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# Amino acid/copper-catalyzed enantioselective allylic benzoyloxylation of olefins in water promoted by diethylene glycol

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**Abstract**—Amino acids, mainly L-proline, in association with diethylene glycol and copper salts have been used in water for a recyclable enantioselective version of the Kharasch–Sosnovsky reaction with e.e.s up to 42%. © 2003 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

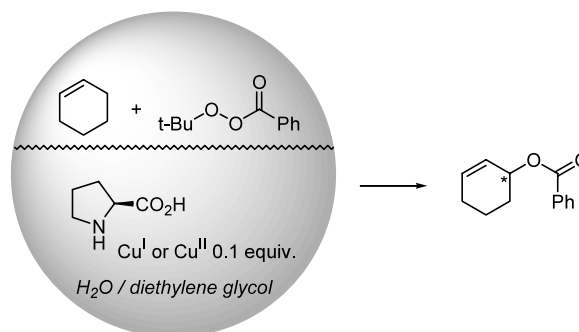
The development of methodologies for the asymmetric functionalization of C–H bonds remains a challenge. The Kharasch–Sosnovsky reaction, in which the allylic carbon of an alkene is acyloxyated, offers access to chiral allylic alcohols and has been the subject of several studies.<sup>1,2</sup> The initial asymmetric version of the Kharasch–Sosnovsky reaction was a diastereoselective oxidation involving the use of *tert*-butyl hydrogen peroxide as oxidizing reagent and  $\alpha$ -ethyl camphorate as the chiral auxiliary; oxidation products were obtained with low d.e.,  $\leq 7\%$ .<sup>3</sup> Later, *tert*-butyl peroxybenzoate and the catalytic L-proline/copper system were found to be superior; optimum selectivity being obtained using a 2/1 ligand/copper ratio.<sup>4</sup> Optimized oxidation of cyclohexene using bis-prolinato-copper catalyst with  $\text{PhCO}_3t\text{-Bu}$  and  $\text{PhCO}_2\text{H}$  in refluxing benzene yielded 59% cyclohexenyl benzoate with 45% e.e.<sup>5</sup> Subsequently, bicyclic amino acid analogs of proline were used.<sup>6</sup> Such ligands were superior in both reactivity and selectivity when a mixture of copper(II)/copper bronze was used as catalyst.

In recent years, organometallic catalysis in aqueous media has developed into an important field of research.<sup>7,8</sup> These procedures make them valuable alternatives and have high economic and environmental impact. Indeed, they do not call for dry solvents, they may allow recycling of catalysts and furthermore unique reactivity and selectivity have been sometimes

observed. The main strategy to obtain suitable water-soluble ligands was the attachment of ionic or polar substituents to standard ligands.<sup>9</sup>

In the above context, we have quite recently developed the aqueous non-enantioselective Kharasch–Sosnovsky reaction by the mean of the hydrophilic ligand  $[(\text{HOCH}_2\text{CH}_2\text{NHCOCH}_2)_2\text{NCH}_2]_2$ : mixing this ligand and  $\text{Cu}(\text{MeCN})_4\text{BF}_4$  in water led to an efficient and reusable catalytic system for the allylic oxidation of olefins by *tert*-butyl perbenzoate.<sup>10</sup>

In the course of investigations to develop asymmetric aqueous oxidation reactions, we thought to exploit the high solubility of amino acids in water to obtain enantioselective water-soluble catalysts. Indeed, the use of simple commercial water-soluble molecules has been rather neglected. Our studies lead us to report the first enantioselective Kharasch–Sosnovsky reaction in water (Scheme 1).



Scheme 1.

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## 2. Results and discussion

### 2.1. Preliminary investigation

Initial experiments in water were performed at 80°C with the water-soluble complex  $\text{Cu}(\text{MeCN})_4\text{BF}_4$  and L-proline as ligand (Table 1, entry 1). After 40 h, cyclohexenyl benzoate was obtained in 13% yield; a white solid isolated during work-up was identified as benzoic acid. Since allylic oxidations in organic medium with copper–amino acid complexes may be improved in the presence of an organic carboxylic acid,<sup>5,11</sup> the effect of the addition of benzoic acid to the biphasic system was then studied. With 0.5 equiv. of this acid, the reaction was faster and afforded a better yield of 55%, however with a very low e.e. (entry 2). Increasing the amount of  $\text{PhCO}_2\text{H}$  to 1.5 equiv. improved slightly the yield to 62% and the e.e. to 12% (entry 3). Under these conditions, the water phase was catalytically active for recycling experiments.

