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REACTION OF NITRILES WITH SOLVATED ELECTRONS II(1). ELECTROCHEMICAL CLEAVAGE OF NITRILES

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Recent work has shown that electrochemical means can be used to advantage for the solvated electron cleavage of the carbon-halogen bond. This affords a convenient synthesis(2) of strained cycloalkanes from α,ω-dihalides.(2) As part of a study on the new reaction(1) of solvated electrons with nitriles, we have found that electrochemically generated electrons in anhydrous amine media similarly cleave the carbon-nitrile bond.

Accordingly, reductive intradimerization and reductive decyanation of 1,1'-dicyanobicyclohexyl(3) produced bicyclohexylidene (20%) and bicyclohexane (80%). This composition was based on the relative intensities of the molecular ion peaks(4) at m/e 167 and 166. Decyanation of dehydroabietonitrile(5), cycloheptyl cyanide, and n-octyl nitrile produced dehydroabietene, cycloheptane, and n-heptane, respectively, in 60-80% yield. The aromatic ring B of dehydroabietonitrile was not affected by the electrolytic process. This was surprising in view of the reported(6) electrolytic reduction of aromatic and unsaturated compounds.

The electrolysis setup used was similar to that already described(6a), which was adapted from previous(7) electrochemical work. In a typical experiment, a 0.12-molar solution of lithium chloride in anhydrous ethylamine containing 0.01 mole of nitrile was electrolyzed under a current of 0.5-0.7 ampere and 31 to 43 volts for a period of three to four hours. The ethylamine was then allowed to evaporate through a fractionating column and the residue was taken into a mixture of 100 ml of ether and 50 ml of water. The ether layer was separated from the aqueous phase, and the products obtained from the ether phase were analyzed via vapor-phase chromatography and spectrometric methods(8) as well as by direct comparison with authentic samples where possible.

The electrolytic generation of solvated electrons provides reductive selectivity with sensitive nitriles and avoids the side reaction encountered with the chemical methods of generating solvated electrons, for example, the competitive reduction(9) of some primary and secondary nitriles to their corresponding amines. In addition, electrochemical decyanation *may have general application for the quantitative determination*(9) *of the cyano group.*

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(8) Infrared spectra were obtained on a P.E. 137 spectrophotometer, while molecular weight was determined from MS-9 mass spectrometric data. Proton magnetic-resonance spectra were obtained on an A-60 with T.M.S. as internal standard. Analytical gas chromatograms were obtained on a Varian Aerograph 202 with a thermal-conductivity detector and an Aerograph Hy-Fi (A-600-D) gas chromatograph equipped with a hydrogen-flame detector. Columns employed were 0.25 in x 10 ft, 20 percent M TPA on 60/80-mesh Chromosorb W; 0.13 x 20 ft, 5 percent squalene on 70/80 ABS; and 0.25 in x 6 ft Porasil.

(9) These and other results as well as the analytical procedure for the cyano determination in t-nitriles will soon be published.