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The investigation of a novel conversion of hydroxybenzaldehydes and acetophenones into hydroquinone monoalkyl ethers

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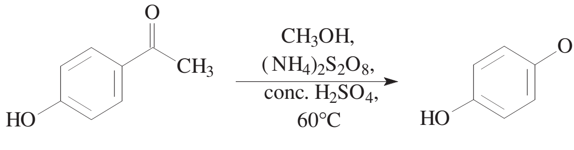
The scope and mechanism of a novel conversion reaction of hydroxyacetophenones and hydroxybenzaldehydes into hydroquinone monoalkyl ethers when reacted with an oxidant and an alcohol in the presence of a strong acid catalyst are reported here.

Keywords: hydroquinone monoalkyl ethers, oxidation

There are many reports that discuss the synthesis of hydroquinone monoalkyl ethers, important organic building blocks to larger, more complex molecules.[1-10] Several of these reactions have disadvantages: low yields of the desired ethers are obtained, complex separations of product mixtures are required, or the reactions are multi-stepped and complex. It was discovered in our laboratories that when 4-hydroxybenzaldehyde or 4-hydroxyacetophenone is reacted with methanol and ammonium peroxydisulfate in the presence of a strong acid catalyst, 4-methoxyphenol is obtained as product in high yield and selectivity (Scheme 1). Reaction conditions are simple, requiring one pot at 60°C. Since this conversion is novel, an extensive investigation was conducted in order to ascertain the scope and mechanism of the reaction. Though other methods of obtaining hydroquinone monoalkyl ethers from simpler substrates are known,[10] this study has led to interesting insights into the mechanism by which this reaction, and indeed those using the simpler substrates, occurs.

It was discovered that only 4-hydroxyacetophenones and 4-hydroxybenzaldehydes could successfully be converted into the ethers. Furthermore, only saturated and unsaturated monoalcohols effectively served as alkylating agents, but a number of different acidic catalysts and oxidants were efficient in this reaction. A mechanism was proposed in which the conversion is envisaged to proceed by an initial Baeyer-Villiger oxidation step to afford, after *in situ* hydrolysis, the corresponding hydroquinone, some of which is further oxidized to the benzoquinone. A stabilized charge-transfer complex between these latter two species is then thought to be involved in the final etherification step (Scheme 2).



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Scheme 1 Preparation of 4-methoxyphenol from 4-hydroxyacetophenone.

Schemes: 2

Scheme 1. Preparation of 4-methoxyphenol from 4-hydroxyacetophenone

Scheme 2. The proposed mechanism

Tables: 1

Table 1. Variation of reagents, catalysts and reaction conditions, and the corresponding product yields

Figures: 1

Figure 1. Variation in substrate, intermediates and product quantities with reaction time

References: 16

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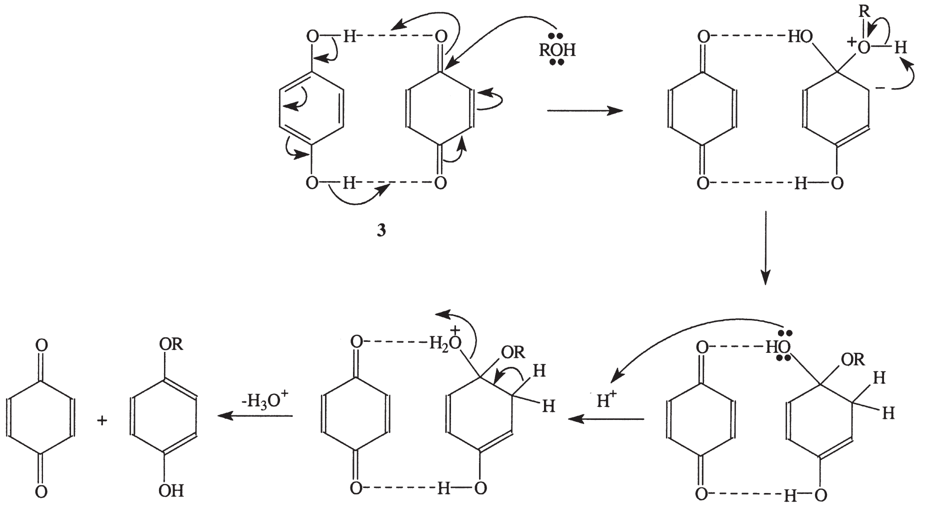

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Scheme 2 The proposed mechanism.

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