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Ullmann Ether Synthesis in DMI. Preparation of m-Phenoxybenzyl Alcohol

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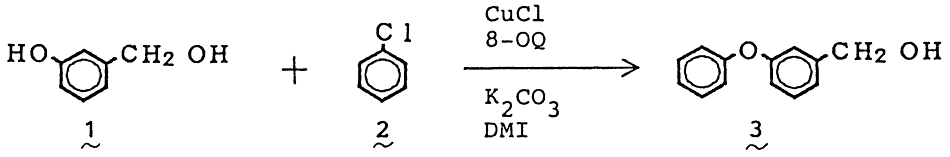
The condensation of m-hydroxybenzyl alcohol with chlorobenzene was examined in several different solvents, and an effective route to m-phenoxybenzyl alcohol has been developed by using 1,3-dimethyl-2-imidazolidinone (DMI) as a solvent.

m-Phenoxybenzyl alcohol (3), which is an important intermediate of prominent pyrethroids, has received much attention in the insecticide chemistry.1) The majority of the hitherto disclosed procedures for the synthesis of 3 relies upon partial oxidation of m-phenoxytoluene. For example, the halogenation of phenoxytoluene followed by hydrolysis2) has been intensively investigated, but product selectivity is not necessarily satisfactory. On the other hand, as an alternative route to 3, we have already established the electrosynthesis of m-hydroxybenzyl alcohol (1) and the condensation of 1 with bromobenzene.3) This time, we studied the condensation of 1 with chlorobenzene (2);4) 2 is a more attractive starting compound than bromobenzene from the economical sense as well as scientific interest.5)



Addition of catalytic amount of 8-hydroxyquinoline6) along with copper(I) chloride was effective for this Ullmann-type reaction. Because of low reactivity of 2, however, the yield of 3 is still low (Table 1, entries 1 and 2). By using bipolar aprotic solvent, the yield of 3 was improved (entries 3 - 5). Especially, the reaction in DMI7) achieved the yield of 3 up to 88% (entry 5).

Typical procedure: A mixture of 1 (51.5 g, 96.5% purity, 0.40 mol), 2 (135.1 g, 1.20 mol), K_2CO_3 (33.4 g, 0.24 mol), CuCl (0.8 g, 0.008 mol), and 8-hydroxyquinoline (1.2 g, 0.008 mol) in DMI (155.2 g, 1.36 mol) was stirred under reflux for 15 h. Generated water by the reaction of 1 with K_2CO_3 was removed during the course of condensation by using chlorobenzene as an azeotrope. The reaction temperature was gradually raised with the consumption of 2 from 150 °C to 170 °C. The mixture was cooled to the room temperature and the insoluble salts were removed by filtration. The filtrate was distilled to afford 3 (65.9 g, 98.5% purity, 81.0% yield) after the recoveries of 2 and DMI.

Table 1. Condensation of **1** with Chlorobenzene

Entry	Catalyst	Solvent	Conditions	Yield of **3**[a]/%
1	CuCl	Chlorobenzene	reflux, 40 h	3
2	CuCl, 8-OQ[b]	Chlorobenzene	reflux, 40 h	10
3	CuCl, 8-OQ	DMF	150 - 170 °C, 20 h	21
4	CuCl, 8-OQ	DMSO	150 - 170 °C, 15 h	58
5	CuCl, 8-OQ	DMI	150 - 170 °C, 15 h	88(81)[c]

a) Analyzed by gas chromatography based on **1**. b) 8-Hydroxyquinoline. c) Isolated yield based on **1**.

DMI, which has high dielectric constant and high solvating capability, is not still so popular among organic chemists, but its excellent potency will be useful for the organic synthesis.

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5) No condensation of this less reactive m-substituted phenol (**1**) with chlorobenzene has been reported so far.

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