Recyclable Palladium Catalyst in PEG/CH$_3$CN Biphasic System for Electro-oxidative Wacker-type Reaction

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ABSTRACT

Electro-oxidative Wacker-type reaction has been developed in PEG/CH$_3$CN thermomorphic biphasic system. The heterogeneous solution was turned into homogeneous solution with heating to 60°C, and electro-oxidative Wacker-type reactions of alkenes bearing long alkyl chains proceeded smoothly to afford methyl ketones in good yields. The recycling of PEG phase containing Pd has also been achieved.

1. Introduction

Transition metal-catalyzed homogeneous reactions have been known as powerful tools for organic synthesis, but one of the drawbacks of homogeneous catalysis is the difficulty of the separation of catalyst from the reaction mixture. The typical way to overcome this problem is to use solid-supported catalysts while their activity is usually lower than that of homogeneous catalysts. Another approach to the immobilization of homogeneous catalysts is thermomorphic biphasic system, in which phases become homogeneous during the reaction with heating and could be readily separated after cooling the reaction mixtures (Fig. 1). This strategy is also effective for electro-chemical reactions, and Chiba and co-workers have reported several pioneer works in this area.13

In the decade, we have studied recyclable electrochemical reactions,14-17 and recently also studied Pd-catalyzed electro-oxidative reactions in homogeneous media.18-24 This time, we turned our attention to the integration of these two areas and designed a recycling system of Pd catalysts in the electrochemical reactions. Herein, we report the first application of PEG/organic solvent thermomorphic biphasic system25 to electro-oxidative Wacker-type reactions, and recycling of the PEG phase including a Pd catalyst.

2. Experimental

2.1 General procedure of electro-oxidative Wacker-type reaction using recyclable Pd catalyst in PEG/CH$_3$CN biphasic system

The anodic oxidation was carried out in a divided cell equipped with two platinum electrodes (1.0 × 1.5 cm$^2$). In the anodic chamber, a solution of alkene (0.20 mmol), Pd(OAc)$_2$ (4.6 mg, 0.02 mmol) and $p$-benzoquinone (6.8 mg, 0.06 mmol) in 0.05 M LiClO$_4$ or Et$_4$N$OT$s solution of CH$_3$CN/H$_2$O (8.75/1.25 mL). In the cathodic chamber, a solution of CH$_3$CN/H$_2$O (8.75/1.25 mL) was placed. A regulated constant current was passed (5 mA, 3.0 F/mol) at 60°C with magnetic stirring. After the electrolysis, the resulting mixture in the anodic chamber was extracted with hexane (3 × 10 mL). The combined organic phase was concentrated under reduced pressure. The yield of the product was determined by GC analysis (Tables 1 and 2) or the product was isolated by column chromatography on silica gel (Tables 3 and 4). When the PEG phase was recycled, the PEG phase was concentrated to solid under reduced pressure, and reused for the next run.
3. Results and Discussion

We first optimized the mediators for the electro-oxidative Wacker-type reaction in PEG/Organic thermomorphic biphasic system using dodecane (1a) as a model compound (Table 1). At 60°C, 3 F mol⁻¹ of electricity was passed through a CH₃CN/H₂O (7/1) solution of 1-dodecene 1a (0.2 mmol), PEG 2000 (2 g), CH₃CN/H₂O (7/1, 10 mL), 5 mA, 3 F mol⁻¹. The use of p-benzoquinone (pbq), which has been known as an efficient mediator for Pd-catalyzed electro-oxidative reaction, was not suitable for the reaction and the yield of 2a decreased to 43% (entry 2). Triphenylamine was also not effective (46% yield, entry 3). Although the use of p-hydroquinone gave the unsatisfactory result (48% yield, entry 4), the yield of 2a drastically increased to 76% with p-benzoquinone (pbq). The choice of electrolyte was also significant for the reaction. When LiClO₄ was used as an electrolyte, the yield of 2a increased to 86% (entry 5). Among so far tried mediators, pbq gave the best result. The use of pbq in the reaction was better than that of TEMPO, which was the best mediator in the previous electro-oxidative Wacker-type reactions. It is assumed that pbq might be relatively stable under heat conditions.

To evaluate the effect of the temperature, the electro-oxidative Wacker-type reaction of 1a was carried out at room temperature to 80°C (Table 2). At room temperature, the PEG phase and organic phase were separated during the electrolysis, and methylketone 2a was obtained in only 60% yield (entry 1). At 40°C, the yield of 2a increased slightly to 72% (entry 2). Increasing the reaction temperature to 60°C, PEG phase and organic phase were fused into homogeneous solution and methylketone 2a was obtained in 86% yield (entry 3). At 80°C, the organic phase was boiled vigorously and the yield of 2a decreased (entry 4).

