CN). Compound (IIc) had m.p. 139.5—140.5 °C (lit.,[9a] 139—140 °C); δ(CDCl$_3$) 2.76 (s, OH), 3.23 (s, CH$_2$CN), and 7.30 (s, Ph); $\nu_{max.}$ (Nujol) 3 360 (s, OH) and 2 260 cm^{-1} (m, CN). *cis*-Cinnamonitrile was prepared from α-cyano-β-phenylacrylic acid and benzaldehyde.[16] It had b.p. 110—112 °C at 3 mmHg; δ(CDCl$_3$) 5.42 (d, *J* 12 Hz, CHCN), 7.10 (d, *J* 12 Hz, PhC*H*), and 7.3—7.9 (m, Ph). 3-Phenylcinnamonitrile (IIIc) was prepared by dehydrating (IIc) using sulphuric acid in acetic acid.[17] It had m.p. 45.5 °C (from methanol) (lit.,[17] 45 °C); δ(CDCl$_3$) 5.70 (s, CH), and 7.38 (m, Ph); $\nu_{max.}$ (CCl$_4$) 2 210 cm^{-1} (s, CN). 3,3-Diphenylpropiononitrile (IVc) was prepared by hydrogenating (IIIc) in acetic acid at atmospheric pressure (65 h) over 10% Pd–C. It had m.p. 88—89 °C (from methanol) (lit.,[18] 88.5 °C); $\delta(CDCl_3)$ 3.03 (d, J 7.5 Hz, CH_2-CN), 4.38 (t, J 7.5 Hz, CH), and 7.27 (s, Ph). 3,3-Diphenylglutaronitrile (Vc) was prepared from (IIIc) in a similar manner to (IIc).[9a] It had m.p. 119.5—126 °C (lit.,[9a] 124—125 °C); $\delta(CDCl_3)$ 3.33 (s, CH_2) and 7.0—7.5 (m, Ph); $\nu_{max.}$ ($CHCl_3$) 2 250 cm^{-1} (CN) [contaminated with (Ic) and (IIIc)].

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