NITRILE CLEAVAGE UPON THE ELECTROCHEMICAL OXIDATION OF HYDRAZONE DERIVATIVES OF BENZALDEHYDES

V. Z. Latypova, M. Yu. Kitaeva,
Yu. M. Kargin, and A. V. Il'yasov

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Upon oxidation at a platinum electrode in acetonitrile with $NaClO_4$ as the base electrolyte, the diphenylhydrazone of benzaldehyde undergoes dihydrodimerization with the formation of dibenzylideniminio-N,N'-diphenyl-N,N'-benzidine in about 50% yield [1, 2].

We are the first to establish that the electrochemical oxidation of a series of hydrazones of aromatic aldehydes may initiate their nitrile cleavage: the electrolysis of the dimethyl hydrazone and diphenylhydrazone of benzaldehyde and the dimethylhydrazone of p-nitrobenzaldehyde on a platinum electrode in acetonitrile with Et_4NClO_4 as the base electrolyte at the potentials of the limiting current of the first oxidation waves (0.60, 0.80, and 0.85 V relative to Ag/Ag^+, respectively) led to the formation of the corresponding nitriles in yields from 20 to 30% along with the previously described products; the nitriles were identified by gas liquid chromatography in the reaction mixture after the electrolysis and by polarography.

The formation of the nitriles is apparently initiated by the deprotonation of the carbon atom of the azomethine group in the radical-cation with subsequent breakage of the nitrogen–nitrogen bond in the radical, which competes with the previously described dehydrodimerization reaction [1].

LITERATURE CITED

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A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch of the Academy of Sciences of the USSR. V. I. Ul'yanov-Lenin Kazan State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, p. 958, April, 1986. Original article submitted December 5, 1985.

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