

CATHODIC AMINATION OF CARBONYL COMPOUNDS

- Abstract -

The first part of the dissertation describes the reductive amination at a mercury cathode as a method for the preparation of secondary amines (Fig. 1). Examples for various classes of compounds are given.

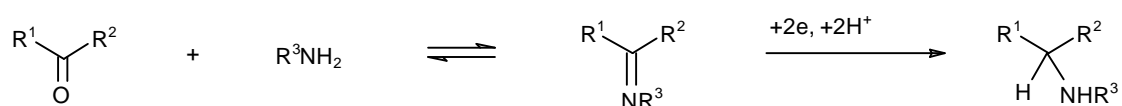


Fig. 1

During reductive amination of ketones containing other reducible substituents, no reduction of an olefinic double bond, a cyclopropanyl or trifluoromethyl-phenyl group occurs. This excellent chemoselectivity makes the electrochemical method advantageous compared to many other reductive methods, e.g. catalytic hydrogenation.

Reaction of 2-alkoxyketones in presence of primary amines at the mercury cathode occurs under stereoelectronic control. If the C-O bond can orientate orthogonally to the plane of the carbonyl group, dealkoxylation is observed. In the opposite case, secondary amines are generated (Fig. 2).

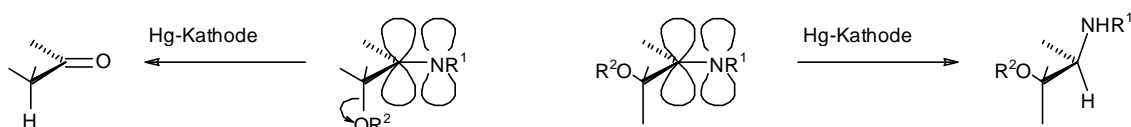


Fig. 2

Cathodic amination of 2-oxocarboxylic acids leads to a mixture of the stereoisomeric N-allylic acids in medium to good yields (Fig. 3). An analogous reaction can be achieved at graphite electrodes.

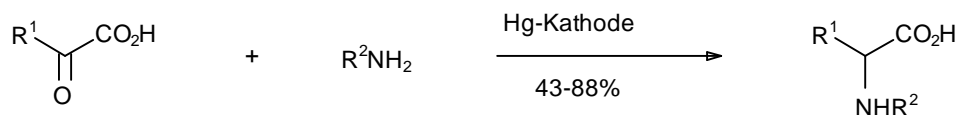


Fig. 3

Reduction of 1,4-diketones in a borate buffered ammonium solution at the mercury cathode produces 2,5-Dialkylpyrrolidines in good to excellent yield (Fig. 4). In case of acyclic diketones, *cis*-dialkyl-pyrrolidines are obtained with good stereoselectivity.

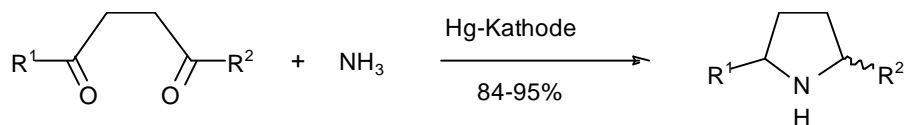


Fig. 4

In the second part of the dissertation the mechanism of the cathodic amination of pyruvic acid and phenoxyacetone is investigated by means of cyclic voltammetry. Programs for recording, editing and simulation of voltammograms on microcomputers are described.

By comparison of measured and simulated voltammograms it is shown that in case of the reaction of pyruvic acid, a semiaminal occurs as intermediate in high equilibrium concentrations. Supported by the findings, it is supposed that in alkaline solution the dissociation of a hydroxide anion is the velocity determining step of imine formation. For the reaction of ethylamine a faster reaction is observed compared to isopropylamine.

In case of the reaction of phenoxyacetone, the semiaminal can be neglected as intermediate and the reaction with ethylamine can be treated as a one step equilibrium. By analysis of the voltammograms, equilibrium and velocity constants can be determined.