

SHORT COMMUNICATION

ON THE ELECTROCHEMICAL REDUCTION OF BENZYL CYANIDE

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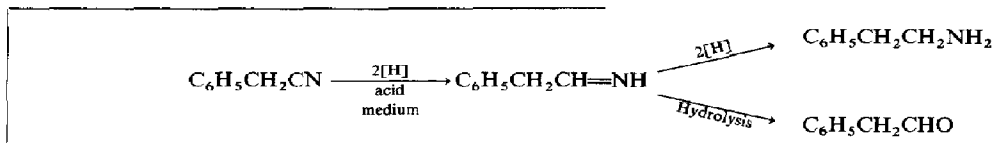
The electro-reduction of benzonitrile to benzylamine has already been communicated[1]. In the present communication, the electro-reduction of benzyl cyanide to β -phenylethylamine is described in detail. There are number of methods available for the preparation of β -phenylethylamine. For example, benzyl cyanide can be reduced catalytically using precious metals adsorbed over carbon under high pressure or with sodium or lithium in alcoholic medium containing ammonia[2]. Benzyl cyanide has also been reduced using Raney nickel in hydrogen atmosphere[3]. There are certain disadvantages in the catalytic method in the use as well as in the preservation of the catalyst. These have been well explained in our earlier communication[1]. An Indian Patent on the electrochemical preparation of β -phenylethylamine hydrochloride has been filed[4].

In the present approach, a novel electro-reduction technique, which involves a combination of *in situ* electrochemical generation of pure hydrogen and the adsorption of the same on a thinly deposited palladium black over graphite cathode acting as the catalyst, is adopted. This electro-reduction technique which has already been employed with much success for the preparation of benzyl-

amine took place. It was also observed by using galvanostatic polarization experiments, there is no depolarization with benzyl cyanide when higher overvoltage cathodes were used. At present, we feel that this reduction may be by chemisorbed hydrogen since it is well known that the surface concentration of hydrogen is very high on a palladized surface.

Benzyl cyanide was reduced under two different conditions: (i) The reduction was carried out using a 10% aqueous methanolic hydrochloric acid as catholyte in a divided cell. In this case, the yield of β -phenylethylamine (as hydrochloride) was around 70%. (ii) When a solution of aqueous methanolic hydrochloric acid containing acetic acid was used as the catholyte in a divided cell, the yield of β -phenylethylamine hydrochloride was around 85%. The current efficiency was found to be poor in both the cases. Under both conditions, the intermediate imine is found to be hydrolysed to the aldehyde to a certain extent. But the formation of aldehyde is greater in aqueous methanolic HCl than in aqueous methanolic HCl containing acetic acid.

The sequence of the electrochemical reduction of benzyl cyanide can be written as follows:



amine[1] and at present for the synthesis of β -phenylethylamine, has opened up a new route for the preparation of primary amines in high yields from corresponding nitriles.

Deposited palladium black cathodes over graphite substrates were prepared both under stationary and rotating conditions as described in our earlier communication[1]. Galvanostatic polarization studies carried out with and without benzyl cyanide using saturated calomel as the reference electrode revealed a considerable depolarization only in the low *cd* region both under stationary and rotating deposited palladium black over graphite cathodes. At the concentrations employed here, it appears that the reduction of the nitrile on an electrode such as palladium black can be by chemisorbed hydrogen. Since this reduction is not a diffusion controlled process, a rotating electrode technique will not have any advantage over the stationary system. Hence, in the present study a cell with a stationary electrode is employed for the preparation of the amine. When higher hydrogen overvoltage cathodes like Hg, Cd and Pb were used for the reduction experiments with benzyl cyanide, it was observed that no reduc-

The yield of amine hydrochloride was at a maximum at low *cd* (1-2 A/dm²); whereas, at higher current densities (4 to 6 A/dm²), the yield is lowered with a poor current efficiency.

β -phenylethylamine hydrochloride was neutralised with alkali and then extracted with ether which on evaporation gave β -phenylethylamine. The amine was converted to its N-benzoyl derivative by the standard method. β -phenylethylamine hydrochloride isolated was found to be very pure as indicated by the melting point and by thin layer chromatographic analysis. β -phenylethylamine was also converted to β -phenylethanol on treatment with NaNO₂ and HCl.

As there is a possibility of the aldehyde getting adsorbed with the amine, various analytical data have been used to confirm the purity of the amine. The estimated C, H, N and Cl values agreed well with the required data. The infrared spectrum of β -phenylethylamine hydrochloride showed bands characteristic of a primary amine having an aromatic nucleus. Mass spectral analysis confirmed its molecular weight and hence its purity also. The other fragments of the mass spectrum are in agreement with the

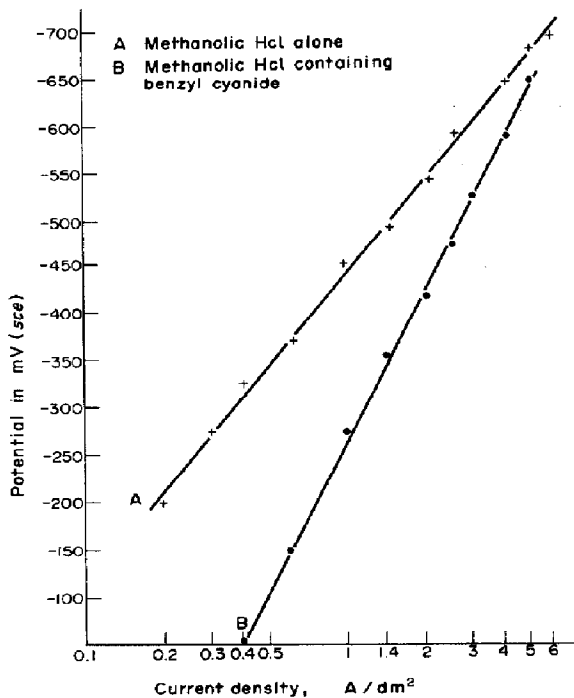


Fig. 1.

structure of the compound. Yet another confirmation regarding the purity of the amine comes from NMR spectrum. There are mainly two sets of signals viz around 7.2 δ denoting the presence of five aromatic protons and a multiplet in the region of 3.0 δ -3.6 δ pertaining to four methylene protons.

REFERENCES

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