AMINONITRILE CLEAVAGE DURING THE ELECTROCHEMICAL REDUCTION OF N,N-DISUBSTITUTED HYDRAZONES

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The electrochemical reduction of N-mono- and N,N-disubstituted hydrazones takes place, as a rule, with cleavage of the N—N bond [1]. It is assumed [1, 2 and refs. therein] that an amine HNR^1R^2 and an imine [for example, $PhC(R^3)=NH$] are formed in this process and that the latter is subsequently reduced to an alkylamine.

We have established that, during the electrochemical reduction of the N,N-diphenyl- (I, $R^1 = R^2 = Ph$, $R^3 = H$), N-methyl-N-phenyl- (II, $R^1 = CH_3$, $R^2 = Ph$, $R^3 = H$), and N-methyl-N-(3-chloropyridazinyl-6-hydrazones of benzaldehyde (III, $R^1 = CH_3$, $R^2 = C_4H_2ClN_2$, $R^3 = H$) and the N,N-diphenylhydrazone of benzoyl chloride (IV, $R^1 = R^2 = Ph$, $R^3 = Cl$) in dimethylformamide (DMF) with Et_4NClO_4 as the supporting electrolyte, formation of the corresponding secondary amine and benzonitrile occurs.

$$PhC(R^3)=N-NR^1R^2 \xrightarrow{2e} PhCN + HNR^1R^2$$

The formation of PhCN during the electrochemical reduction of hydrazones was confirmed by ESR (recording of the spectrum of $PhCN^-$), cyclic voltammetry, and IR and UV spectroscopy and, during the electrolysis of the hydrazone (IV), it was isolated preparatively.

The direction in which the electrochemical reduction reaction proceeds depends on the nature of R^2 and R^3. For instance, in the electrochemical reduction of the phenylhydrazone of benzoyl chloride ($R^1 = Ph$, $R^2 = H$, $R^3 = Cl$), aminonitrile cleavage was observed as a parallel process, while it did not occur during the electrochemical reduction of the phenylhydrazone of benzaldehyde ($R^2 = R^3 = H$). Aminonitrile cleavage has only previously been observed during the electrochemical reduction of trialkylaldehydrazonium salts [3].

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