

Studies on the Kolbe Electrolytic Synthesis

VIII.* Further Investigations on the Electrolysis of α -Cyanocarboxylates

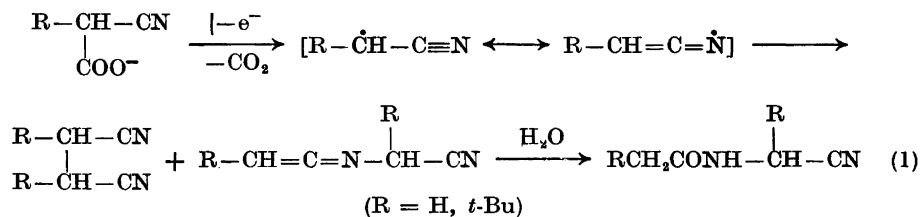
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Isopropyl-, *t*-butyl-, cyclohexyl-, and dimethylcyanoacetic acid have been electrolyzed in methanolic solution and the radical coupling products determined quantitatively. *t*-Butylcyanoacetic acid has also been electrolyzed in water, acetonitrile, and *N,N*-dimethylformamide. From this acid a very low yield of a rearrangement product, 2-cyano-3-methyl-2-butene, was obtained on electrolysis in methanol at a Pt anode; the same low yield was observed when a carbon anode was used.

The behavior of anodically generated α -cyanoalkyl radicals is very similar to that of α -cyanoalkyl radicals generated in homogeneous solution, both with regard to the stereochemistry of the reaction and to the proportion between C-to-C- and C-to-N-coupling products.

Some years ago, one of us¹ demonstrated that cyanoacetic and *t*-butylcyanoacetic acid give good yields of coupling products on anodic oxidation in methanolic solution (eqn. 1). Both carbon-to-carbon and carbon-to-nitrogen



coupling products were formed, the latter (a ketenimine) being converted to an *N*-acylglycinonitrile by traces of water present in the electrolyte and by water produced by esterification of part of the α -cyanocarboxylic acid used, as indicated by the isolation of a fair yield of its methyl ester. Thus, the behavior of anodically generated α -cyanoalkyl radicals is qualitatively similar to that of radicals thermally²⁻⁵ and photochemically⁶ generated in homogeneous media.

* Part VII, see *Acta Chem. Scand.* 20 (1966) 739.

On preparative workup, the mixture of meso- and rac-2,3-di-*t*-butylsuccinonitrile from *t*-butylcyanoacetic acid was found to consist predominantly of the racemic form, less than 1 % of the meso form being isolated.⁷ However, when these compounds later were prepared from the easily available 2,3-di-*t*-butylsuccinic diamides,⁷ it was found that the meso form is a somewhat volatile compound, very soluble in the common organic solvents. Since the isolation procedure involved a fractionated crystallization to separate the racemic form from the amide, followed by evaporation of the residue and distillation of a partly decomposing liquid in *vacuo*, it might well be that heavy losses of the meso form had occurred during these operations as well as in the final recrystallization from petroleum ether, in which it is very soluble.

With this in mind, we have reinvestigated the electrolysis of *t*-butylcyanoacetic acid in several solvents, using modern analytical techniques, to see if the reaction really displays any stereospecificity. In this connection it is of obvious interest to get quantitative data in order to be able to compare with results from homogeneous systems.⁸ We have also extended the investigations to some other cyano acids, *viz.*, isopropyl-, cyclohexyl-, and dimethylcyanoacetic acid. Finally, we have looked for possible carbonium ion mediated products resulting from further oxidation of cyanoalkyl radicals, both on a platinum and a carbon anode, the latter being chosen in order to see if a carbon anode would switch the mechanism to a predominant carbonium ion mediated one, as has been demonstrated to occur in the electrolysis of simple aliphatic acids.⁹

RESULTS

Isopropyl-, *t*-butyl-, cyclohexyl-, and dimethylcyanoacetic acid were first electrolyzed in methanolic solution at a platinum anode in order to isolate and identify the coupling products. Using these compounds as standards, the

Table 1. Yields of dinitriles, ketenimines (analyzed as the corresponding *N*-acylglycinonitriles), and methyl esters of starting materials on electrolysis of alkyl substituted α -cyanoacetic acids in methanol.^a

α -Cyanoacetic acid	Dinitrile, % ^b		Ketenimine, % ^b	Methyl ester, % ^b
	Meso	Racemic		
Isopropyl	13 ^c	12 ^c	18	+ ^d
<i>t</i> -Butyl	13 ^c	17 ^c	31	35
Cyclohexyl	14	8 ^e	8	+ ^d
Dimethyl		24	6	5