To expand the scope of the system, we next carried out the electro-oxidative Wacker-type reaction using various alkenes (Table 3). The reaction of 1-decene (1b) and 1-undecene (1c), which have shorter chain length than 1a, afforded methylketone 2b and 2c in 43% and 45% yields, respectively (entries 1 and 2). The longer alkenes 1d and 1e gave moderate yields of methylketone 2d and 2e (entries 3 and 4). Higher molecular weight terminal alkenes, which are hardly oxidizable for the usual Wacker reaction, could be used under the same conditions and the corresponding ketones were obtained in good to high yields (entries 5 and 6). In particular, the alkene 1-eicosene (1f) afforded methylketone 2-eicosanone (2f) in 91% yield (entry 5). We next examined the tolerance of functional groups under these conditions. The electro-oxidative Wacker-type reaction of terminal alkenes bearing polar functional groups was performed in 43–58% (entries 6–10). These yields were lower than that of the electro-oxidative Wacker-type reactions without PEG phase. These results are reasonably explainable by assuming that

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature (°C)</th>
<th>Yield (%)</th>
<th>Recov. 1a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Room temp.</td>
<td>60</td>
<td>N.D.</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>72</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>86</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>80</td>
<td>61</td>
<td>N.D.</td>
</tr>
</tbody>
</table>

*Reaction conditions: 1a (0.2 mmol), Pd(OAc)₂ (10 mol%), pbq (30 mol%), LiClO₄ (0.05 M), PEG2000 (2 g), CH₃CN/H₂O (7/1, 10 mL), 5 mA, 3 F mol⁻¹.

*Isolated yield.

<table>
<thead>
<tr>
<th>Entry</th>
<th>1</th>
<th>2</th>
<th>Yield (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>n-C₁₂H₂₅</td>
<td>n-C₁₂H₂₅</td>
<td>48</td>
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<tr>
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<td>n-C₁₄H₂₉</td>
<td>n-C₁₄H₂₉</td>
<td>74</td>
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<tr>
<td>3</td>
<td>n-C₁₆H₃₃</td>
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<td>86</td>
</tr>
<tr>
<td>4</td>
<td>n-C₁₈H₃₇</td>
<td>n-C₁₈H₃₇</td>
<td>91</td>
</tr>
<tr>
<td>5</td>
<td>n-C₂₀H₄₁</td>
<td>n-C₂₀H₄₁</td>
<td>43</td>
</tr>
<tr>
<td>6</td>
<td>n-C₂₂H₄₅</td>
<td>n-C₂₂H₄₅</td>
<td>58</td>
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<tr>
<td>7</td>
<td>n-C₂₄H₅₉</td>
<td>n-C₂₄H₅₉</td>
<td>45</td>
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<tr>
<td>8</td>
<td>n-C₂₆H₆₅</td>
<td>n-C₂₆H₆₅</td>
<td>48</td>
</tr>
</tbody>
</table>

*Reaction conditions: 1 (0.2 mmol), Pd(OAc)₂ (10 mol%), pbq (30 mol%), LiClO₄ (0.05 M), PEG2000 (2 g), CH₃CN/H₂O (7/1, 10 mL), 5 mA, 3 F mol⁻¹.

*Isolated yield.
significant amounts of such polar products would remain in PEG phase after the extraction of the ketones. In contrast, the less polar products 1b–g were obtained in higher yields.

Next, recycling of Pd catalyst in PEG/Organic thermomorphic biphasic system was investigated using 1f as a model compound (Table 4). PEG phase including the Pd catalyst was dried after extraction of the product, and the remaining solids containing the Pd catalyst was reused for the next reaction 5 times. During the 2nd and 3rd runs, the reused PEG media was quite essential for the reaction and 2f was obtained in 88% and 91% yields, respectively. The yield of 2f decreased gradually after 4th run. This results exhibited that the activity of Pd catalyst was kept in the recycled PEG media at least 3 cycles. The decrease of the yield after 4th runs was probably due to the decreasing amount of Pd catalyst, and/or the gradually increasing some contaminants though the previous runs.

4. Conclusion

In summary, we designed a novel thermomorphic biphasic system consisting of PEG and organic phase and applied it to electro-oxidative Wacker-type reaction. Several terminal alkenes could be converted to methylketones in moderate to good yields. The PEG phase including Pd catalyst could be recycled to afford the target ketones in 64–91% yields. Further application of PEG/CH3CN biphasic system is under investigation in our laboratory.

Table 4. Recycling of PEG phase in PEG/Organic thermomorphic biphasic system.Δ

<table>
<thead>
<tr>
<th>Run</th>
<th>1st</th>
<th>2nd</th>
<th>3rd</th>
<th>4th</th>
<th>5th</th>
<th>6th</th>
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<tbody>
<tr>
<td>Yield/recov. (%)</td>
<td>91/4</td>
<td>88/11</td>
<td>91/1</td>
<td>75/22</td>
<td>73/13</td>
<td>64/25</td>
</tr>
</tbody>
</table>
|ΔReaction conditions: 1 (0.5 mmol), Pd(OAc)2 (10 mol%), pbq (30 mol%), LiClO4 (0.05 M), PEG2000 (2 g), CH3CN/H2O (7/1, 10 mL), 5 mA, 3 F mol⁻¹.Δ²Isolated yield.

Acknowledgment

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References