The use of a  $\text{Cu}^{\text{II}}$  complex,  $\text{Cu}(\text{L-prolinato})_2 \cdot 2\text{H}_2\text{O}$ , increased the e.e. to 18% (entry 4). As with  $\text{Cu}^{\text{I}}$ , decreasing the amount of benzoic acid afforded lower e.e. (entry 5). A catalyst in situ prepared from  $\text{Cu}(\text{OTf})_2$ , L-proline and NaOH led also to 18% e.e. (entry 6). Lower reaction rates were obtained in the absence of NaOH (entry 7). In contrast to reactions performed in an organic medium,<sup>12</sup> addition of anthraquinone-2-sulfonic acid has no effect under these aqueous conditions (entry 8). Decrease of the reaction temperature with  $\text{Cu}^{\text{I}}$  or  $\text{Cu}^{\text{II}}$  catalysts (entries 9, 10) afforded only traces of product even if usual co-solvents used in biphasic process such as acetone or ethanol,<sup>13</sup> were added. In contrast, when the catalytic system was a *syn*-proportionation of  $\text{Cu}(\text{OAc})_2$  (0.1

equiv.) and copper bronze (0.5 equiv.) as the source of  $\text{Cu}^{\text{I}}$ , the reaction was complete in 18 h at room temperature yielding 95% allylic ester but with very low e.e. (entry 11). When lower amounts of  $\text{Cu}^{\text{I}}$  (from 0.5 to 0.1 equiv.) were used in association with  $\text{Cu}(\text{OAc})_2$ , the reaction rates decreased regularly and enantioselectivities were not improved.

In conclusion, in these preliminary experiments, the oxidation of cyclohexene with copper/proline associations in water affords the corresponding allylic ester in fair yield but with low e.e. However, some experiments have shown that after catalysis the water phase keeps a blue color and was still catalytic active, this result urges us to pursue the study to improve the enantioselectivity. After a great deal of experimentation, we have found out that the addition of diethylene glycol to the reaction mixture was able to fulfil in part our objectives.

### 2.2. Effect of diethylene glycol

Oxidation of cyclohexene could be performed at room temperature in 18 h using  $\text{Cu}(\text{OTf})_2$ , L-proline, NaOH, and  $\text{PhCO}_2\text{H}$  in a mixture of water (30 equiv.)/diethylene glycol (9.4 equiv.), the allylic ester being isolated in low yield (31%) but with 38% e.e. (Table 2, entry 1). When the amount of diethylene glycol was reduced to 5.2 equiv., reaction required 8 days to go to the completion and e.e. decreased to 34% but yield was improved to 62% (entry 2). Monitoring the reaction by TLC has shown that only traces of allylic ester were produced during the first 5 days; after this induction period, the product was generated regularly until complete disappearance of *tert*-butyl peroxybenzoate. This observation led us to look for a procedure to reduce or suppress this induction period.

