

SHORT
COMMUNICATIONS

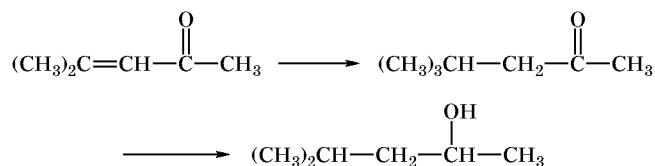
Chemical Aspects of Electrocatalytic Reduction of Carbonyl Compounds. Mesityl Oxide

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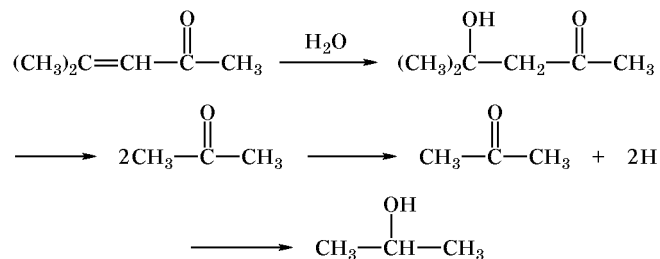
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Interest in the reduction of mesityl oxide (4-methyl-3-penten-2-one) originates from the fact that this process results in formation of either 4-methylpentan-2-one which is widely used in varnish-and-paint industry or 4-methylpentan-2-ol which is an efficient flotation reagent for large-scale coal beneficiation.



Kirilyus *et al.* [1] described a procedure for electrocatalytic reduction of mesityl oxide to 4-methylpentan-2-one in 92% yield. We believe that aqueous-alkaline medium (where the reaction was carried out) should necessarily give rise to side processes, specifically to aldol-like condensation. Our attempts to reproduce experiments described in [1] showed that 0.0438 mol of mesityl oxide in 3 h absorbs only 0.066 mol of hydrogen. Moreover, it was impossible to attain more than 30% yield of 4-methylpentan-2-one because of concurrent aldol condensation.



When the reaction was performed until hydrogen was no longer absorbed (contrary to [1]), the yield of

the target product increased almost twofold (see table). There was no doubt that temperature should strongly affect the process. Raising the temperature increases the fraction of isopropyl alcohol among the products, which indicates increased contribution of the retro-aldol reaction and subsequent reduction of the acetone thus formed.

Naturally, it was reasonable to examine electrocatalytic reduction of acetone itself at various temperatures. We have found that at 20°C the reduction of acetone is terminated when the fraction of isopropyl alcohol in the catholyte attains 34%; at 60°C the corresponding fraction of isopropyl alcohol is 66%.

The electrocatalytic reduction of mesityl oxide of chemically pure grade was carried out in a two-chamber Kirilyus electrolyzer [2, 3], whose anode and cathode spaces were separated by an MA-40 ion-exchange membrane. As anolyte we used a 20% aqueous solution of sodium hydroxide (50 ml), the catholyte was 5% aqueous sodium hydroxide (50 ml), the anode was a platinum network, the cathode was

Temperature effect on the composition of products of exhaustive electrocatalytic reduction of mesityl oxide (substrate amount 0.024 mol)

| T, °C | Catholyte composition, % | | | |
|-------|--------------------------|---------------------|--------------------|----------------|
| | 4-methylpentan-2-one | 4-methylpentan-2-ol | Me ₂ CO | <i>i</i> -PrOH |
| 20 | 56.4 | 25.8 | 1.8 | 16.0 |
| 45 | 38.6 | 27.9 | 6.8 | 26.7 |
| 52 | 41.3 | 9.2 | 1.5 | 48.1 |
| 60 | 7.2 | 8.4 | 11.1 | 73.2 |

a copper plate, and the catalyst was Raney nickel (0.5 g); direct current 1 A (8 V). The conditions were the same as in [1]. When the reaction was complete, the products were extracted from aqueous-alkaline solution into diethyl ether using a Soxhlet apparatus.

The product composition was determined by GLC on a Chrom-5 chromatograph (thermal conductivity detector; carrier gas helium, flow rate 80 ml/min; glass column, 3500×3 mm; oven temperature 80°C; stationary phase 5% of PEG on Chromaton N-AW-DMCS); authentic samples of the products were used. The results are given in table.

REFERENCES

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