*Preparation of δ-Cyanovaleric Acid Ester by Cathodic Crossed Coupling**,***

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An electrolytic method for preparing adipodinitrile by the cathodic hydrodimerisation of acrylonitrile has recently been described.[1] We have now attempted to extend this to the preparation of the δ-cyanovaleric acid ester by the cathodic crossed coupling of acrylonitrile and the acrylic acid ester.

After many trials, it has now been found that the desired product can be obtained in a good yield when a mixture of a large amount of acrylonitrile (1 mol.) and a small amount of methyl acrylate (1/5 mol.) is reduced at the mercury cathode at as low a potential as possible (about −1.80 V. vs. SCE) in an electrolyte containing quaternary ammonium salt and with a slight excess of the theoretical amount of current. The yield and the current efficiency were both as high as 60% as calculated on the basis of the methyl acrylate used. A small amount of adipodinitrile was produced as a by-product, but neither dimethyl adipate nor propionitrile was produced. The product can be easily separated from the mixture of reaction products and unreacted starting materials by fractional distillation.

* Organic Electrode Process, Part 28; Part 27; *J. Electrochem. Soc.*, **110**, 918 (1963).

** Just before we read this paper at the Symposium on Organic Synthesis using Free Radical Reaction held at Osaka on September 1964[2], M. M. Baiser had also reported the same process in the July issue of the *Journal of Organic Chemistry*.[3] However, his conditions were somewhat different from the ours, and the yield was lower than that in the present paper. Our patent application to the Japanese patent office is dated July 15, 1964.

1) M. M. Baiser, Extended Abstract of Electro-Organic Division, Fall Meeting of The Electrochemical Society, Sept.-Oct. 1963, p. 14; *J. Electrochem. Soc.*, **111**, 215 (1964).

2) K. Sugino, K. Shirai and T. Nonaka, Extended Abstract of the Symposium on Organic Synthesis using Free Radical Reaction, sponsored by the Chemical Society of Japan, September 1964, p. 31.

3) M. M. Baiser, *J. Org. Chem.*, **29**, 1670 (1964).

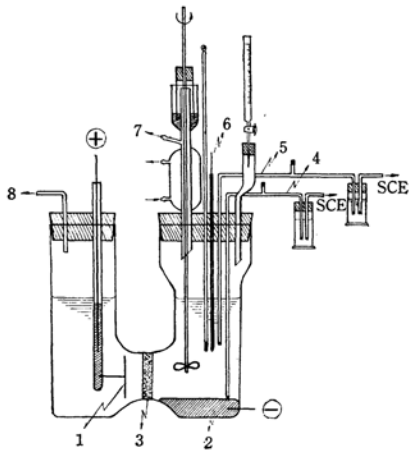

Fig. 1

1. Pt anode
2. Hg cathode
3. Diaphragm
4. Salt bridge for electrolyser use
5. Salt bridge for pH-meter use
6. Antimony electrode
7, 8. Gas outlets

This may be a new and simple route for preparing this compound from raw materials easily obtainable.

Experimental.—The cell used is an H-type cell; it is shown in Fig. 1. A fine-sintered glass diaphragm separated the cathode chamber from the anode chamber. The cathode chamber was closed with a rubber stopper equipped with a burette, a thermometer, a stirrer through the reflux condenser, two salt bridges connected with reference electrodes, and an antimony electrode connected with the pH meter. A mercury pool at the bottom of the cathode chamber served as the cathode. A platinum disk anode was placed vertically near the diaphragm. A controlled potential electrolyser, constructed by the Yanagimoto Co. in Kyoto, was used for the direct current power supply. The temperature was maintained at 30°C by cooling the cell with water.

A mixture of acrylonitrile (17.3 g., 1/3 mol.) and methyl acrylate (5.7 g., 1/15 mol.) was added to a concentrated aqueous solution of tetraethylammonium *p*-toluenesulfonate (consisting of 25 g. of salt and 25 g. of water), which served as the catholyte. The anolyte was the same electrolyte solution. The electrolysis was carried out by controlling the cathode potential at −1.80 V. A current of 0.70 amp. (cathodic current density: 6 amp./dm^2) flowed at the beggining (cell voltage: 17 V.), but it decreased to 0.50 amp. (cell voltage: 13 V.) at the end. The total amount of current passed was 3.57 amp. hr. (the theoretical amount for methyl acrylate). During the electrolysis, the catholyte was vigorously agitated by a stirrer. The pH of the catholyte was controlled at 5∼8 by adding *p*-toluenesulfonic acid.

After the reduction, the catholyte was thoroughly extracted with benzene. The distillation* of the dried (calcium chloride) benzene solution at temperatures up to 100°C left a light-yellow viscous liquid. After the absence of dimethyl adipate had been confirmed by a distillation test, the liquid was analyzed by vapor phase chromatography.** It consisted of 5.8 g. of methyl δ-cyanovalerate and 1.8 g. of adipodinitrile. Then the liquid was distilled under reduced pressure, to give 5.3 g. of methyl δ-cyanovalerate, b. p. 110°C at 7 mmHg and 1.7 g. of adipodinitrile, b. p. 126∼130°C at 7 mmHg.

For further confirmation, a portion of methyl δ-cyanovalerate fraction was hydrogenated in the presence of a nickel catalyst in an ethereal solution at 100∼120°C and 130 atm. to methyl ε-aminocaproate, which, in turn, was converted to ε-caprolactam by heating it in methanol at 220°C under a 60 atmospheric hydrogen pressure.[4] The methyl ε-aminocaproate and ε-caprolactam thus obtained had b. p. of 88∼89°C at 7 mmHg and 126°C at 8 mmHg respectively, and the latter solidified on standing.

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* The distillate was analyzed by vapor phase chromatography. The results showed that propionitrile was not formed and that the unchanged starting materials could be recovered almost quantitatively. As for methyl propionate, it could not be analysed by this method. However, if it existed the amount would be very small.

** Silicone (DC 550): Stationary phase, 2 m.; carrier gas, H_2; flow rate, 40 cc./min., 203°C.

4) Japanese Pat. 218607.