

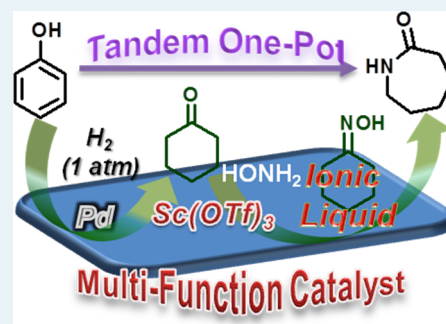
# A Multifunction Pd/Sc(OTf)<sub>3</sub>/Ionic Liquid Catalyst System for the Tandem One-Pot Conversion of Phenol to $\epsilon$ -Caprolactam

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**S** Supporting Information

**ABSTRACT:** A multifunction Pd/Sc(OTf)<sub>3</sub>/ionic liquid catalyst for the tandem one-pot conversion of phenol to  $\epsilon$ -caprolactam is reported. Pd and Sc(OTf)<sub>3</sub> cooperate to catalyze the hydrogenation of phenol to cyclohexanone with excellent conversion (>99.9%) and selectivity (>99.9%), whereas Sc(OTf)<sub>3</sub> and an ionic liquid, [bmim][PF<sub>6</sub>], cooperate to catalyze the tandem transformation of the resulting cyclohexanone to cyclohexanone oxime and the Beckmann rearrangement affording  $\epsilon$ -caprolactam.

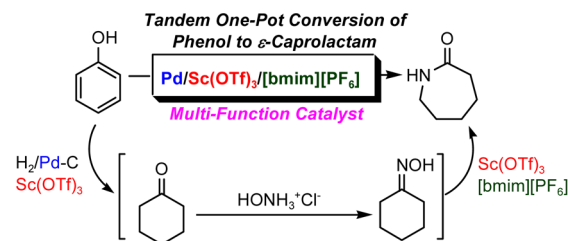


**KEYWORDS:** multifunction catalyst, tandem catalysis, hydrogenation, phenol, caprolactam

Because of the problems associated with energy shortages and environmental pollution that confront our societies, the design and implementation of tandem catalytic reactions have become increasingly important.<sup>1</sup> In biological systems, tens of enzymes selectively cooperate to catalyze a tandem transform of a simple molecule to complex molecules.<sup>2</sup> Mimicking of such multienzymatic tandem catalysis could make synthetic chemistry more sustainable. In this paper, we report the selective cooperation of a multifunction Pd/Sc(OTf)<sub>3</sub>/ionic liquid (IL) catalytic system, which made possible the tandem one-pot conversion of phenol to  $\epsilon$ -caprolactam, a key precursor of nylon-6. Pd and Sc(OTf)<sub>3</sub> cooperate to catalyze the hydrogenation of phenol to cyclohexanone under extremely mild conditions (1 atm of H<sub>2</sub> pressure at room temperature) with excellent conversion (>99.9%) and selectivity (>99.9%) within 2 h. Sc(OTf)<sub>3</sub> and an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF<sub>6</sub>], also cooperate to catalyze the tandem transformation of the resulting cyclohexanone to  $\epsilon$ -caprolactam in three-step overall yield of 67% (Scheme 1). It is noteworthy that this represents the first example of tandem one-pot conversion of phenol to  $\epsilon$ -caprolactam, providing useful grounds for the future design of more practical catalysts.

$\epsilon$ -Caprolactam is produced worldwide on one of the largest scales among commercial chemical products. Its preparation is typically carried out in a three-step procedure:<sup>3</sup> (a) synthesis of cyclohexanone either by oxidation of cyclohexane<sup>4</sup> or by hydrogenation of phenol in the gas phase<sup>5</sup> or liquid phase,<sup>6</sup> (b) formation of cyclohexanone oxime,<sup>7</sup> and (c) Beckmann rearrangement of cyclohexanone oxime to  $\epsilon$ -caprolactam.<sup>8</sup> Because of the ever-increasing industrial demand for  $\epsilon$ -caprolactam, extensive efforts have been devoted to maximizing the efficiency of each reaction step. For example, the

**Scheme 1. Multifunction Pd/Sc(OTf)<sub>3</sub>/Ionic Liquid Catalyst for Tandem One-Pot Selective Conversion of Phenol to  $\epsilon$ -Caprolactam**



development of an efficient catalyst for selective hydrogenation of phenol to cyclohexanone has received a great deal of attention in recent years.<sup>9</sup> Phenol can be hydrogenated to cyclohexanone in a “one-step” or a “two-step” process. The two-step process involves hydrogenation of phenol to cyclohexanol, followed by dehydrogenation to cyclohexanone. Although the direct one-step selective hydrogenation of phenol to cyclohexanone is more efficient than the two-step process, it is difficult to achieve high selectivity at high levels of conversion because cyclohexanone is easily hydrogenated to cyclohexanol under the reaction conditions.