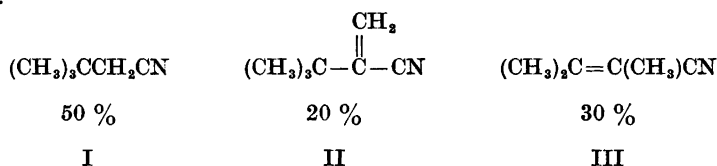
^a Pt anode; the reaction was run until the electrolyte became neutral or slightly alkaline. ^b Based on starting material. ^c For these assignments, see Ref. 7. ^d The + sign indicates that the methyl ester was present but that it could not be quantitatively determined due to interference from other products. ^e This dinitrile was related chemically to low-melting 2,3-dicyclohexylsuccinic acid (see experimental part), which from its pK value and chemical behavior¹⁰ is known to be the racemic form.

electrolyses were repeated and the products analyzed by gas chromatography. The results are shown in Table 1.

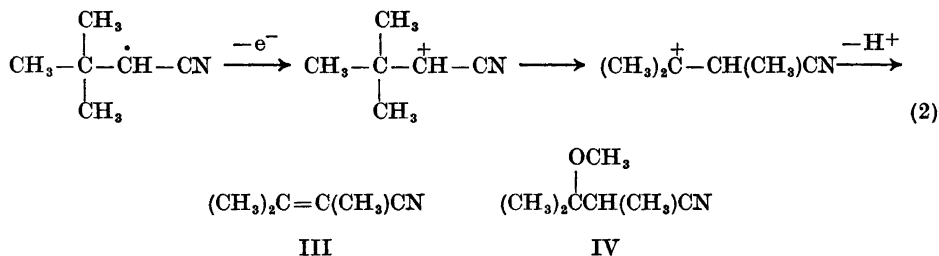
Inspection of Table 1 reveals that the C-to-C-coupling reaction is not stereospecific to any appreciable extent, as the earlier preparative results¹ indicated. In this respect the coupling between anodically generated α -cyanoalkyl radicals is similar to coupling between α -ethoxycarbonylalkyl and α -carboxamidoalkyl radicals.⁸

As would be expected for this type of structure, the *t*-butyl acid gives the best yields of coupling products. Having no hydrogens on the carbon atom β to the radical center, any monomeric products must originate from other reaction paths (see below). From dimethylcyanoacetic acid the disproportionation products, isobutyronitrile and α -methylacrylonitrile, were obtained in 2% yield in an approximate 1:1 ratio. The two other acids gave a very complicated mixture of monomeric products (12–15 components in the VPC traces in a combined yield of less than 10%) due to the fact that both the disproportionation and carbonium ion pathway are available for the intermediate radicals in these cases. It was therefore only possible to demonstrate the presence of the methyl ester of the starting material in this part of the gas chromatograms.

The electrolysis product from *t*-butylcyanoacetic acid was carefully analyzed for other monomeric products than the methyl ester in order to see if further oxidation of the cyanoalkyl radical takes place. A combined yield of about 2% of the following products was separable by preparative gas chromatography:



Compound I may originate either from an attack of the intermediate radical on a C–H-bond in methanol or any of the solutes present or, less likely, from a slow decarboxylation of the cyano acid during the run. Compound II is probably formed from the *t*-butylcyanoacetic acid and formaldehyde, which is formed in small amounts from the simultaneously occurring anodic oxidation of methanol. Compound III has a rearranged carbon skeleton and is most probably formed *via* a second electron transfer from the cyanoalkyl radical, followed by a 1,2-alkyl shift and proton loss:



The alternative possibility, rearrangement of the radical followed by a second electron transfer and subsequent proton loss, is considered unlikely in view of the stability of neopentyl-type radicals towards rearrangement.^{11,12} The methyl ether IV was not found among the products.

Koehl⁹ has shown that the yield of carbonium ion products from the electrolysis of a number of simple fatty acids is considerably increased when a carbon anode is used. For *t*-butylcyanoacetic acid it was found, however, that the electrolysis at a carbon anode did not increase the yield of III, nor did the methoxy compound IV appear among the products. The yield of coupling products in this case was meso-dinitrile 6 %, rac-dinitrile 17 %, ketenimine 38 %, and methyl ester 31 % (cf. Table 1).

