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Wacker oxidation of terminal olefins in a mixture of [bmim][BF_4] and water[☆]

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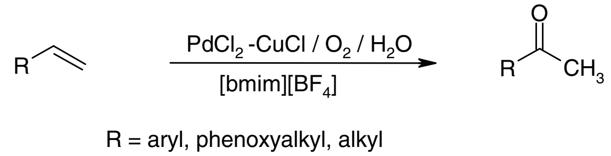
Abstract—A simple and efficient $PdCl_2$/CuCl catalyzed oxidation of alkenes has been successfully developed using a mixture of water and the ionic liquid [bmim][BF_4] as solvent. Starting from various types of terminal olefins, the corresponding ketones have been prepared under mild reaction conditions and obtained in good to excellent yields after a simple extraction with diethyl ether. Furthermore, it was possible to recycle and reuse the ionic liquid and the catalytic system.

The Pd(II) chloride and copper(I) chloride oxidation of alkenes to ketones and aldehydes is an extension of the well-known Wacker process.[1,2] The solvent of the original Wacker reaction is water containing HCl. It affords excellent results in the production of acetaldehyde from ethylene and it is one of the most important industrial process employing transition metal catalysis. However, higher alkenes have very poor solubility in water and therefore exhibit lower rates for the oxidation and furthermore they afford different types of by-products due to the presence of the acid. Therefore, mixtures of water and organic solvents (such as DMF, NMP or sulfolane) have been studied in order to solve this problem.[1,2] In the recent literature, various alternative solutions have been described. They involve the use of surfactants,[3] cyclodextrins[4] or calixarenes,[5] supported catalysts,[6] nonclassical solvents such as fluorous phases[7] or polyethylene glycols (PEGs).[8] During the last decade, room temperature ionic liquids (RTILs) have attracted a lot of interest as a novel type of reaction medium[9] and they have proved to be especially useful in the case of catalytic reactions.[10] Therefore, ionic liquids have also been considered for Wacker oxidations. A Pd-catalyzed selective oxidation of styrene to acetophenone, using H_2O_2 in imidazolium type ionic liquids, has been reported.[11] This has been further extended to super critical (sc) CO_2 and mixtures of ionic liquids and sc CO_2.[12] During the last few years, we have been interested in the use of ionic liquids in synthesis, including oxidation reactions. For instance, we have demonstrated recently that ionic liquids are excellent solvents for the aerobic oxidation of alcohols to carbonyl compounds.[13] As an extension of this study, we demonstrate in this letter that a combination of the ionic liquid [bmim][BF_4] and water is an excellent solvent system for the Wacker oxidation of different types of olefins using the classical Pd/Cu catalysts under an oxygen atmosphere. The corresponding ketones, bearing various substituents as well as different chain lengths, were obtained in good to excellent yields and it was possible to recycle and reuse the ionic liquid and the catalyst (Scheme 1).

A key issue for the success of such a reaction was to obtain the best possible miscibility of all components. The imidazolium ionic liquids are reported to be good solvents for metal salts and therefore they appeared as



Scheme 1.

Keywords: Wacker oxidation; Ionic liquid; $PdCl_2$; CuCl; Alkenes.

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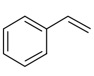
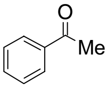
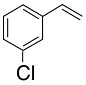
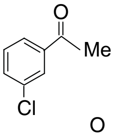
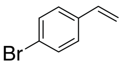
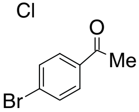
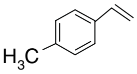
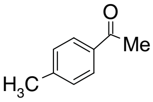
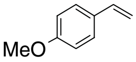
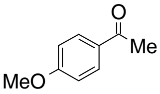
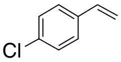
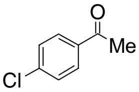
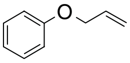
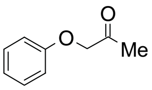
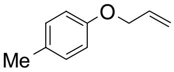
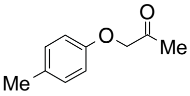
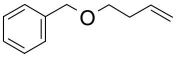
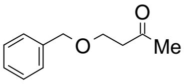
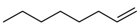
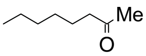
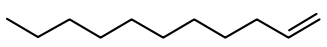
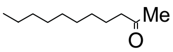
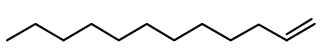
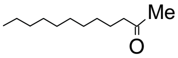
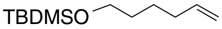
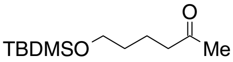
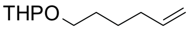
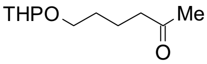
obvious candidates. However, it has also been well established that their miscibility with water was strongly dependent upon the nature of the counter anion.[14] The [bmim][BF_4] ionic liquid was selected for this study since it has an excellent miscibility with H_2O. Styrene was selected as a convenient model alkene to optimize the reaction conditions using such an ionic liquid–water mixture.

In pure [bmim][BF_4], the reaction was very slow, affording only traces of acetophenone. Then, water was added and after a careful optimization of the quantity, it was found that the best ratio was 2/1 by volume. Higher quantities of water gave more degradation products while lower quantities gave less conversion to the desired product. Under these optimized reaction conditions, we found that 95% of the styrene was consumed after 25 h and the isolated yield of carbonyl compound was 90%, just 5% of the starting material being left unreacted.