Recently, by taking advantage of cooperative catalytic activity of dual-function Lewis acid/Pd catalyst,<sup>10</sup> Liu and co-workers have achieved both excellent conversion (>99.9%) and selectivity (99.9%) in the hydrogenation of phenol to cyclohexanone by using a Lewis acid/Pd–C catalyst, in which

**Received:** January 3, 2013

**Revised:** February 8, 2013

**Published:** February 18, 2013

a hydrogen molecule and phenol can be selectively activated by the Pd–C and the Lewis acid, respectively.<sup>9d</sup> More recently, Wang and co-workers developed a catalyst made of Pd nanoparticles supported on a mesoporous graphite carbon nitride that achieves the hydrogenation of phenols to the corresponding cyclohexanones with high selectivity.<sup>9e</sup> Corma and co-workers also achieved the selective conversion of phenol to cyclohexanone using Pd on Al<sub>2</sub>O<sub>3</sub> with a high surface area.<sup>9b</sup> Although these catalytic systems could potentially solve the problems associated with overreduction of phenol to cyclohexanol, they are effective only for the first step of the process and may not be applied to formation of cyclohexanone oxime and subsequent Beckmann rearrangement.

Many Lewis acids, such as AlCl<sub>3</sub>, are sensitive to water, which is formed alongside with cyclohexanone oxime in the reaction of cyclohexanone with hydroxylamine or its salts. Moreover, the AlCl<sub>3</sub>-catalyzed Beckmann rearrangement of cyclohexanone oxime is notorious for its extremely low yields of  $\epsilon$ -caprolactam.<sup>11</sup> A one-step process for the conversion of cyclohexanone to  $\epsilon$ -caprolactam has been developed by Thomas and Raja using a bifunctional catalyst, Mn<sup>III</sup>Mg<sup>II</sup>AlPO<sub>4</sub>, which catalyzed air oxidation of ammonia to hydroxylamine, reacting with cyclohexanone to form cyclohexanone oxime and the Beckmann rearrangement of the resulting oxime to  $\epsilon$ -caprolactam.<sup>12</sup> However, this catalyst could not be applied to the selective hydrogenation of phenol. Therefore, the development of a catalytic system for the tandem one-pot synthesis of  $\epsilon$ -caprolactam from phenol has remained a challenge.

For the tandem one-pot conversion of phenol to  $\epsilon$ -caprolactam, the catalyst should catalyze not only the selective hydrogenation of phenol to cyclohexanone, but also the oxime formation and Beckmann rearrangement. In addition, the catalysts must be stable to water, which is generated during oxime formation. On the basis of these considerations, we chose lanthanide triflates as a Lewis acid partner for the Pd-catalyzed selective hydrogenation of phenol to cyclohexanone because they are well-known Lewis acids with water tolerance.<sup>13</sup> Moreover, although they were not effective in the synthesis of  $\epsilon$ -caprolactam, it has been reported that some lanthanide triflates, such as Yb(OTf)<sub>3</sub>, Y(OTf)<sub>3</sub>, and Nd(OTf)<sub>3</sub>, could catalyze the Beckmann rearrangement of oximes to lactams.<sup>14</sup> In the course of our ongoing study on lanthanide triflate-catalyzed reactions in imidazolium-based ILs, we found that the catalytic activity of lanthanide triflates is often significantly increased in the ILs having noncoordinating anions, such as SbF<sub>6</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, and NTf<sub>2</sub><sup>-</sup>.<sup>15</sup> Considering the positive effects of such ILs on the lanthanide triflate-catalyzed reactions, oxime formation and Beckmann rearrangement,<sup>16</sup> we set about to investigate imidazolium-based ILs bearing noncoordinating anions as one of the components of the catalytic system.