The *t*-butyl acid was also electrolyzed in other solvents in order to see if there is any significant change in distribution between C-to-C- and C-to-N-coupling products. Table 2 shows that this is not the case, the proportions being approximately the same in methanol, acetonitrile, *N,N*-dimethylformamide (DMF), and water. Immediately after the run in DMF it was possible to demonstrate the presence of the ketenimine from the IR spectrum of the reaction mixture. Ketenimines have a characteristic absorption band around 2040 cm⁻¹, which was present in the spectrum of the mixture and slowly disappeared on standing. During workup, the ketenimine was transformed into the amide.

DISCUSSION

The implications of the results shown in Tables 1 and 2 with regard to the problem of adsorbed *vs.* free radicals as product-forming entities in the Kolbe reaction have already been discussed at some length in a previous paper and need no repetition here.^{13,14} However, some comments on the behavior of dimethylcyanoacetic acid are appropriate.

It is known that the thermal decomposition of azobisisobutyronitrile gives an initial distribution between C-to-C- and C-to-N-coupling products of approximately 1:1,⁴ and that the ketenimine is subsequently converted into tetramethylsuccinonitrile as the reaction progresses. The final product mixture has been found² to consist of 84 % tetramethylsuccinonitrile, 3.5 % isobutyronitrile and 9 % 2,3,5-tricyano-2,3,5-trimethylhexane, the latter compound

Table 2. Yields of coupling products from the electrolysis of *t*-butylcyanoacetic acid in different solvents.

Solvent	Dinitrile, %		Ketenimine, %
	Meso	Racemic	
Methanol	13	17	31
Acetonitrile	9	8	20
DMF	4	3	8.5
Water	4	5	5

apparently being formed by addition of two 2-cyano-2-propyl radicals to α -methylacrylonitrile. From these results it was concluded that the ratio between coupling and disproportionation products is about 9:1.

In the electrolysis experiments, we experienced considerable difficulties in analyzing for the amide resulting from hydration of the ketenimine. This amide is known to be very sensitive towards hydrolysis and thus some of it might have been lost during the run and the workup procedure. Besides, the reaction product was found to be very sensitive to alkali, being converted to a black tar within hours if by accident the pH of the electrolyte had exceeded 8 towards the end of the run. This is a possible explanation for the rather high dinitrile/amide ratio of about 4:1 found in the dimethyl acid case as compared to the other cases, in which the amides are stable towards hydrolysis. The ratio between coupling and disproportionation products in the electrolytic reaction is about 15:1, not very much different from the thermal process, especially if one considers the differing reaction conditions. Thus, the fate of anodically generated 2-cyano-2-propyl radicals is not drastically different from that found in homogeneous media.

α -Cyanoalkyl radicals have high ionization potentials as determined by mass spectrometry, generally in the region between 9 and 10 eV. The empirical rule¹⁵ that radicals with ionization potentials above 8 eV should give predominantly radical coupling (or disproportionation) products instead of being further oxidized to carbonium ions, is thus obeyed by α -cyanoalkyl radicals; in the case where the formation of a carbonium ion mediated product could be unambiguously demonstrated, the yield was very low.

It has recently been shown that the same empirical rule is valid for lead tetraacetate oxidation of radicals.¹⁶

EXPERIMENTAL

Gas chromatographic analyses were carried out on a Perkin-Elmer 116 Fractometer and preparative gas chromatographic separations on an Aerograph A-700 instrument. NMR spectra were recorded on a Varian A-60 NMR spectrophotometer. Elementary analyses were carried out at the Department of Analytical Chemistry, University of Lund.

Preparation of isopropylcyanoacetic acid. Ethyl isopropylcyanoacetate was dissolved in ethanol and an equivalent amount of potassium hydroxide dissolved in ethanol/water was slowly added with rapid stirring at room temperature. The ethanol was distilled off, water added and the aqueous solution acidified with hydrochloric acid. The isopropylcyanoacetic acid was extracted by ether. After evaporation of the ether, the crude acid was recrystallized from carbon tetrachloride, giving a 56 % yield of isopropylcyanoacetic acid, m.p. 25°, lit.¹⁷ 31° (Found: Equiv. wt. 127.0. Calc. 127.2).

Preparation of t-butylcyanoacetic acid. This acid was prepared according to the method given by Widequist,¹⁸ m.p. 97–98°, lit.¹⁸ 98–99° (Found: Equiv. wt. 142.0. Calc. 141.2).

