AN EFFICIENT AND ENVIRONMENTALLY BENIGN BIPHASIC SYSTEM FOR THE AEROBIC OXIDATION OF BENZYLIC ALCOHOLS

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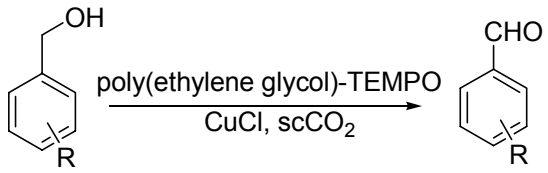
The selective catalytic oxidation of alcohols to their corresponding carbonyl compounds is an important but challenging task for modern organic synthesis and the chemical industry, especially the selective oxidation of benzylic alcohols to aldehydes, as these aldehydes are important intermediates in the synthesis of other organic compounds, ranging from pharmaceuticals to plastic additives as well as in the processing of perfume and flavouring compounds and in the preparation of certain aniline dyes in the textile industry.[1] Many catalytic systems were developed for the transformation.[2] Of particular interest are the catalytic systems consisting of an inexpensive transition-metal compound and TEMPO for mild and selective aerobic benzylic alcohol oxidations. However, TEMPO is a rather expensive chemical agent. Therefore, recycling of TEMPO is highly desirable, especially when the reactions are run on a large scale.

Herein, we envisioned poly(ethylene glycol) supported TEMPO and CuCl catalytic system for the oxidation of benzylic alcohol under supercritical carbon dioxide (Scheme 1). To our delight, the designed catalytic system displays low toxicity and reusability and is highly active for the oxidation under 60 ^{o}C and 9 MPa, with the yield (above 90 %) and the selectivity for aldehyde > 99 %. Moreover, the products can be extracted by the $scCO_2$ and reused by further supplying the substrates.



Scheme 1 An aerobic oxidation of benzylic alcohols in $scCO_2$/PEG

References

[1] (a) B. M. Choudary, *Catal. Today* 2000, 57, 17;
(b) M. Musawir, P. N. Davey, G. Kelly, I. V. Kozhevnikov, *Chem. Commun.* **2003**, 1414 .
[2] March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 4th ed.; John Wiley & Sons: New York, 1992.