We began our investigation to find a catalytic system for the selective hydrogenation of phenol to cyclohexanone using Pd–C and lanthanide triflates. These results are summarized in Table 1. As shown in Table 1, all lanthanide triflates can, in the presence of a Pd catalyst, perform the selective hydrogenation of phenol to cyclohexanone within a few hours in dichloromethane under 1 atm of H<sub>2</sub> at room temperature. More specifically, the catalyst composed of Sc(OTf)<sub>3</sub>/Pd–C showed extremely high catalytic activity and hydrogenated phenol to afford cyclohexanone with >99.9% conversion and 99.9% selectivity in only 2 h (entry 1, Table 1). In addition, the Pd–C/Sc(OTf)<sub>3</sub> catalyst can be reused four times without any loss of selectivity (entry 1, Table 1). The reaction rate and

**Table 1. Selective Hydrogenation of Phenol to Cyclohexanone using Pd/Ln(OTf)<sub>3</sub> Catalyst<sup>a</sup>**

entry	Ln(OTf) <sub>3</sub>	time (h) <sup>b</sup>	conv. (%) <sup>c</sup>	selectivity <sup>c</sup>	
				C=O	C–OH
1 <sup>d</sup>	Sc(OTf) <sub>3</sub>	2.0	>99.9	>99.9	<0.1
2 <sup>e</sup>	Sc(OTf) <sub>3</sub>	3.5	>99.9	97.7	2.3
3 <sup>f</sup>	Sc(OTf) <sub>3</sub>	2.0	>99.9	>99.9	<0.1
4 <sup>g</sup>	Sc(OTf) <sub>3</sub>	3.5	>99.9	94.2	5.8
5	Ce(OTf) <sub>3</sub>	3.5	>99.9	>99.9	<0.1
6	Pr(OTf) <sub>3</sub>	3.0	>99.9	>99.9	<0.1
7	Nd(OTf) <sub>3</sub>	3.5	>99.9	>99.9	<0.1
8	Sm(OTf) <sub>3</sub>	2.5	>99.9	>99.9	<0.1
9	Eu(OTf) <sub>3</sub>	2.5	>99.9	>99.9	<0.1
10	Gd(OTf) <sub>3</sub>	3.0	>99.9	>99.9	<0.1
11	Tb(OTf) <sub>3</sub>	2.5	>99.9	>99.9	<0.1
12	Dy(OTf) <sub>3</sub>	2.5	>99.9	>99.9	<0.1
13	Ho(OTf) <sub>3</sub>	3.0	>99.9	>99.9	<0.1
14	Er(OTf) <sub>3</sub>	3.0	>99.9	>99.9	<0.1
15	Tm(OTf) <sub>3</sub>	2.0	>99.9	>99.9	<0.1
16	Yb(OTf) <sub>3</sub>	2.5	>99.9	>99.9	<0.1
17	Lu(OTf) <sub>3</sub>	2.5	>99.9	>99.9	<0.1
18	Y(OTf) <sub>3</sub>	2.5	>99.9	>99.9	<0.1
19	La(OTf) <sub>3</sub>	3.0	>99.9	>99.9	<0.1
20	Zn(OTf) <sub>2</sub>	5.0	>99.9	>99.9	<0.1

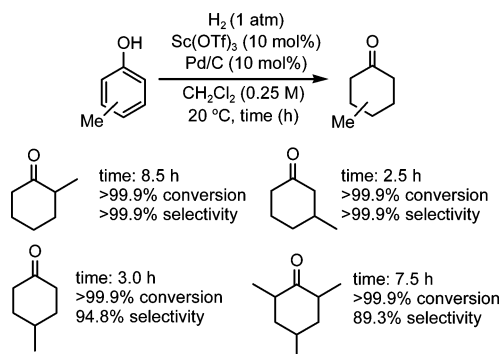
<sup>a</sup>Unless otherwise noted, the reaction was carried out with 0.5 mmol of phenol in the presence of 10 mol % (based on Pd contents) of Pd/C (10 wt %) and 10 mol % of lanthanide triflate in dichloromethane under 1 atm of H<sub>2</sub> at room temperature (see the Supporting Information for experimental details). <sup>b</sup>Time for complete conversion of phenol by GC. <sup>c</sup>Determined by GC using *n*-decane as an internal standard (see the Supporting Information for experimental details). <sup>d</sup>The catalyst was reused four times. <sup>e</sup>Reaction was carried out in the presence of 1.0 mol % of Sc(OTf)<sub>3</sub>. <sup>f</sup>Reaction was carried out in dichloroethane. <sup>g</sup>Pd on alumina was used instead of Pd/C.

selectivity (97.7%) were decreased as the amount of Sc(OTf)<sub>3</sub> decreased to 1.0 mol % (entry 2, Table 1). This result suggests that activation of phenol with Sc(OTf)<sub>3</sub> is crucial to obtain high selectivity.