Preparation of cyclohexylcyanoacetic acid. This acid was prepared according to the method given by Ives and Sames,¹⁹ m.p. 81–82°, lit.¹⁹ 82° (Found: Equiv. wt. 167.0. Calc. 167.7).

Preparation of dimethylcyanoacetic acid. The following procedure was found to give a fairly good yield of this acid: Sodium (2 moles) was dissolved in absolute methanol (500 ml). Methyl cyanoacetate (2 moles) was added, followed by the dropwise addition of methyl iodide (2 moles). After boiling for one hour, the solution had become neutral. A solution of sodium (2 moles) in absolute methanol (500 ml) was added and methyl iodide (2 moles) was then added dropwise. Finally the reaction mixture was stirred under

reflux for 6 h. Acetic acid (10 ml) was added and the methanol distilled off at water pump pressure. After addition of water, the organic material was taken up in ether and the ether extract dried with anhydrous magnesium sulphate. Final distillation gave methyl dimethylcyanoacetate (74 %), b.p. 65–67°/10 mm, almost free from the monomethyl derivative according to VPC analysis.

The hydrolysis of this ester was carried out at room temperature in methanol in the same way as described for ethyl isopropylcyanoacetate. It is essential that the addition of the potassium hydroxide solution is made *at a very slow rate*, so that there is never any excess of base in the reaction mixture. The crude dimethylcyanoacetic acid was recrystallized from carbon tetrachloride, m.p. 50–56°, lit.¹⁹ 60–61° (Found: Equiv. wt. 113.8. Calc. 113.0).

Preparation of cyclohexylmalonamic acid. Ethyl cyclohexylcyanoacetate (0.48 mole) was stirred with sodium hydroxide (1.44 moles) in water (230 ml) on a water-bath at 100° for 4 h. After cooling, the solution was acidified and the product extracted with ether. Evaporation of the ether and recrystallization of the residue from formic acid gave a 73 % yield of cyclohexylmalonamic acid, m.p. 168–176° (decomp), lit.⁴⁵ 184° (Found: Equiv. wt. 185.5. Calc. 185.2).

Electrolysis procedure. Electrolyses were carried out as described elsewhere.^{10a} Platinum was the anode material unless otherwise stated. The temperature of the electrolyte was kept at 20–25° and the electrolysis was stopped when the electrolyte had become neutral or slightly alkaline. The current density was about 0.5 A/cm².

Electrolysis of isopropylcyanoacetic acid in methanol. A. Preparative run. Isopropylcyanoacetic acid (0.1 mole) and potassium hydroxide (0.2 g, 3.5 mole %) were dissolved in absolute methanol (200 ml) and electrolyzed until the electrolyte had turned neutral (this required 2.4 times the theoretically calculated amount of charge). On cooling to 0°, crystals (1.9 g, m.p. 155–157° after recrystallization from ethyl acetate) separated from the solution. This compound was identified as meso-2,3-diisopropylsuccinonitrile by comparison (IR, m.p.) with an authentic sample.⁷

The mother liquor was then evaporated to a volume of about 30 ml and cooled to 0°. A second crop of crystals (0.7 g) was obtained, m.p. 71–73° after recrystallization from petroleum ether, identified as rac-2,3-diisopropylsuccinonitrile by comparison with an authentic sample.⁷

The mother liquor from the second filtration was evaporated to dryness, leaving behind a sticky mass (7.0 g) which was subjected to chromatography on silica gel. Chloroform-ether eluted a viscous liquid (4.9 g) which after repeated chromatography on silica gel analyzed as a single compound on VPC (1 m × 0.6 cm 10 % Carbowax 1500 column at 225°). It was identified as *N*-(isopropylacetyl)-isopropylglycinonitrile on the basis of its IR spectrum, which had N–H stretching frequencies at 3270 and 3030 cm⁻¹, a C≡N stretching frequency at 2237 cm⁻¹, and two amide bands at 1645 and 1520 cm⁻¹, and its NMR spectrum, which had signals at 7.9 ppm (doublet), 4.7 ppm (quartet), 1.8–2.3 ppm (multiplet) and 0.9–1.2 ppm (three overlapping doublets) with integrated band areas in the proportions 1:1:4:12. The doublet at 7.4 ppm is assigned to the amide proton and the quartet at 4.7 ppm to the methine proton at the asymmetric carbon atom. The multiplet in the region 1.8–2.3 ppm is assigned to the methine hydrogens of the isopropyl group and the methylene group. The three doublets in the 0.9–1.2 ppm region originate from methyl groups, one of them from the isopropylacetyl part of the molecule, and two of them from the isopropyl group situated at the asymmetric carbon atom.¹² Elementary analyses were in good agreement with the formula C₁₀H₁₈N₂O (Found: C 65.4; H 10.0; N 15.2. Calc. for C₁₀H₁₈N₂O: C 65.9; H 10.0; N 15.4).

