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# Application of ionic liquids in palladium(II) catalyzed homogenous transfer hydrogenation

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This article is dedicated to Professor András Lipták on the occasion of his 70th birthday

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**Abstract**—The first application of palladium(II) catalyzed homogenous transfer hydrogenations in ionic liquids is described. Cinnamic acid and its derivatives were reduced in high yields under mild conditions using ammonium formate as hydrogen donor.

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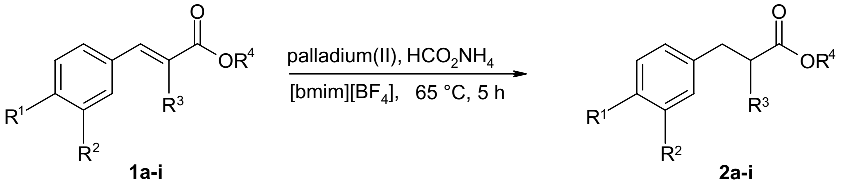
Catalytic transfer hydrogenation is an important synthetic method for the reduction of organic compounds.[1–3] Such reactions can generally be performed in various organic solvents, but in some cases water can serve as solvent.[4–6] Bertold and co-workers were the first to report the application of ionic liquids[7–11] in heterogeneous transfer hydrogenation.[12] In their process the catalyst was Pd/C, the solvent was [bmim][$PF_6$] and the reaction took place under microwave irradiation. Geldbach and Dyson reported the asymmetric transfer hydrogenation of acetophenone with a ruthenium complex in 2-methyl-[bmim][$PF_6$], using triethylammonium formate as the hydrogen donor.[13] Very recently, Ohta and co-workers published the transfer hydrogenation of ketones with a modified ruthenium complex in ionic liquids.[14] In both cases ionic liquids were not only the solvents of the reactions, but they also had a role in stabilization of the ruthenium complexes.

We have found that ionic liquids are suitable solvents for the palladium(II) catalyzed homogenous transfer hydrogenation of α,β-unsaturated carboxylic acids (Scheme 1).

Cinnamic acid **1a** was reduced in high yield under mild conditions using a catalytic amount of palladium(II) acetate or palladium(II) chloride and ammonium formate as hydrogen donor in different ionic liquids (Table 1).

Both $Pd(OAc)_2$ and $PdCl_2$ were found to be effective catalysts for the transfer hydrogenation. Of the ionic liquids studied, [bmim][$BF_4$], ECOENG™-212 and ECOENG™-500 were the most effective, resulting in >99% hydrogenated product. In contrast, ionic liquids containing the [$PF_6^-$] anion furnished only 2% product and in typical organic solvents such as ethanol, toluene



**Scheme 1.**

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*Keywords*: Ionic liquids; Homogenous catalytic transfer hydrogenation; Palladium(II) acetate; Palladium(II) chloride.

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**Table 1.** $Pd(OAc)_2$ catalyzed transfer hydrogenation of **1a** in various ionic liquids using $HCO_2NH_4$ as the hydrogen donor

| Entry | Solvent | Yield[a] (%) |
|---|---|---|
| A | $[bmim][BF_4]$ | >99 |
| B | [bmim][Cl] | 46 |
| C | $[bmim][PF_6]$ | 2 |
| D | $[emim][PF_6]$ | 2 |
| E | ECOENG™-212[b] | >99 |
| F | ECOENG™-500[b] | >99 |

[a] HPLC yield.

[b] Solvent-innovation GmbH.[15]

**Table 2.** $Pd(OAc)_2$ catalyzed transfer hydrogenation in $[bmim][BF_4]$

| Compound **1** | $R^1$ | $R^2$ | $R^3$ | $R^4$ | Yield of **2**[a] (%) |
|---|---|---|---|---|---|
| **a** | H | H | H | H | >99 |
| **b** | OMe | H | H | H | >99 |
| **c** | OH | OH | H | H | 69 |
| **d** | OMe | OMe | H | H | 98 |
| **e** | H | H | Me | H | >99 |
| **f** | H | H | Ph | H | >99 |
| **g** | H | H | $NHCOCH_3$ | H | 52 |
| **h** | H | H | $–NCH(CH_3)–$ |  | 46 |
| **i** | H | H | H | Me | >99 |

