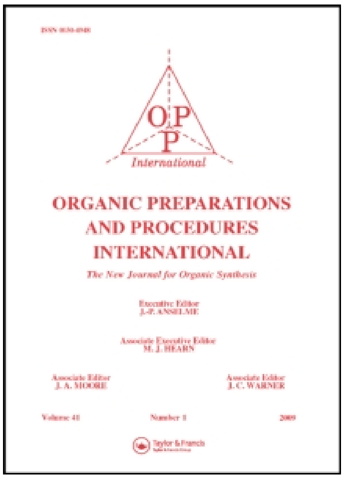

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ORGANIC ELECTROSYNTHESES VII.[1]

CONVENIENT PREPARATION OF p-AMINOBENZYLCYANIDE BY CATHODIC REDUCTION OF p-NITROBENZYLCYANIDE

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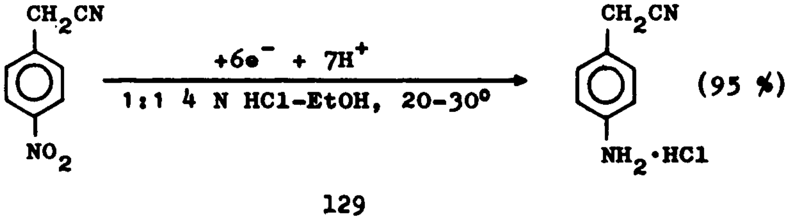
p-Aminophenylacetonitrile was needed for condensation[2] with 2-chlorocyclohexanone to give 6-cyanomethyl-1,2,3,4-tetrahydrocarbazole. The reported procedures[3,4] involving catalytic hydrogenation of p-nitrobenzylcyanide over a nickel catalyst failed in our hands and it was accordingly decided to try electrochemical reduction.

The nitro compound showed normal polarographic behaviour at a DME in acid solution. Preparative scale reductions at a mercury cathode at controlled potential in a 1:1 mixture of 4 N hydrochloric acid and ethanol gave the crude hydrochloride of the required compound in about 95 % yield. The hydrochloride could either be purified as such or converted into the free base.



The electrolytic reduction has been performed on batch sizes up to about 0.1 mole with reproducible high yields and a current efficiency of nearly 100 %. The cathodic reduction is thus an efficient and convenient alternative to catalytic hydrogenation which, for selective reduction, requires a catalyst of carefully specified activity. A more active catalyst may cause reduction of the cyano group as well. This is difficult to do electrochemically, and acid hydrolysis of the cyano function does not apparently occur under the conditions used. Electrochemical cleavage of the benzylic cyano group is also precluded in the conditions used.

EXPERIMENTAL

Apparatus. Electrolyses were performed in a divided all-glass cell of conventional design[5] with a catholyte volume of about 400 ml and surrounded by a water bath. The cell voltage was supplied and the cathode potential controlled by a Juul Electronic 40V/25A potentiostat. Electricity consumption was measured by a 5A DC Kwh-meter.

Material. Commercial p-nitrobenzylcyanide from Hopkins & Williams, Ltd., was used without further purification.

p-Aminophenylacetonitrile hydrochloride. All three cell compartments were filled with a 1:1 mixture of 4 N hydrochloric acid and ethanol and p-nitrobenzylcyanide (10-15 g) was added to the cathode compartment. The reference electrode was a silver wire in 4 N hydrochloric acid which avoided contamination of the product with inorganic material and thus facilitated work-up.[6] The electrolysis was performed overnight at potentials more anodic than -0.9 V vs Ag/AgCl, and towards the end of the experiment a white precipitate of the amine hydrochloride was formed in the slightly brownish catholyte. Because of the limited cooling capacity of a 10 l water bath it was necessary to restrict the current to about 3A, exchange the water after 2-3 h, and gradually alter the cathode potential to the final value of -0.9 V.

After electrolysis the mercury was separated and washed with water. The aqueous extract was added to the catholyte mixture and the combined mixture evaporated to dryness under reduced pressure using a rotatory evaporator. The last traces of water and hydrochloric acid were removed by the addition of 25-50 ml of absolute ethanol to the solid residue and re-evaporation. The yield of crude light brown p-aminophenylacetonitrile hydrochloride was 90-96 %, m.p. 222-224° (dec.). The crude material was purified by boiling with about 100 ml of ethanol followed by cooling to -15° and filtration to give 80-82 % of yellowish crystals, m.p. 224-226° (dec.), (lit.[4] 217-220°). A further crop of 8-10 %, m.p. 209-210° (dec.), was obtained by addition of a fivefold volume of ether to the mother liquor, cooling and filtration.

p-Aminophenylacetonitrile. The crude hydrochloride was treated with excess aqueous potassium carbonate solution, shaken with ether (x2), and the combined ether layers dried (K_2CO_3). Evaporation of the filtered solution gave 91 % of the free amine, m.p. 36-7° suitable for use in the tetrahydrocarbazole synthesis. The residue was redissolved in 200 ml of ether, the solution decanted from a little tarry material and re-evaporated, leaving 89 % of an orange solid, m.p. 47-8° (lit.[3] 46°).

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