CLEAVAGE DIRECTION OF C – O BOND IN ANION RADICALS OF METHYL ESTERS OF AROMATIC ACIDS IN APROTIC SOLVENTS

V. P. Gul'tai, T. Ya. Rubinskaya, and L. M. Korotaeva

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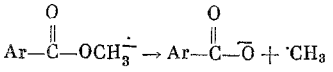
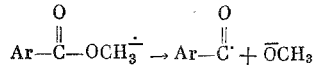
During electrolytic reduction (ER) of aliphatic esters of aromatic acids (AEAA) in proton-donor solvents, a mixture of aromatic alcohols and esters hydrogenated in the aromatic ring is formed [1]. According to [2], in aprotic solvents (in particular, in DMFA), ER of phenyl esters of aliphatic acids (phenyl acetate) leads to aliphatic acids and aromatic hydrocarbons. From the results of a two-electron ER of methyl benzoate under similar conditions, it was concluded [2] that also during one-electron ER (generation of anion-radicals of AEAA) the formation of the corresponding alcohols should be expected. Thus, in contrast to the anion radicals of phenyl acetate, the anion radicals of methyl benzoate should undergo a cleavage of the C–O bond with the formation of a methylate ion. However, the EPR spectra of anion-radicals of methyl benzoate electrochemically generated in DMFA in the presence of Alk_4N^+ salts [3] show that the conjugation chain is extended in them to the methyl group protons, which makes it possible to predict the decomposition of these anion radicals equally probably at the terminal C–O bond



(1)

and at the C–O bond with the participation of the carbonyl group carbon atom



(2)

In contrast to the point of view advanced in [2], a preparative electrolysis of methyl benzoate and methyl ester of 2-thiophenecarboxylic acid on a mercury cathode in DMFA solutions in the presence of 0.25 M $(C_4H_9)_4NClO_4$ at the formation potentials of their anion radicals (1 F of electricity per mole) leads to a quantitative formation of benzoic and 2-thiophenecarboxylic acids (reaction 1), respectively. Thus a one-electron ER of AEAA can serve as a preparative method for the removal of the ester protection.

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