

SHORT
COMMUNICATIONS

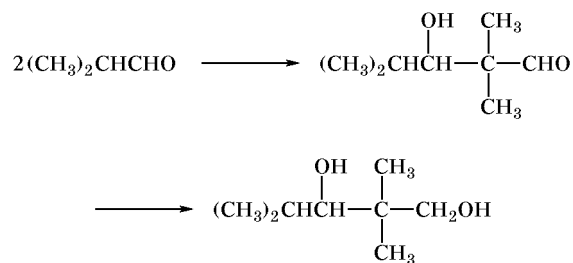
Chemical Aspects of Electrocatalytic Reduction of Carbonyl Compounds. Aldehydes

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In continuation of our studies on electrocatalytic reduction of carbonyl compounds in alkaline medium over Raney nickel [1], we examined the reduction of a series of aldehydes. The hydrogenation of benzaldehyde, which is incapable of undergoing aldol condensation, gave benzyl alcohol. The reaction with isobutyraldehyde under the same conditions led to aldol condensation and subsequent hydrogenation of the resulting β -hydroxy aldehyde to afford 2,2,4-trimethylpentane-1,3-diol in high yield.



The concentration of 2-methyl-1-propanol in the products was as low as 2.6%. The reduction of acetaldehyde and butyraldehyde followed an analogous pattern. The hydrogenation of crotonaldehyde also involved intermediate formation of β -hydroxy aldehyde and gave the same product as that obtained from acetaldehyde, 1,3-butanediol.

The electrocatalytic reduction was carried out in a two-chamber electrolyzer whose anode and cathode chambers were separated by an MA-40 ion exchange membrane. The cathode chamber was equipped with a stirrer operating at a speed of 300 rpm. A platinum network was used as anode, and a titanium plate, as cathode.

Reduction of benzaldehyde. As anolyte we used 50 ml of 20% aqueous sodium hydroxide. Raney nickel, 0.5 g, was placed in the cathode chamber together with 50 ml of 5% aqueous sodium hydroxide. The reduction was performed at 20°C at a constant current (1 A, 8 V). Before addition of benzaldehyde, the catalyst was saturated with hydrogen over a period of 20 min. Benzaldehyde, 5 ml (5.2 g, 0.05 mol), was then added, and the electrocatalytic reduction was conducted for 2 h. When the reaction was complete, the products were extracted from the catholyte with diethyl ether, and volatile fractions were distilled off from the extract. According to the GLC data, the yield of benzyl alcohol was 96% (current-based yield 75%).

From isobutyraldehyde and butyraldehyde we obtained, respectively, 2,2,4-trimethylpentane-1,3-diol (chemical yield 92%, current-based yield 65%) and 2-ethylhexane-1,3-diol (chemical yield 90%, current-based yield 62%). In the synthesis of 1,3-butanediol from acetaldehyde, the chemical yield was 85%, and current-based yield, 62%. In the reduction of crotonaldehyde, the chemical yield was 80%, and current-based yield, 63%.

The products were identified by GLC on a Chrom-5 chromatograph using authentic samples; thermal conductivity detector, carrier gas helium (80 ml/min), glass column (3500 × 3 mm), stationary phase 5% of polyethylene glycol on Chromaton N-AW-DMCS, oven temperature 80°C.

REFERENCE

1. Shchelkunov, S.A., Mazakova, S.V., Bekenova, U.B., Amirkhanova, A.K., and Shchelkunov, A.V., *Russ. J. Org. Chem.*, 2001, vol. 37, p. 446.