B. Analytical run. The electrolysis was performed as in the experiment above. The methanol solution was evaporated directly and the residue dissolved in benzene. This solution was analyzed for the coupling products by VPC on a 1 m × 0.6 cm 10 % Carbowax 1500 column at 225°, using tetramethylsuccinonitrile as an internal standard. VPC at lower temperatures revealed the presence of methyl dimethylcyanoacetic and a number of other products in small amounts. Due to the complexity of this region of the VPC trace, no attempt was made to identify these compounds.

Electrolysis of t-butylcyanoacetic acid. A. Preparative run in methanol. The isolation and identification of the coupling products and the methyl ester have been described previously.^{1,7}

To identify the low-boiling products formed, *t*-butylcyanoacetic acid was electrolyzed in methanol in the usual manner. The product was distilled and low-boiling fractions between 65°/760 and 140°/20 were collected. These fractions were separated into their components by preparative VPC on a 3 m × 0.6 cm 20 % Carbowax column at 80°. Apart from the predominant methyl *t*-butylcyanoacetate, the products were identified as 1) 3,3-dimethylbutyronitrile (I) by comparison with an authentic specimen (IR, NMR) prepared by decarboxylation of *t*-butylcyanoacetic acid, 2) 2-cyano-3,3-dimethyl-1-butene (II) on the basis of its IR spectrum (bands at 2221 cm⁻¹ due to a conjugated nitrile group, at 1620 cm⁻¹ from the C=C-bond, and at 1465 cm⁻¹ due to the in-plane deformation vibration of the C=CH₂ group) and its NMR spectrum (a singlet at 1.21 ppm, and two slightly broadened singlets at 5.68 and 5.76 ppm with integrated band areas in the proportions 9:1:1), and 3) 2-cyano-3-methyl-2-butene, identified by comparison with an authentic specimen (IR, NMR), prepared by dehydration of 2,3-dimethyl-3-butenic amide⁷ by treatment with P₂O₅.

B. Analytical run in methanol, Pt or C anode. These experiments were run with 0.1 mole of the acid as described for the isopropyl acid. The carbon anode was a cylindrical charcoal plate, 50 × 23 × 5 mm. VPC analyses were made on a 1 m × 0.6 cm 10 % Carbowax column at 225°.

C. Analytical run in DMF. This experiment was performed as described before with 0.1 mole of the acid and 0.2 g of potassium hydroxide in 200 ml of DMF (analytical grade). An IR spectrum taken on the reaction mixture during and after the electrolysis had a medium strong band at 2040 cm⁻¹, indicative of a ketenimine.³ Exposure of the reaction mixture to atmospheric moisture caused this band to disappear within half an hour.

D. Analytical run in acetonitrile. The electrolyte consisted of *t*-butylcyanoacetic acid (0.1 mole), acetonitrile (200 ml), potassium hydroxide (0.2 g), and water (2 ml). It was necessary to add this amount of water in order to get a homogeneous solution.

E. Analytical run in water. *t*-Butylcyanoacetic acid (0.028 mole) was dissolved in water (200 ml) and potassium hydroxide (0.2 g) was added. The products were extracted by ether and analyzed as before.

Electrolysis of cyclohexylcyanoacetic acid in methanol. A. Preparative run. The electrolyte consisted of cyclohexylcyanoacetic acid (0.1 mole), potassium hydroxide (0.2 g), and methanol (200 ml). Immediately after the run, high-melting 2,3-dicyclohexylsuccinonitrile (1.7 g) could be filtered off directly, m.p. 235° after recrystallization from ethyl acetate (Found: C 78.4; H 10.0; N 11.2. Calc. for C₁₆H₂₄N₂: C 78.6; H 10.0; N 11.5).

The mother liquor was then evaporated *in vacuo* at room temperature. The residue was extracted with benzene in order to separate small amounts of potassium salts. After evaporation of the benzene, ethyl acetate (20 ml) was added to the residue, which precipitated low-melting 2,3-dicyclohexylsuccinonitrile (1.0 g), m.p. 155–159° after recrystallization from ethyl acetate (Found: C 78.4; H 9.8; N 11.6. Calc. for C₁₆H₂₄N₂: C 78.6; H 10.0; N 11.5).

