Rapid and Reusable Copper Catalytic System for Allylic Oxidation of Olefins in Hexafluoroisopropanol as Solvent

Fabienne Fache,* Olivier Piva

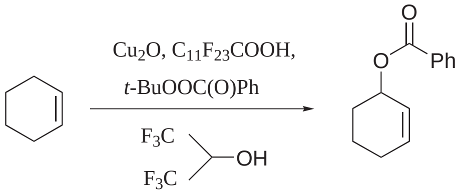
Laboratoire de Chimie Organique, Photochimie et Synthèse, Université Claude Bernard Lyon 1, Unité Mixte de Recherche CNRS 5622, Bât. Raulin, 43 bd du 11 novembre 1918, 69622 Villeurbanne Cedex, France
Fax +33(4)72448136; E-mail: fache@univ-lyon1.fr

Received 13 September 2002

Abstract: Cu_2O mixed with perfluorododecanoic acid $C_{11}F_{23}COOH$ and *t*-butyl peroxybenzoate in hexafluoroisopropanol led to a rapid and reusable catalytic system for the Kharasch–Sosnovsky reaction.

Key words: allylic oxidation, olefins, copper catalyst, HFIP, recycling

Allylic oxidation of olefins with copper catalysis and organic peroxyester as oxidant is a powerful reaction, which has been extensively studied since the seminal work of Kharasch and Sosnovsky.[1] Numerous asymmetric versions of this reaction have been also reported.[2–4] Among the different systems published in the literature, only few of them could be recycled. Thus, Sartori et al.[5] used copper-exchanged zeolites, while, Le Bras and Muzart[6] reported a reusable water-soluble copper catalyst. This nice system is competitive in terms of isolated yields with the best results published in the literature[2] but reaction times to go to completion were quite long (few days). In a search to improve the reactivity of the copper catalytic system for allylic oxidation of olefins, we took into account the great advantages of fluorinated alcohols in oxidation reactions.[7,8] We thus explored the potentiality of hexafluoro-2-propanol (HFIP) with copper catalyst and *t*-butyl perbenzoate as the oxidant (Scheme 1).

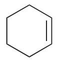
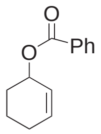
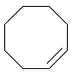
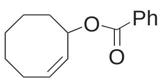
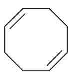
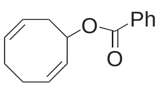
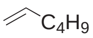
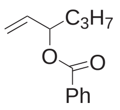
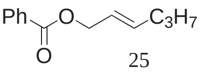
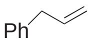
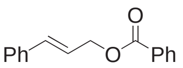


Scheme 1 Allylic oxidation of cyclohexene in a fluorinated medium.

In a typical procedure, Cu_2O (0.05 mmol) was mixed with the commercially available perfluorinated acid $C_{11}F_{23}COOH$ (0.1 mmol) in HFIP (1.5 mL) to ensure its complete solubility. The solution took rapidly a deep blue colour. Olefin (5 mmol) and *t*-BuOOC(O)Ph (1 mmol) were then added and the reaction was heated to reflux (59 °C) under stirring until complete conversion (TLC control). Without the fluorinated acid or even with an excess of benzoic acid, no reaction occurred. When benzene was used instead of HFIP, even in the presence of $C_{11}F_{23}COOH$, the reaction mixture remained heterogeneous with some red particles of starting Cu_2O. The catalytic system thus could not be recovered properly.

HFIP could be recycled by careful distillation and the final product was isolated by flash chromatography over SiO_2 (petroleum ether/EtOAc, 95:5). The catalytic system could be recovered very easily. When all the perester was consumed, HFIP was evaporated and the resulting crude product was rinsed three times with petroleum ether (15 mL). The catalytic system was thus isolated by simple decanting the insoluble turquoise blue solid. It could be reused without further addition of copper and acid. All the results are summarised in Table 1.

Table 1 Comparative Results Using New Cu_2O Catalyst and a Pretreated One

Entry	Olefin	Reaction time (h)	Product	Yield (%)[a]	
				Cu_2O (initial)	Cu_2O[b] (recycled)
1		3		30	72
2		15		20	33
3		24		42[c]	52[c]
4		20	 75  25	23	10
5		18		30	50

[a] Isolated yield.
[b] Cu_2O recycled from a cyclohexene reaction.
[c] No C=C migration occurred.