**Table 1.** Allylic oxidation of cyclohexene in water

| Entry           | Cu (0.1 equiv.)                                             | L-Proline (equiv.) | NaOH (equiv.) | $\text{PhCO}_2\text{H}$ (equiv.) | T (°C) | Time (h) | Yield (%) <sup>a</sup> | E.e. (%) <sup>b</sup> |
|-----------------|-------------------------------------------------------------|--------------------|---------------|----------------------------------|--------|----------|------------------------|-----------------------|
| 1               | $\text{Cu}(\text{MeCN})_4\text{BF}_4$                       | 0.25               | 0             | 0                                | 80     | 40       | 13                     | nd                    |
| 2               | $\text{Cu}(\text{MeCN})_4\text{BF}_4$                       | 0.25               | 0             | 0.5                              | 80     | 17       | 55                     | 5                     |
| 3               | $\text{Cu}(\text{MeCN})_4\text{BF}_4$                       | 0.25               | 0             | 1.5                              | 80     | 17       | 62                     | 12                    |
| 4               | $\text{Cu}(\text{L-prolinato})_2 \cdot 2\text{H}_2\text{O}$ | 0                  | 0             | 1.5                              | 80     | 17       | 50                     | 18                    |
| 5               | $\text{Cu}(\text{L-prolinato})_2 \cdot 2\text{H}_2\text{O}$ | 0                  | 0             | 0.5                              | 80     | 17       | 44                     | 13                    |
| 6               | $\text{Cu}(\text{OTf})_2$                                   | 0.45               | 0.20          | 1.5                              | 80     | 17       | 70                     | 18                    |
| 7               | $\text{Cu}(\text{OTf})_2$                                   | 0.45               | 0             | 1.5                              | 80     | 40       | 71                     | 18                    |
| 8 <sup>c</sup>  | $\text{Cu}(\text{OTf})_2$                                   | 0.45               | 0.20          | 1.5                              | 80     | 17       | 66                     | 17                    |
| 9               | $\text{Cu}(\text{OTf})_2$                                   | 0.45               | 0.20          | 1.5                              | 50     | 72       | Traces                 | nd                    |
| 10              | $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$              | 0.45               | 0.20          | 1.5                              | 50     | 72       | Traces                 | nd                    |
| 11 <sup>d</sup> | $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$                | 0.45               | 0             | 1.5                              | rt     | 18       | 95                     | 5                     |

<sup>a</sup> Isolated yield calculated on the amount of  $\text{PhCO}_3t\text{-Bu}$  introduced.

<sup>b</sup> *S*-Configuration of the main enantiomer.

<sup>c</sup> Reaction carried out in the presence of anthraquinone-2-sulfonic acid (4.0 equiv.).

<sup>d</sup>  $\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.1 equiv.) and  $\text{Cu}^{\text{I}}$  (0.5 equiv.) were used.

**Table 2.** Allylic oxidation of cyclohexene in water in the presence of diethylene glycol

| Entry <sup>a</sup> | Cu (0.1 equiv.)                                     | NaOH (equiv.) | Diethylene glycol (equiv.) | Time (h) | Yield (%) <sup>b</sup> | E.e. (%) <sup>c</sup> |
|--------------------|-----------------------------------------------------|---------------|----------------------------|----------|------------------------|-----------------------|
| 1                  | Cu(OTf) <sub>2</sub>                                | 0.20          | 9.4                        | 18       | 31                     | 38                    |
| 2                  | Cu(OTf) <sub>2</sub>                                | 0.20          | 5.2                        | 192      | 62                     | 34                    |
| 3 <sup>d</sup>     | Cu(OTf) <sub>2</sub>                                | 0.20          | 5.2                        | 72       | 70                     | 34                    |
| 4 <sup>d</sup>     | Cu(OTf) <sub>2</sub>                                | 0             | 5.2                        | 96       | 69                     | 29                    |
| 5 <sup>e</sup>     | Cu(OTf) <sub>2</sub>                                | 0.20          | 5.2                        | 96       | 72                     | 33                    |
| 6                  | Cu(CH <sub>3</sub> CN) <sub>4</sub> BF <sub>4</sub> | 0.20          | 5.2                        | 72       | 60                     | 33                    |

