BRIEF COMMUNICATIONS

Electrochemical Methoxylation of Anethole on a Graphite Anode

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Abstract—A procedure is suggested for electrochemical methoxylation of anethole in an electrolyzer with a graphite cathode and potassium *p*-toluenesulfonate in methanol as supporting electrolyte; a mixture of two products is formed in the process.

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Electrochemical alkoxylation of organic compounds on platinum, carbon, and graphite anodes has been reported [1]. The source of the methoxylating agent was methanol, acting as a solvent for both the organic substance and the electrolyte. Alcoholic solutions of alkalis and alcoholates were recommended for electrochemical alkoxylation of hydrocarbons, tertiary amines, and ethers. The alkoxylation pathway is strongly influenced by the concentration of the organic substrate [1]. If dimerization occurs concurrently with alkoxylation, the contribution of the former process, as a rule, increases with the concentration of the organic substrate.

The methoxylation of aryl-substituted unsaturated hydrocarbons, styrene and its derivatives, has been studied in detail; it was shown that electrochemical methoxylation of styrene gives dimethoxyphenylethane in 30% yield [1]. Anodic methoxylation of anethole (1-methoxy-4-propenylphenol) is of interest as a route to anisaldehyde (aubepine) diacetal, which can be readily converted by hydrolysis into the free aldehyde, a valuable fragrance compound and an intermediate for organic synthesis. Methoxylation of alkenylarenes, including anethole, in a methanolic solution of potassium or sodium trifluoroacetate in a diaphragmless electrolyzer with graphite electrodes was reported in [2]. However, the electrolyses may be complicated by anodic decomposition of trifluoroacetate. The goal of this study is to simplify this process and extend its potentialities.

Previously [3] we have demonstrated the possibility in principle of electrochemical methoxylation of anethole at $55-65^{\circ}$ C on a graphite anode in methanol, with potassium *p*-toluenesulfonate as supporting electrolyte. An advantage of this system is that the salt crystallizes and precipitates on cooling, and it can be readily separated by filtration. The filtrate is treated with 10% sulfuric acid and extracted with toluene; the extract is washed with a sodium carbonate solution and vacuum-distilled. In the process, anethole is gradually added to the electrolyte, because at low concentrations its oxidative dimerization is suppressed.

We examined the influence exerted on the methoxylation by the temperature, current density, amount of electricity, and electrolyte concentration. The best results were obtained under the following conditions: $55-65^{\circ}$ C, anodic current density 0.02–0.05 A cm⁻², amount of electricity 5.5–6 F per mole of anethole, 3–5% supporting electrolyte concentration, and up to 0.4 M concentration of anethole in the electrolyte. Anisaldehyde and methyl *p*-methoxybenzoate were obtained in yields of up to 70 and 25%, respectively. The electrochemical methoxylation and hydrolysis follow the scheme

It should be noted that methyl *p*-methoxybenzoate (anisic acid methyl ester) is used as a stabilizer for fragrance compounds. As a target product we obtained a mixture of anisaldehyde and methyl *p*-methoxybenzoate. Their boiling points are close (248 and 256°C, respectively [4]), making difficult their separation by distillation.

EXPERIMENTAL

Anethole, toluene, and potassium *p*-toluenesulfonate were reagent-grade. The electrolyzer was a cylindrical glass vessel with a temperature-control jacket. Current leads and tubes for the stirrer, addition of anethole, and removal of the gas were fixed on the lid. The electrolyzer was charged with a mixture of 150 g of methanol and 3.5 g of potassium p-toluenesulfonate; the mixture was stirred at 55-65°C until the salt dissolved completely, and the electrolysis was performed at a current density of 0.03 A cm⁻² (3 A current) with gradual addition of anethole (15 g in total; the running concentration did not exceed 0.4 M). The electricity was passed in an amount of 6 F per mole of anethole. After the electrolysis completion, the solution was cooled to ensure complete precipitation of the salt, the salt was separated, and the filtrate was evaporated to remove methanol, treated with 15 ml of 10% H₂SO₄, and extracted with toluene $(3 \times 20 \text{ ml})$. The toluene extract was washed with an aqueous solution of sodium carbonate and then distilled; toluene was distilled off at atmospheric pressure and vapor temperature of up to 110°C, and the target product, at reduced pressure (8–9 mm Hg) and vapor temperature of 120-125°C. An oily liquid (14 g) with a pleasant hawthorn odor was obtained; according to the chromatographic analysis, it contained 69% anisaldehyde and 25% methyl p-methoxybenzoate (total yield based on anethole 94%). The product can be used as a component of odorants, cosmetics, and aromatic food essences [5], and also as a component of agricultural chemicals for rodent and pest control [6, 7]. Anisaldehyde can be isolated from the product via bisulfite derivative. The product components were identified by gas chromatography (comparison of the retention times with those of the authentic samples).

CONCLUSION

The procedure developed for electrochemical methoxylation of anethole in methanol on a graphite anode with potassium *p*-toluenesulfonate as supporting electrolyte, yields a mixture of two valuable products, anisaldehyde and methyl *p*-methoxybenzoate and allows simplification of the process and extension of its potentialities.

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