[a] HPLC yield.

and chloroform low yields or no reactions were observed. With either sodium formate or triethylammonium formate as hydrogen donor, the reactions occured with similar yields as when using ammonium formate. The reduction of cinnamic acid **1a** gave the best results at 65 °C for 5 h in $[bmim][BF_4]$ using 10 mol % of catalyst and 4 equiv of ammonium formate as hydrogen donor.[16,17]

After the successful reduction of **1a** under these conditions, the method was extended to a variety of α- and aryl-substituted cinnamic acids (Table 2). Aryl-substituted compounds bearing methoxy (**1b**), dihydroxy (**1c**) or dimethoxy (**1d**) groups were reduced in good yields. Of the α-substituted derivatives investigated, the α-methyl (**1e**) and α-phenyl (**1f**) substituted examples provided the corresponding hydrogenated products in good yields. The α-acetamido (**1g**) derivative and the readily available azalactone (**1h**) were converted directly to the *N*-acyl derivatives in moderate yields. The methyl ester of cinnamic acid (**1i**) was also hydrogenated in excellent yield.

In conclusion, we have found a new application of ionic liquids in the homogenous transfer hydrogenation of α,β-unsaturated carboxylic acids with commercially available, nonpyrophoric palladium(II) catalysts. This method offers an efficient and attractive alternative to currently available procedures.

## Acknowledgements

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## References and notes

1. Brieger, G.; Nestrick, T. J. *Chem. Rev.* **1974**, *74*, 567–580.
2. Johnstone, R. A. W.; Wilby, A. H.; Entwistle, S. D. *Chem. Rev.* **1985**, *85*, 129–170.
3. Palmer, M. J.; Wills, M. *Tetrahedron: Asymmetry* **1999**, *10*, 2045–2061.
4. Tour, J. M.; Pendalwar, S. L. *Tetrahedron Lett.* **1990**, *31*, 4719–4722.
5. Arterburn, J. B.; Pannala, M.; Gonzalez, A. M.; Chamberlin, R. M. *Tetrahedron Lett.* **2000**, *41*, 7847–7849.
6. Sharma, A.; Joshi, B. P.; Sinha, A. K. *Chem. Lett.* **2003**, *32*, 1186–1187.
7. Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH, 2003, pp 40–118.
8. Welton, T. *Chem. Rev.* **1999**, *99*, 2071–2083.
9. Holbrey, J. D.; Seddon, K. R. *Clean Products Process.* **1999**, *1*, 223–236.
10. Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772–3789.
11. Hua, Z.; Shanjay, M. V. *Aldrichim. Acta* **2002**, *35*, 75–83.
12. Bertold, H.; Schotten, T.; Hönig, H. *Synthesis* **2002**, *11*, 1607–1610.
13. Geldbach, T. J.; Dyson, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 8114–8115.
14. Kawasaki, I.; Tsunoda, K.; Tsuji, T.; Yamaguchi, T.; Shibuta, H.; Uchida, N.; Yamashita, M.; Ohta, S. *Chem. Commun.* **2005**, 2134–2136.
15. ECOENG™-212: $[emim][EtSO_4]$; ECOENG™-500: $[(C_{13}H_{27})(CH_3)N[(CH_2CH_2O)_2H][(CH_2CH_2O)_3H]][MeSO_4]$.
16. In a typical procedure, cinnamic acid (0.1 g, 0.66 mmol) and 10 mol % $Pd(OAc)_2$ (15 mg, 0.066 mol) were added to a stirred solution of 3 mL $[bmim][BF_4]$. Ammonium formate (200 mg, 2.4 mmol) was added and the reaction mixture was heated to 65 °C for 5 h. After cooling to room temperature, the mixture was extracted with diethyl ether (2 × 8 mL) and the extract was dried with $Na_2SO_4$. The pure product, hydrocinnamic acid (0.09 g, 90% yield), was isolated after removal of the solvent in vacuum.
17. In some batches of $[bmim][BF_4]$, formic acid was a suitable hydrogen donor, due to the basic impurities of the ionic liquid.[18]
18. Scammels, P. J.; Scott, J. L.; Singer, R. D. *Aust. J. Chem.* **2005**, *58*, 155–169.