It is interesting to note that under these conditions it was not necessary to add any acid, contrary to the classical Wacker process. This may be due to the hydrolysis of BF_4^- liberating HF during the reaction, which may act as the catalyst.[15]

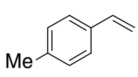
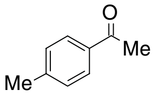
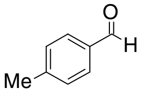
Table 1. Ionic liquid mediated Wacker oxidation of terminal olefins

Entry	Alkenes	Products[a]	Conversion[b] (%)	Reaction time/h	GC ratio ketone/aldehyde	Yield[c] (%)
a			95	25	92:6.5	90
b			90	24	97.5:2.4	88
c			88	24	96.2:3.1	85
d			92	24	80:18	80
e			90	28	95.1:3.5	85
f			95	30	94.1:4.2	82
g			90	33	83.4:8.8	70
h			90	25	90.2:6.9	78
i			88	25	91:7.5	80
j			85	45	81.1:13.3	70
k			84	50	72:13.6	60
l			86	48	72.1:11.5	62
m			84	58	73.1:10.3	60
n			85	64	74:12.6	62

[a,b] All products were characterized by GC analysis and ^1H NMR.

[c] Yield refers to the pure ketones after column chromatography.

Table 2. Reuse of the solvent system for the Wacker oxidation of methyl styrene to ketone

Entry	Olefin	Run	Conversion (%)	Ketone	(%)[a]	Aldehyde	(%)[a]
a		1	92		80		18
b		2	96		76		15
c		3	95		78		14
d		4	94		82		12
e		5	94		85		11
f		6	90		90		7
g		7	89		92		—
h		8	85		96		—

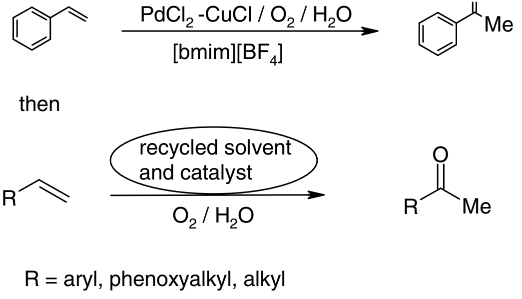
[a] GC ratio of the ketone taken from 100% product ratio.

These reaction conditions could be extended to various types of alkenes as indicated in Table 1. These included various styrenes (entries a–f), as well as aliphatic derivatives (entries j–l). Several examples (entries g–i and m–n) demonstrated that functional groups could be tolerated in this process. In each case, the conversions were excellent (84–95%). Furthermore, these reactions afforded excellent (in the case of aromatic) to good yields (in the case of aliphatic derivatives) as shown in Table 1.

The possibility of recycling the solvent and the catalysts is one of the key advantages in the use of ionic liquids as solvents. This was demonstrated using 4-methylstyrene as a model (Table 1, entry d). It was possible to recycle the system up to eight times with only a slight decrease in the conversion (96–85%). However, at the same time, an increase in the selectivity was observed since the excess of the ketone increased from 70% to 96% (Table 2) with less tolylaldehyde being obtained. At this stage, there is no clear explanation for this intriguing result.

In addition to recycling of the solvent and catalyst for the same substrate, it was found suitable for being reused for different types of substrates. This was demonstrated in different reactions using the same solvent–catalyst system and taking either aromatic alkenes (such as entries a, d and e) or aliphatic derivatives (such as entries j and k, Table 1), as shown in Scheme 2. In each case, the yields were equal to previous ones and NMR and GC analysis of the products indicated no contamination due to the earlier product. In all cases, the aldehyde yield decreased.

In conclusion, a mixture of [bmim][BF_4] and water appears to be an efficient solvent system for the aerobic Wacker oxidation of higher and functionalized alkenes.[16] Under these reaction conditions, the classical catalytic system of $PdCl_2/CuCl$ and O_2 can be used. The catalyst/solvent system can be recycled several times with only a slight decrease in the yield of the expected ketones. Extension of these reactions and their applications in total synthesis are under active study in our laboratories.



Scheme 2.

Acknowledgements

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15. Anbar, M.; Guttmann, S. *J. Phys. Chem.* **1960**, *64*, 1896.
16. *Typical procedure*: A mixture of $PdCl_2$ (36 mg, 0.2 mmol, 10 mol %), CuCl (200 mg, 2 mmol) in ionic liquid [bmim]-[BF_4] (2 mL, 8.4 mmol) and H_2O (1 mL, 55.5 mmol) was stirred at 60 °C for 1 h under an oxygen atmosphere (the colour of the reaction mixture changed from greenish to dark and then again to greenish). Then styrene (208 mg, 2 mmol) was added dropwise and slowly over 30–40 min. After complete addition, the reaction mixture was further stirred at the same temperature under an oxygen atmosphere and the progress of the reaction was monitored by GC. After completion of the reaction, the product was extracted with ether. The organic phase was dried ($MgSO_4$) and concentrated under vacuum. Acetophenone was isolated by flash chromatography on SiO_2 and fully characterized by NMR and by comparison with an authentic sample. Similar reactions were performed with other alkenes. The corresponding ketones had spectroscopic data (IR, ^1H NMR) in agreement with the literature. A further comparison by GC analysis was also performed in the case of commercially available ketones. *Recycling and reuse of the ionic liquid and catalyst*: After extraction of the product, the ionic liquid containing $PdCl_2$ and CuCl was dried at 60 °C under vacuum for 4 h before the next run. Then, 1 mL of H_2O was added and the mixture was stirred at 60 °C for 1 h under an oxygen atmosphere before the slow addition of the olefin as described previously.