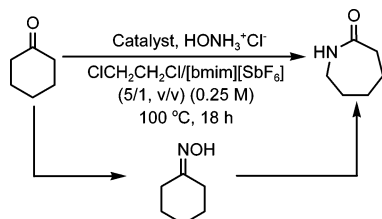
The reactivity and selectivity were retained in high-boiling 1,2-dichloroethane solvent, which is a necessity in Beckmann rearrangement (entry 3, Table 1); however, it was found that the support material could influence the reaction efficiency,<sup>9b,e</sup> and thus, the use of palladium on alumina decreased reactivity and selectivity, requiring 3.5 h to afford 94.2% of cyclohexanone along with 5.8% of overreduced cyclohexanol (entry 4, Table 1). Under the same reaction conditions, Zn(OTf)<sub>2</sub> also catalyzed the selective hydrogenation of phenol to cyclohexanone but required a prolonged reaction time (entry 20, Table 1). The Pd–C/Sc(OTf)<sub>3</sub> catalyst can hydrogenate methyl-substituted phenols to the corresponding methylated cyclohexanones with full conversion and high selectivities at room temperature within hours (Scheme 2).

With the optimal dual-function catalyst, Pd–C/Sc(OTf)<sub>3</sub>, in hand for the selective hydrogenation of phenol to cyclohexanone, we then attempted to find a multifunction catalytic system for the one-pot conversion of cyclohexanone to  $\epsilon$ -caprolactam using Sc(OTf)<sub>3</sub> as a catalyst (Table 2).

**Scheme 2. Selective Hydrogenation of Methylated Phenols to the Corresponding Cyclohexanones using Pd–C/Sc(OTf)<sub>3</sub> Catalyst**



**Table 2. One-Pot Conversion of Cyclohexanone to  $\epsilon$ -Caprolactam Using Sc(OTf)<sub>3</sub>/[bmim][SbF<sub>6</sub>] Catalyst<sup>a</sup>**



entry	catalyst			oxime <sup>b</sup> %	lactam %
	Pd/C	Sc(OTf) <sub>3</sub>	IL		
1 <sup>c</sup>		10 mol %		93	
2		10 mol %	IL	5	89
3			IL	96	3
4	10 mol %	10 mol %	IL	7	88

<sup>a</sup>Unless otherwise noted, a solution of cyclohexanone (1.5 mmol) and hydroxylamine hydrochloride (1.65 mmol) in a mixture of 1,2-dichloroethane (5.0 mL) and [bmim][SbF<sub>6</sub>] (1.0 mL) was stirred for 18 h at 100 °C in the presence of catalyst (see the Supporting Information for experimental details). <sup>b</sup>Determined by GC using *n*-decane as an internal standard. <sup>c</sup>Reaction was carried out in 1,2-dichloroethane (6.0 mL) only.

Through the systematic variation of catalyst compositions, we found that both Sc(OTf)<sub>3</sub> and an ionic liquid are critical for the one-pot conversion of cyclohexanone to  $\epsilon$ -caprolactam. In the reaction of cyclohexanone with hydroxylamine hydrochloride in dichloroethane at 100 °C for 18 h in the presence of 10 mol % of Sc(OTf)<sub>3</sub>, only cyclohexanone oxime was formed in 93% yield. No sign for the formation of  $\epsilon$ -caprolactam was observed (entry 1, Table 2). When the same reaction was carried out in a mixture of dichloroethane and [bmim][SbF<sub>6</sub>] (5/1, v/v), the desired  $\epsilon$ -caprolactam was formed in 89% yield along with 5% of cyclohexanone oxime (entry 2, Table 2). In contrast, only tiny amounts (~3%) of  $\epsilon$ -caprolactam were formed in the absence of Sc(OTf)<sub>3</sub>, and cyclohexanone oxime was formed as a major product in 96% conversion (entry 3, Table 2). The reaction efficiency was not diminished in the presence of Pd catalyst (entry 4, Table 2).

Finally, the tandem one-pot conversion of phenol to  $\epsilon$ -caprolactam was investigated using the multicomponent catalytic system composed of Pd–C/Sc(OTf)<sub>3</sub>/IL (Table 3).

