Water-soluble and reusable copper catalyst for the allylic benzoyloxylation of olefins

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Abstract—Simple mixing of [(HOCH2CH2NHCOCH2)2NCH2]2 with Cu(MeCN)4BF4 in water led to an efficient and reusable catalytic system for the allylic oxidation of olefins by tert-butyl perbenzoate. © 2002 Elsevier Science Ltd. All rights reserved.

The Kharasch–Sosnovsky reaction involves the allylic oxidation of olefins by an organic peroxyester in the presence of catalytic amounts of a copper salt.1,2 This simple and general method for the synthesis of allyl esters which has been known for almost half a century, has been carried out in various organic solvents; we3 and others4 have proposed enantioselective versions of this process. Presently, there is considerable interest in the development of water-soluble ligands,5 which allows metal-catalyzed reactions to take place in either water6 or biphasic systems;7 these approaches frequently result in an improvement of the productive process from both economical and ecological points of view.8 We were interested in the use of such ligands to carry out Kharasch–Sosnovsky reactions in water as well as the aim of obtaining catalyst recycling.

One of the most useful water-soluble ligand is TPPTS;9 this phosphine cannot however be used in an oxidizing medium. During our research on the synthesis of new N-donor ligands, we discovered that highly hydrophilic [(HOCH2CH2NHCOCH2)2NCH2]2 (1), which is easily prepared from ethylenediaminetetraacetic acid permethyl ester10 and 2-aminoethanol (Eq. (1)),11 was able to fulfill our objectives; thus, we report here our main results (Eq. (2), Table 1).

The catalytic system was in situ prepared by mixing Cu(MeCN)4BF412 with 1equiv. of 1 in degassed water. After addition of neat cyclohexene (50 equiv./Cu), tert-butyl perbenzoate (10 equiv./Cu) and heating at 80°C, the aqueous phase was blue-colored while the organic phase was very lightly yellow. Stirring this mixture at 80°C for 48 h led to the disappearance of the perester; the subsequent workup yielded 67% of 2-cyclohexenyl-1-benzoate.13 An array of olefins was then reacted under similar conditions (Table 1). Cycloheptene and 1,5-cyclooctadiene (entries b and d) were oxidized in good yields in 48 h, while the reaction with cyclooctene required several days (entry c). The benzoyloxylation of linear 1-alkenes, allylbenzene and 1-octene, was accompanied by migration of the double bond, affording a mixture of the corresponding esters, the main one being the secondary isomer in both cases (entries e and f).

Keywords: catalysis; copper; perester; olefins; allylic oxidation; water.

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Table 1. Catalyzed allylic oxidation of olefins with Cu(MeCN)$_4$BF$_4$/I in water.$^{13}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Olefin 2</th>
<th>Time (h)</th>
<th>Product 3</th>
<th>Yield (%)$^{a}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td></td>
<td>48</td>
<td></td>
<td>67</td>
</tr>
<tr>
<td>b</td>
<td></td>
<td>48</td>
<td></td>
<td>64</td>
</tr>
<tr>
<td>c</td>
<td></td>
<td>120</td>
<td></td>
<td>42</td>
</tr>
<tr>
<td>d</td>
<td></td>
<td>48</td>
<td></td>
<td>75</td>
</tr>
<tr>
<td>e</td>
<td></td>
<td>72</td>
<td></td>
<td>47</td>
</tr>
<tr>
<td>f</td>
<td></td>
<td>240</td>
<td></td>
<td>13</td>
</tr>
</tbody>
</table>

$^{a}$Isolated yield calculated on the amount of PhCO$_2$-Bu introduced.

and with a low yield when 1-octene was the starting material.

The aqueous phase recovered from workup of such an oxidation remains blue-colored and more interestingly, was catalytic active. For example, the oxidation of cyclohexene (entry a) was repeated four times in using the recovered aqueous phase: an increase in efficiency from 67% in the first cycle to 80% in the last cycle was observed. The very low coloration of the organic phase in the course of these recycling experiments and their efficiencies show that most of the copper complex remains thus in the aqueous phase.

To examine the role of I, the oxidation of cyclohexene was carried out as in entry a but in the absence of this additive. Some differences were observed: (i) the organic phase was blue-colored as soon as the mixture was heated to 80°C; (ii) the perester was fully consumed in 24 h; (iii) the yield of 2-cyclohexenyl-1-benzoate was slightly reduced (65%) and (iv) more importantly, the recycling of the catalyst was much less efficient, the yield of the fourth run being less than 20% instead of the 77% obtained under the previous recycling conditions. These experiments indicate that in the absence of I: (i) a large part of the copper complex is transferred to the organic phase and (ii) the oxidation proceeds mainly in the organic phase. Comparison of the results demonstrates the value of I in obtaining an effective recycling of the catalyst.

In conclusion, we have described a new and recyclable water-soluble system to efficiently catalyze the allylic oxidation of olefins. Our future work will be concentrated on the nature of the active species and on the development of this copper–salt with different additives such as β-cyclodextrins.

Acknowledgements

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References


11. Preparation of 1. A mixture of acid permethyl ester (1.08 g, 3.1 mmol) and 2-aminoethanol (0.75 ml, 12.4 mmol) was heated (oil bath 80°C) for 20 h. A solid precipitated out. Triturating and washing this precipitate with acetone removed the colored impurities and gave a white solid (1.32 g, 92%). Mp 130–132°C. 1H NMR (250 MHz, D2O): δ 2.69 (s, 4H), 3.27 (s, 8H), 3.33 (t, J = 5.4 Hz, 8H), 3.63 (t, J = 5.4 Hz, 8H); 13C NMR (63 MHz, D2O): δ 43.7, 55.4, 60.9, 62.4, 176.2. IR (KBr, cm−1): 1643, 3307, 3239. Anal. calcd for C18H36N6O8: C, 46.54; H, 7.81; N, 18.09; found: C, 46.66; H, 8.03; N, 17.85.

12. Cu(MeCN)4BF4 was freshly prepared prior to use from Cu2O and HBF4 as reported: Kubas, G. J. Inorg. Synth. 1979, 19, 90–92.

13. A solution of 1 (93 mg, 0.2 mmol) in water (2 ml) was freeze–pump–thaw–degassed three times and then added under an argon atmosphere to a Schlenk flask containing Cu(MeCN)4BF4 (62.8 mg, 0.2 mmol). The alkene (10 mmol, distilled over CaH2 under argon to remove peroxides) was added, followed by dropwise addition of tert-butyl perbenzoate (0.38 ml, 2.0 mmol). The biphasic mixture was heated (oil bath 80°C) until the disappearance of the perbenzoate (TLC analysis). After cooling the mixture to rt, the organic phase was extracted with petroleum ether (3×20 ml), dried over MgSO4, filtered and concentrated by rotary evaporation. Flash chromatography of the residue (SiO2, petroleum ether/ethyl acetate 95/5) led to the esters (Rf = 0.5–0.6).