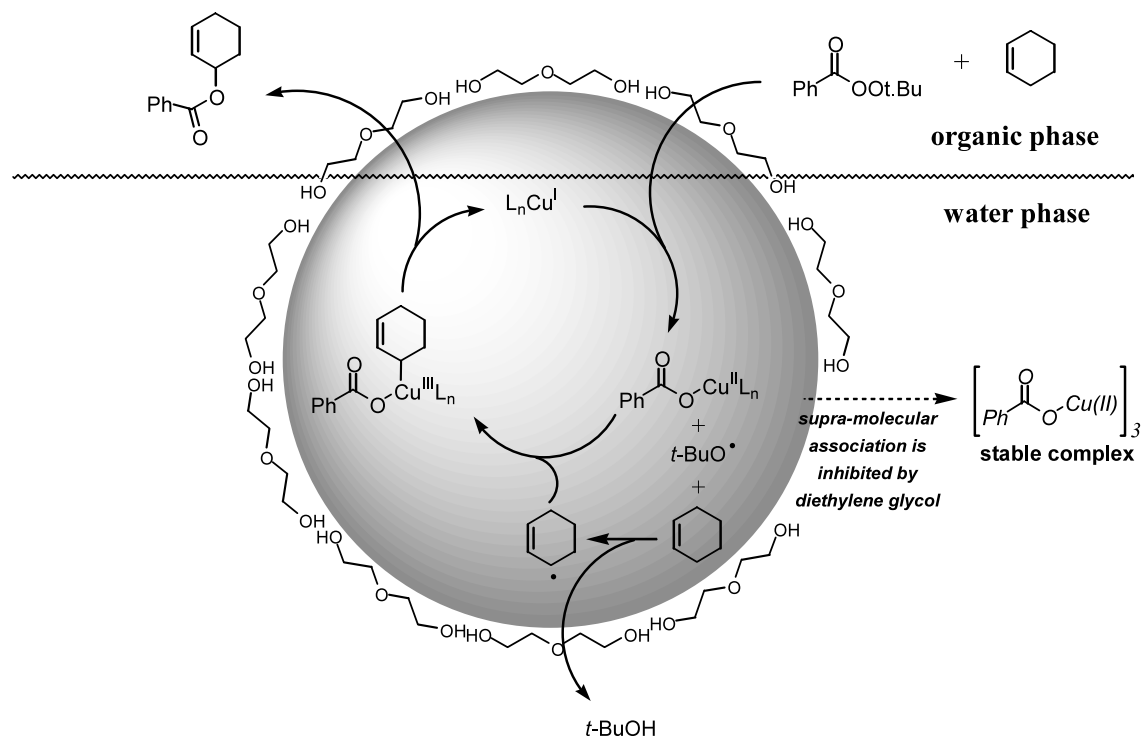
<sup>a</sup> Conditions: L-proline (0.45 equiv.), PhCO<sub>2</sub>H (1.5 equiv.), room temperature.

<sup>b</sup> Isolated yield calculated on the amount of PhCO<sub>2</sub>*t*-Bu introduced.

<sup>c</sup> *S*-Configuration of the main enantiomer.

<sup>d</sup> The system was activated with 0.1 equiv. of *tert*-butyl peroxybenzoate at 80°C for 30 min.

<sup>e</sup> The system was activated with 0.05 equiv. of *tert*-butyl peroxybenzoate at 80°C for 30 min.

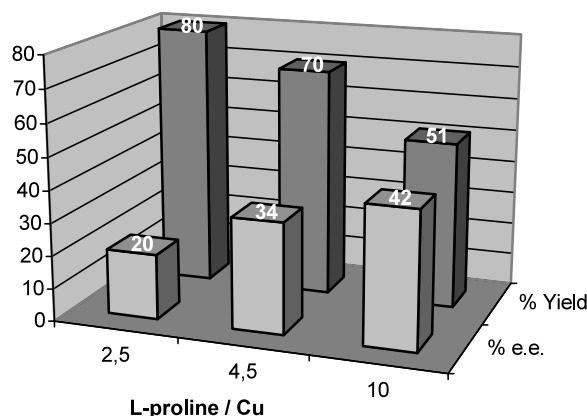


### Scheme 2.

The system was activated by heating at 80°C for 30 min a solution of the catalyst in water/diethylene glycol in the presence of a catalytic amount of *tert*-butyl peroxybenzoate (0.1 equiv. based on the total amount used later), the turn of the initial blue color to blue–green or yellow indicated that Cu<sup>I</sup> species were probably produced. After cooling to room temperature, cyclohexene and *tert*-butyl peroxybenzoate were added. Following the reaction by TLC has shown no induction period and the allylic ester was then produced over 3 days at room temperature in 70% yield and 34% e.e. (entry 3). Slight reduction of activation and e.e. were obtained in the absence of base (entry 4). When 0.05 equiv. of oxidizing agent was used for initiation, reaction time was increased to 4 days (entry 5), while no activation was observed in the absence of *tert*-butyl peroxybenzoate. The use of Cu<sup>I</sup> was also examined in the presence of diethylene glycol, no induction period was observed and similar results were obtained (entry 6).

