ELECTROCHEMICAL METHOXYLATION OF ALLYLBENZENE

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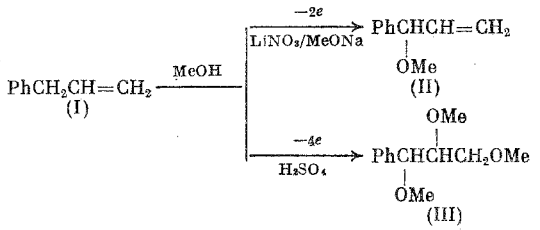
The anodic methoxylation of alkylbenzenes leads to α-methoxyalkylbenzenes and the oxidation products of these methoxy derivatives [1]. Phenylethylenes under analogous conditions form 1,2-dimethoxyphenylethanes [2, 3]. 1-Phenyl-1,3-dimethoxyalkanes are obtained in the anodic methoxylation of phenylcyclopropanes [4]. There has been no report of the electrochemical methoxylation of 1-alkenes.

We discovered that the anodic oxidation of allylbenzene in methanol with $LiNO_3$, NH_4NO_3, or MeONa base electrolyte leads to 1-methoxy-1-phenyl-2-propene (II), which is the expected reaction product. Only 1-phenyl-1,2,3-trimethoxypropane (III) is obtained upon carrying out the electrolysis in methanol containing sulfuric acid.



Apparently, propane derivative (III) is the product of the additional methoxylation of (II). The most likely precursor for (III) is 1-phenyl-3-methoxy-1-propene (which is isomeric to (II)). Small amounts of (III) were detected upon carrying out the electrolysis with sulfuric acid as the base electrolyte in the reaction mixture. Thus, the direction of the electrochemical methoxylation of allylbenzene is altered with change in the base electrolyte.

The electrolysis of 9 g (76 mmoles) (I) and 1 ml 95% H_2SO_4 in absolute methanol in a diaphragmless electrolyzer on a platinum anode with 220 mA/cm^2 current density at 55-60°C (Q = 5 F/mole) leads to the formation of 5.8 g (III) (two diastereomers) in 45% yield relative to converted (I) (the conversion of (I) was 75%), bp 127-132°C (17 mm). Found: C, 68.46; H 8.56%. Calculated for $C_{12}H_{18}O_3$: C, 68.57; H 8.57%. PMR spectrum (δ, ppm): 3.08 s, 3.11 s, 3.18 s and 3.28 s (9H, CH_3O), superimposed on signals (3H, C$\underline{H}$OCH_3 and C$\underline{H}_2$OCH_3), 4.15 d (1H, PhC$\underline{H}$OCH_3), 7.18 (5H, C_6H_5).

LITERATURE CITED

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