Petroleum ether was then added to the mother liquor and the solution cooled to 0°. A second crystal fraction (1.0 g), m.p. 125–126° after recrystallization from benzene, was obtained. Its IR spectrum had a very weak nitrile band at 2240 cm⁻¹ (the nitrile band is known²¹ to be very weak or absent in compounds having electron-withdrawing groups α to the cyano group) and amide bands at 1640 and 1535 cm⁻¹. Elementary analyses (Found: C 74.0; H 9.8; N 10.9. Calc. for C₁₆H₂₆N₂O: C 73.2; H 10.0; N 10.7) were in agreement with the formula of *N*-(cyclohexaneacetyl)-cyclohexylglycinonitrile, as was also the NMR spectrum.

B. Analytical run. This was performed as described above. VPC analyses were made on a 1 m × 0.6 cm 10 % Carbowax 1500 column at 230°.

Configurational assignments of the 2,3-dicyclohexylsuccinonitriles.⁷ A. Electrolysis of cyclohexylmalonic acid. Cyclohexylmalonic acid (0.16 mole), methanol (300 ml), and potassium hydroxide (0.2 g) was electrolyzed until the electrolyte became neutral (this took some 15 times more than the theoretically calculated amount of charge; oxidation of methanol takes place simultaneously). The solid (7.7 g) formed was filtered off. By repeated washing with hot acetic acid, followed by high-vacuum sublimation, the high-melting diamide was obtained pure, m.p. 392° (decomp.).

By evaporation of the methanol solution from the first filtration a second crystal crop was obtained (0.5 g), m.p. 146–148° (decomp.), identified as the low-melting 2,3-dicyclohexylsuccinic diamide through its IR spectrum.

B. Dehydration of high- and low-melting 2,3-dicyclohexylsuccinic diamide. High-melting diamide (300 mg) was refluxed with POCl_3 (2 ml) for 10 min. The reaction mixture was poured on ice and the solid filtered off. After recrystallization from ethyl acetate, the product was identified as the high-melting 2,3-dicyclohexylsuccinonitrile (mixed m.p., IR).

The low-melting diamide on the same treatment gave the low-melting 2,3-dicyclohexylsuccinonitrile.

C. Hydrolysis of low-melting 2,3-dicyclohexylsuccinic diamide. Low-melting diamide (200 mg) was dissolved in acetic acid (10 ml) and concentrated hydrochloric acid (1 ml). Sodium nitrite (2 g) in water (10 ml) was then added dropwise with rapid stirring. After standing overnight, water (50 ml) was added and the organic material taken up in ether. The ether was evaporated and the residue neutralized with dilute potassium hydroxide solution. Barium chloride solution was then added and the precipitated barium salt was filtered off. From the barium salt low-melting 2,3-dicyclohexylsuccinic acid was liberated by treatment with hydrochloric acid and identified by comparison with an authentic sample.^{10a} Since the low-melting acid, as judged from its pK value and its chemical behavior, must be the racemic form, the low-melting diamide and the low-melting dinitrile must also be the racemic forms.^{7,22}

The high-melting diamide was recovered unchanged on the same treatment as well as from runs at higher temperatures, probably due to its exceedingly low solubility in the medium used. Other hydrolysis methods also failed, at least those which would be expected to retain the configuration of the starting material.

Electrolysis of dimethylcyanoacetic acid in methanol. A. Preparative run. Dimethylcyanoacetic acid (0.50 mole), methanol (200 ml), and potassium hydroxide (0.2 g) was electrolyzed until the solution had a pH of about 6 (above 7, the reaction mixture darkens very quickly and tar formation takes place). After evaporation of the methanol, part of the residue was subjected to column chromatography on silica gel. Ether eluted tetramethylsuccinonitrile, identified by comparison with an authentic sample (prepared by thermal decomposition of azobisisobutyronitrile in CCl_4), whereas *N*-(isobutyryl)- α -aminoisobutyronitrile was eluted by acetone and identified by comparison with an authentic sample.⁸

The rest of the residue from the methanol evaporation was subjected to small-scale preparative gas chromatography on a 1 m \times 0.6 cm 10 % diisodecylphthalate column at 50° in order to identify the low-boiling products. Isobutyronitrile, α -methylacrylonitrile, and methyl dimethylcyanoacetate were isolated and identified by comparison with authentic specimens.

B. Analytical run. This was performed as described before. VPC analyses were made on a 1 m \times 0.6 cm 10 % Carbowax 1500 column at 200°.

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