These results suggest that under these conditions, the real active species is a copper(I); this is generally admitted for Kharasch–Sosnovsky reactions and proposed mechanisms start most of the time with a copper(I) (Scheme 2).<sup>14</sup> Under the present aqueous conditions, diethylene glycol plays an important role, since in its absence no reaction occurs at room temperature. In a previous work,<sup>15</sup> we have suggested that supramolecular associations of active species could lead to a stable and non-catalytic active copper complex, this phenomenon being suppressed in the presence of an excess of substrate. In the reactions summarized in Tables 1 and 2, substrate and catalyst are in two separate phases and auto-association of copper species in the water phase could be promoted. However, this phenomenon seems to be prevented in elevating the temperature (Table 1) or in adding diethylene glycol (Table 2). Hence, we suspect that diethylene glycol either coordinates to copper species or forms a third catalyst-rich phase as observed with PEG<sup>16</sup> (Scheme 2).

Surprisingly, concentration of ligand had an effect on the enantioselectivity (Fig. 1). In organic medium<sup>5,11</sup> and in the experiments performed in water in the absence of diethylene glycol, best ratio for L-proline/copper was around 2. In the presence of diethylene glycol, increasing the amount of the chiral ligand from 25 to 100 mol%, improved the e.e. from 20 to 42% but yield dropped from 80% to 51% (Fig. 1).



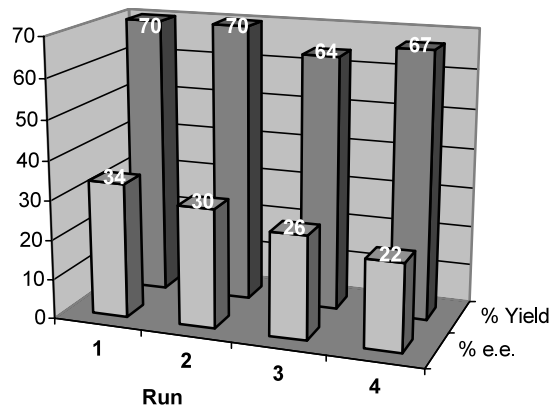
**Figure 1.** Evolution of e.e. and yield with L-proline/Cu ratio.

Non-cyclic amino acids were tested and afforded lower enantioselectivities as already observed in organic media.<sup>4</sup> For example, when L-proline was substituted by L-valine and oxidation performed as reported in entry 3, Table 2, the reaction was completed in 24 h yielding 62% allylic ester with 13% e.e.

Two other substrates were subjected to the procedure. The oxidation of cyclopentene under conditions of entry 3, Table 2, was faster than with cyclohexene (44 h instead of 72 h) affording (*S*)-cyclopentenyl benzoate in 70% yield and 32% e.e. The oxidation of cyclooctadiene was not efficient and no traces of expected compound were observed even after 9 days.

Recycling experiments were performed under atmosphere of argon. First cycle was run according to entry 3, Table 2, the aqueous phase recovered from work-up remains blue colored and was catalytically active as shown in Figure 2. More interestingly, activity of catalyst was improved after the first cycle and reaction time passed from 72 to 48 h. Yields of allylic ester were quite constant but e.e.'s decreased regularly from 34 to 22%. When experiments were performed in air, activity of the catalyst decreased and reaction required 4 days for the second cycle and 8 days for run 3 with, respectively, 70, 71, 57% yield and 33, 30, 26% e.e.

The very low coloration of organic phases and their low catalytic activities when they were used for recycling experiments have shown that most of the copper complex remains thus in the aqueous phase.



**Figure 2.** Recycling experiments under argon.

### 3. Conclusion

In conclusion, enantioselective allylic oxidation could be performed in a biphasic-water-organic medium with amino acids and copper complexes. The presence of diethylene glycol is required to obtain active catalysis at room temperature, which led to the formation of the allylic ester with fair yield and enantiomeric excesses up to 42%. Performing the reaction under an argon atmosphere allows the recycling of catalyst; yields were not affected while enantioselectivity decreased slightly from run to run. Work is in progress to improve the e.e. with other water-soluble molecules and to understand the influence of the different parameters on the activity and enantioselectivity.

