OXIDATION OF NITROBENZENES BY OXYGEN IN A KOH–ORGANIC SOLVENT–18-CROWN-6 ETHER SYSTEM

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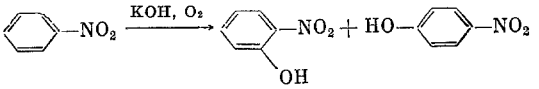
The conversion of nitrobenzene to nitrophenols in an alkaline medium is known [1]. However, since the oxidizing agent in this reaction is apparently nitrobenzene itself, the maximum yield of nitrophenols theoretically cannot be greater than 50% and is less in practice.

We have shown that the conversion of nitrobenzene to nitrophenols may be readily accomplished in a heterogeneous system consisting of a solid alkali, organic solvent, 18-crown-6 ether, and oxygen. Thus, the oxidation of nitrobenzene by oxygen in the KOH–dimethoxyethane–18-crown-6 ether at 60-70°C for 6 h leads to the formation of a mixture of nitrophenols in 90-95% yield. The o-nitrophenol fraction is 90-95% and the remainder is p-nitrophenol. The yield of the nitrophenol mixture is only 65-70% when running this reaction at 20°C for 20-25 h with 98-99% o-nitrophenol content



The oxidation of nitrobenzene in benzene at 60-70°C for 9 h leads to the formation of a nitrophenol mixture in 80-85% yield. The content of the ortho isomer was 85-90%. The reaction in benzene with 10% added dimethyl sulfoxide reduces the yield of nitrophenols to about 50%.

We should note that the oxidation in dimethoxyethane also proceeds without the crown ether, although the initial rate is reduced by a factor of 2-4. The oxidation does not proceed in benzene without crown ether.

We have also shown that p-nitrochlorobenzene is also oxidized by oxygen in the KOH–dimethoxyethane–18-crown-6-ether system and the reaction product is 2-nitro-5-chlorophenol in 85-87% yield.

LITERATURE CITED

1. A. Wohl, Chem. Ber., 32, 3486 (1899).

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