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LETTERS TO THE EDITOR

Electrochemical Amination of Anisole to Anisidines in a Mixture Aqueous Sulfuric Acid and Acetonitrile

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Electrochemical amination of aromatic substrates by hydroxylamine with Ti(IV)/Ti(III)system as mediator provides a fundamental possibility of one-stage synthesis of mono- and diaminocompounds [1, 2]. In the aqueous sulfuric acid up to 7 M concentration the only substitution products are monoamines. But when the substrates insoluble or poorly soluble in catholyte are exposed to amination even under the most favorable conditions (1–3 M H_2SO_4 solutions) the current yields of monoaminocompounds do not exceed 11% [3, 4], the main part of the aminyl radicals is reduced with Ti(III) ions to ammonia.

In this study we showed by an example of anisole functionalization that using in the process of amination of aromatic compounds acetonitrile, the organic solvent more inert to the aminoradical intermediates [5], permits to increase significantly the efficiency of substitution and to prepare monoamines in the sufficiently high yields with respect to the aminoradical source.

The amination of anisole was carried out in the glass electrochemical cell with the cathode and the anode spaces separated with a ceramic diaphragm. The catholyte, 25 ml of water solution, contained 0.2 M of NH_2OH, 0.1 M of Ti(IV), and also the required concentrations of sulfuric acid and acetonitrile. Electrolysis of the highly dispersed emulsion of 5 ml of anisole in the catholyte deaerated with argon was carried out at 40°C and the current density on the mercury anode 2 mA cm^{-2}. For the sake of comparison of the results of investigation with the data of [4] the amount of electricity passed through the emulsion in the course of electrolysis as a rule was 250 Coulombs.

After the completion of amination the catholyte was diluted with water to the H_2SO_4 concentration 1–1.5 M, cooled and alkalinized to the weak acidic reaction with NaOH solution and then neutralized with $NaHCO_3$. The products of amination of anisole were extracted with chloroform and analyzed on a Chrom-4 chromatograph. For more exact analysis of the nature of products the flame ionization detector, the katharometer, and the XE-60, the SE-30, and the OV-17 phases were used. The quantitative analysis of anisidines was carried out on a 2500 × 3 mm steel column filled with 5% of XE-60 on Chromaton N-AW (0.169–0.200 mm) at 150°C using the flame-ionization detector.

The electrolyses carried out in 1.5 M H_2SO_4 showed that the dependence of the current yield on the acetonitrile concentration passes through the minimum point in 11 M solution, but at high concentrations of organic solvent the efficiency of the target electrochemical process does not significantly exceed 11%. Therefore considering the effect of H_2O/H_2SO_4 ratio on the results of substitution [4] we have carried out the amination of anisole in the electrolytes containing 2–7 M of H_2SO_4 and the concentrations of acetonitrile close to the maximum possible.

In the media with high content of solvent the products of amination of anisole are *ortho*- and *para*-anisidines. The highest yield of aminocompounds was obtained in the catholyte containing 6 M of H_2SO_4 and 11.6 M of CH_3CN. Due to the chain mechanism of the electrochemical process the current yield of anisidines (*para/ortho* ratio ~1.8) under these conditions exceeded 100% and reached 147%. When the electrolysis was carried out with consumption of the amount of electricity theoretically required for the complete conversion of hydroxylamine in the one-electron process (Q_t 482.4 Coulombs) the catholyte turned violet as characteristic of the Ti(III) solutions. Decoloration of the catholyte probe at the addition of hydroxylaminium sulfate indicated the complete consumption of the source of aminoradicals in the process with the consumption of Q_t. Hence, the current yield of anisidines in this electrolysis equal to 78% corresponds to their yield with respect to hydroxylamine.

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