### 4. Experimental

#### 4.1. General

All reactions were monitored by TLC (TLC plates, 60 F<sub>254</sub>, Merck); detection was effected by UV light and phosphomolybdic acid indicator. Water and diethylene glycol were freeze-pump-thaw degassed three times. Petroleum ether was either used as received or was freeze-pump-thaw degassed three times when used in recycling experiments. Cyclohexene was distilled over CaH<sub>2</sub> under Ar; all other commercially available reagents were used as received. Cu(MeCN)<sub>4</sub>BF<sub>4</sub> was prepared from Cu<sub>2</sub>O, MeCN and HBF<sub>4</sub> just prior to use.<sup>17</sup> Cu(L-prolinato)<sub>2</sub>·2H<sub>2</sub>O was prepared by treatment of copper(II) carbonate with a hot water solution of (*S*)-proline followed by filtration and slow evaporation of the resulting solution.<sup>18</sup> Enantiomeric excesses were determined by chiral HPLC: Chiracel OD, hexane-isopropanol (99.9:0.1), flow rate 1 mL/min, UV detection at 220 nm, cyclohexenyl benzoate: *t* = 12 (*S*), *t* = 13 (*R*) min, cyclopentenyl benzoate: *t* = 14 (*S*), *t* = 18 (*R*). Perkin-Elmer-241 automatic polarimeter has been used for optical rotation measurements. Absolute configuration was determined by comparison of specific rotations with literature data.<sup>5</sup>

#### 4.2. Catalysis with Cu<sup>II</sup> and Cu<sup>I</sup> at high temperature

A Schlenk flask was charged with L-proline (103 mg, 0.9 mmol), NaOH (16 mg, 0.4 mmol) and water (1 mL). After stirring for 5 min, catalyst (0.2 mmol) was added against an Ar counterflow. Five minutes later, PhCO<sub>2</sub>H (366 mg, 3.0 mmol), cyclohexene (1.0 mL, 10.0 mmol) and *t*-BuOOC(O)Ph (0.38 mL, 2.0 mmol) were successively added. The mixture was heated (oil bath 80°C) until the disappearance of the perbenzoate (TLC analysis). After cooling to rt, the mixture was extracted with petroleum ether (3×20 mL), dried over MgSO<sub>4</sub>, filtered. Partial evaporation of the organic phase afforded a white solid (PhCO<sub>2</sub>H). After filtration, the mother liquor was concentrated and subjected to flash-chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate 95/5, *R*<sub>F</sub>=0.55).

#### 4.3. Catalysis with Cu<sup>II</sup>, diethylene glycol and activation process

A Schlenk flask was charged with L-proline (103 mg, 0.9 mmol), NaOH (16 mg, 0.4 mmol) and water (1 mL). After stirring for 5 min, Cu(OTf)<sub>2</sub> (72 mg, 0.2 mmol) was added against an Ar counterflow. Five minutes later, diethylene glycol (1 mL), PhCO<sub>2</sub>H (366 mg, 3.0 mmol) and *t*-BuOOC(O)Ph (0.04 mL, 0.2 mmol) were successively added. The mixture was placed in an oil bath at 80°C for 30 min. After cooling to rt, cyclohexene (1.0 mL, 10.0 mmol) and *t*-BuOOC(O)Ph (0.38 mL, 2.0 mmol) were added and the mixture was stirred until the disappearance of the perbenzoate. Work-up was performed as described above.

#### 4.4. Catalysis with Cu<sup>I</sup> and diethylene glycol

A Schlenk flask was charged with L-proline (103 mg, 0.9 mmol), NaOH (16 mg, 0.4 mmol) and water (1 mL). After stirring for 5 min, the solution was transferred via cannula to a Schlenk containing Cu(MeCN)<sub>4</sub>BF<sub>4</sub> (62.9 mg, 0.2 mmol). Five minutes later, diethylene glycol (1 mL), PhCO<sub>2</sub>H (366 mg, 3.0 mmol), cyclohexene (1.0 mL, 10.0 mmol) and *t*-BuOOC(O)Ph (0.38 mL, 2.0 mmol) were added successively and the mixture was stirred at room temperature until the disappearance of the perbenzoate. Work-up was performed as described above.

#### 4.5. Recycling experiments

The reaction medium is extracted with degassed petroleum ether (3×20 mL). Work up of the organic phase was performed as described above. PhCO<sub>2</sub>H (366 mg, 3.0 mmol), cyclohexene (1.0 mL, 10.0 mmol) and *t*-BuOOC(O)Ph (0.38 mL, 2.0 mmol) were successively added to the aqueous phase under an Ar flow and the mixture was stirred until the disappearance of the perbenzoate.

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