When phenol was hydrogenated in a mixture of dichloroethane/[bmim][SbF<sub>6</sub>] (5/1, v/v, 0.3 M) in the presence of 10 mol % of Pd/C and 10 mol % of Sc(OTf)<sub>3</sub> under 1 atm of H<sub>2</sub>

**Table 3. Tandem One-Pot Conversion of Phenol to  $\epsilon$ -Caprolactam Using Pd–Sc(OTf)<sub>3</sub>/Ionic Liquid Catalyst.<sup>a</sup>**

Reaction conditions:  $\text{H}_2$  (1 atm),  $\text{Pd}/\text{C}$  (10 mol%),  $\text{Sc}(\text{OTf})_3$  (10 mol%),  $\text{ClCH}_2\text{CH}_2\text{Cl}$  (0.25 M), [bmim][X], 20 °C, 3 h;  $\text{HONH}_3^+\text{Cl}^-$  (1.1 equiv), 100 °C, 21 h.

entry	[bmim][X]	yield (%) <sup>b</sup>
1	[bmim][SbF <sub>6</sub> ]/200 mol %	34
2	[bmim][BF <sub>4</sub> ]/200 mol %	<5
3	[bmim][NTf <sub>2</sub> ]/200 mol %	22
4	[bmim][PF <sub>6</sub> ]/200 mol %	63
5	[bmim][PF <sub>6</sub> ]/300 mol %	67

<sup>a</sup>Reaction conditions: the reaction was carried out with 0.5 mmol of phenol in the presence of 10 mol % (based on Pd contents) of Pd/C (10 wt %), 10 mol % of Sc(OTf)<sub>3</sub>, and [bmim][X] in dichloroethane (6.0 mL) under 1 atm of H<sub>2</sub> pressure at room temperature. After complete conversion of phenol to cyclohexanone, determined by GC, hydroxylamine (1.65 mmol, 1.1 equiv) was added and stirred for 21 h at 100 °C (see the Supporting Information for experimental details).

<sup>b</sup>Determined by GC using *n*-decane as an internal standard.

at room temperature, only 75% of the phenol was converted to cyclohexanone during 6 h. Fortunately, the catalytic activity of Pd/C and Sc(OTf)<sub>3</sub> was restored when IL was used as an additive. With addition of 200 mol % of [bmim][SbF<sub>6</sub>], phenol was completely converted to cyclohexanone with >99.9% selectivity within 3 h. Unfortunately, the tandem reaction of the resulting cyclohexanone with hydroxylamine hydrochloride afforded the desired  $\epsilon$ -caprolactam in only 34% yield (entry 1, Table 3). Changing the counteranion of the ionic liquid to [BF<sub>4</sub>] (entry 2, Table 3) or [NTf<sub>2</sub>] anion (entry 3, Table 3) did not improve the yield of  $\epsilon$ -caprolactam. To our delight, when [bmim][PF<sub>6</sub>] was used as an additive, the tandem one-pot conversion of phenol to  $\epsilon$ -caprolactam could be achieved with overall 63% yield (entry 4, Table 3). In the presence of 300 mol % of [bmim][PF<sub>6</sub>], the yield was further increased to afford  $\epsilon$ -caprolactam in 67% overall yield (entry 5, Table 3); however, the catalytic activity of the recovered catalyst was dramatically decreased, and the origin of the decreased catalytic activity is not clear at the present time. Nevertheless, it is clear that the Lewis acidic Sc(OTf)<sub>3</sub> could accelerate the hydrogenation of phenol to cyclohexanone, but suppress its reduction to cyclohexanol.<sup>9d,10</sup> In addition, IL may play a dual function:<sup>15a</sup> increasing Lewis acidity of Sc(OTf)<sub>3</sub> via anion exchange and lowering the activation energy for Beckmann rearrangement via stabilization of the charged intermediate formed during Beckmann rearrangement to ultimately afford  $\epsilon$ -caprolactam.

In summary, a new multifunction catalyst, consisting of Pd–C/Sc(OTf)<sub>3</sub>/[bmim][PF<sub>6</sub>], has been developed for the tandem one-pot synthesis of  $\epsilon$ -caprolactam from phenol in 67% overall yield. Similar to the multienzymatic catalytic reactions, Pd catalyzed the hydrogenation of phenol to cyclohexanone in the presence of Sc(OTf)<sub>3</sub> with >99.9% selectivity in >99.9% conversion. Furthermore, Sc(OTf)<sub>3</sub> catalyzed the oxime formation and Beckmann rearrangement in the presence of [bmim][PF<sub>6</sub>] to afford  $\epsilon$ -caprolactam. The cooperative action of multicomponent catalytic systems will therefore be a valuable concept in the design of future catalysts demonstrating greater practicality.

**■ ASSOCIATED CONTENT****■ Supporting Information**

Details of the experimental procedures and GC chromatograms for the conversion of phenol (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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**Notes**

The authors declare no competing financial interest.

**■ ACKNOWLEDGMENTS**

This work was supported by the Korean Research Foundation (KRF-20120005673). We thank to Prof. J. Bouffard for helpful comments.

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