Synlett 2002, No. 12, Print: 02 12 2002.
Art Id.1437-2096,E;2002,0,12,2035,2036,ftx,en;G27302ST.pdf.

ISSN 0936-5214

Isolated yields were based on peroxyester consumption. The reaction was rapid (always < 24 h) and in the case of cyclohexene only three hours were necessary for the reaction to go to completion (entry 1). The first cycle of the catalytic system led to moderate isolated yields, irrespective of the substrate. In contrast, with cyclohexene, 72% (isolated yield) of the desired oxidation product was obtained using a recycled catalyst and the reaction was repeated thrice without loss of activity (70–72% isolated yield in 4 hours). We assumed that some of the peroxyester was consumed in the first cycle to form the active copper species, which should explain the lower yields. In the second cycle, all the peroxyester could be used to form the final product. Moreover, with this catalytic system recovered from cyclohexene, the oxidation process occurred nicely irrespective of the nature of the substrate with isolated yields similar to those published in the literature.[2] Thus, gram amounts of Cu_2O have been pre-treated with cyclohexene under the reaction conditions described above and then used successfully with other olefins (Table 1). This new catalyst is very easy to prepare and to handle.

In the case of allylbenzene, a complete regioselective oxidation took place to deliver only the terminal primary alcohol derivative with 50% isolated yield (entry 5) whereas reported systems usually led to a mixture[2] of regioisomers. Acyclic olefins like *n*-hexene gave poorer yields as already observed[4] (entry 4).

In conclusion, we have described a new catalytic system for allylic oxidation of olefins, which is rapid and easily recycled. An asymmetric version of this system is currently in progress, to take advantage of the fluorous phase.

In a typical procedure, Cu_2O (7 mg, 0.05 mmol) was mixed with $C_{11}F_{23}COOH$ (61 mg, 0.1 mmol) in HFIP (1.5 mL) to ensure its complete solubility. The solution rapidly became a deep blue colour. Olefin (5 mmol) and 190 μL (1 mmol) of *t*-BuOOC(O)Ph were then added and the reaction was heated to reflux (59 °C) under stirring until complete conversion (TLC control). When all the perester was consumed, HFIP was evaporated. The solid thus obtained was rinsed with petroleum ether (3 × 15 mL). The resulting organic phase was evaporated and the desired product was purified by flash-chromatography over silica gel (petroleum ether/EtOAc, 95:5).

For recycling experiments: the solid obtained above after being rinsed with petroleum ether was dried by simple evaporation of residual petroleum ether. Recycled catalyst (50 mg) was recovered. Then HFIP (1.5 mL), *t*-BuOOC(O)Ph (190 μL) and the olefin (5 mmol) were stirred under reflux until complete conversion of the perester. The desired product was recovered according to the above procedure.

References

(1) Kharasch, M. S.; Sosnovsky, G. J. *J. Am. Chem. Soc.* **1958**, *80*, 756.
(2) Malkov, A. V.; Bella, M.; Langer, V.; Kocovsky, P. *Org. Lett.* **2000**, *2*, 3047.
(3) Levina, A.; Muzart, J. *Tetrahedron: Asymmetry* **1995**, *6*, 147.
(4) For reviews, see: (a) Brunel, J.-M.; Legrand, O.; Buono, G. *C. R. Acad. Sci.* **1999**, *2*, 19. (b) Eames, J.; Watkinson, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 3567. (c) Andrus, M. B.; Lashley, J. C. *Tetrahedron* **2002**, *58*, 845.
(5) Carloni, S.; Frullanti, B.; Maggi, R.; Mazzacani, A.; Bigi, F.; Sartori, G. *Tetrahedron Lett.* **2000**, *41*, 8947.
(6) Le Bras, J.; Muzart, J. *Tetrahedron Lett.* **2002**, *43*, 431.
(7) Van Vliet, M. C. A.; Arends, I. W. C. E.; Sheldon, R. A. *Synlett* **2001**, 248.
(8) Legros, J.; Crousse, B.; Bourdon, J.; Bonnet-Delpon, D.; Bégué, J.-P. *Tetrahedron Lett.* **2001**, *42*, 4463.