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ORIGINAL ARTICLE

A facile and green microwave-assisted synthesis of new functionalized picolinium-based ionic liquids

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Abstract A facile preparation of a series of 17 new functionalized picolinium-based ionic liquids under "green chemistry" conditions is described. For the first time, target ionic liquids were prepared using standard methodology and under microwave irradiation in short duration of time with quantitative yields. Their structures were characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, ^{11}B, ^{19}F, ^{31}P and mass spectra.

1. Introduction

Considerable stress to replace a lot of volatile organic compounds that were used as solvents in synthetic organic chemistry has been laid on many chemical industries. Chlorinated hydrocarbons and many other toxic substances having hazardous effect caused many serious environmental problems which led to make their use prohibitive. A suitable solution for these problems is found by using the ionic liquid as a clean medium of working and avoiding the solvent effect as well as the catalyst recycling problems (Sheldon, 2001; Carmichael, 2000; Seddon, 1998).

Ionic liquids (ILs) are salts consisting of ions, which exist in the liquid state at ambient temperatures. They have many unique physicochemical properties, such as negligible vapor pressure, high thermal and chemical stabilities, high ionic conductivity, excellent solubility with many substances (Davis, 2004). They have been also widely investigated for a variety of applications: the use as solvents or catalysts for chemical synthesis (Liu et al., 2003; Wang et al., 2007), media for electrodeposition of metals (Endres, 2002; Lin and Sun, 1999), electrolyte for electrochemical devices such as battery (Takahashi et al., 1999; Brennecke and Magin, 2001), supercapacitors (Ue et al., 2003; Balducci et al., 2004) and, in particular, fluids for thermal storage and exchange in solar concentrating power plants (Moens et al., 2003).

It is found that the cation and anion modifications with special functional groups led to a pronounced change in the properties of ionic liquids (ILs). Incorporating of the ILs with more than one functional group has attractive great interest in chemical synthesis, separation science,

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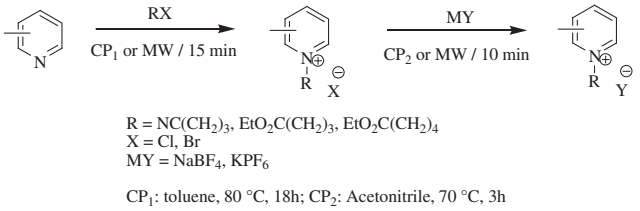
electrochemistry, instrumental analysis and energy sources (Chen, 2010).

On the other hand, different procedures are recommended for green chemistry (Anastas and Warner, 1998) involving: solvent-free reactions, non-classical modes of activation such as ultrasounds or microwaves. The use of MW irradiation leads to large reductions in reaction times, enhancements in conversions, sometimes in selectivity, with several advantages of the eco-friendly approach (Loupy, 2004; Aupoix et al., 2010; Yi et al., 2005; Singh et al., 2005; Deetlefs and Seddon, 2003).



Scheme 1 Synthesis of picolinium-based ionic liquids by conventional preparation (CP) and under microwave irradiation (MW).

2. Materials and methods

2.1. Experimental

All new compounds were synthesized and characterized by ^{1}H NMR, ^{13}C NMR, IR and LCMS.

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured in DMSO at room temperature at 400 MHz. Chemical shifts (d) were reported in ppm to a scale calibrated for tetramethylsilane (TMS), which is used as an internal standard. The LCMS spectra were measured with a Micromass, LCT mass spectrometer. IR spectra were recorded in NaCl disc on a Schimadzu 8201 PC, FTIR spectrophotometer (ν_{max} in cm^{-1}). The microwave-assisted reactions were performed using a controllable single-mode microwave reactor, CEM Discovery, designed for synthetic use. The reactor is equipped with a magnetic stirrer as well as pressure, temperature and power controls. The maximum operating pressure of the reactor is 20 bar. The power and temperature ranges are 15–300 W and 60–250 °C, respectively.

2.2. Synthesis

2.2.1. General procedures for the synthesis of picolinium halides (1, 4, 7, 10, 13 and 16) using conventional method

To the solution of picoline (1 eq) in toluene, was added alkyl halide (1.1 eq) at room temperature, followed by stirring at 80 °C for 18 h. The completion of the reaction was marked by the separation of oil from the initially obtained clear and homogenous mixture of picoline and alkyl halide in toluene. The product was isolated by extraction to remove the unreacted starting materials and solvent. Subsequently, the picolinium salt was washed with ethyl acetate. In each case, the IL/salt was finally dried at a reduced pressure to get rid of all the volatile organic compounds.

Table 1 Different entries, reaction conditions and reaction yields for the synthesis of picolinium-based ionic liquids using conventional preparation (CP) and under microwave irradiation (MW).

Entry	Amine	RX	Yield (%) N-alkylation (first step)		MY	Yield (%) Anion metathesis (second step)	
			CP[a]	MW[b]		CP[c]	MW[d]
1	2-Picoline	$NC(CH_2)_3Cl$*	67	78			
2					$NaBF_4$	91	98
3					KPF_6	92	98
4	3-Picoline	$NC(CH_2)_3Cl$*	64	76			
5					$NaBF_4$	92	98
6					KPF_6	93	98
7		$EtO_2C(CH_2)_3$ Br	78	89			
8					$NaBF_4$	94	97
9					KPF_6	93	97
10		$EtO_2C(CH_2)_4$ Br	81	90			
11					$NaBF_4$	92	97
12					KPF_6	94	98
13	4-Picoline	$EtO_2C(CH_2)_3$ Br	79	90			
14					$NaBF_4$	94	98
15					KPF_6	93	97
16		$EtO_2C(CH_2)_4$ Br	81	91			
17					$NaBF_4$	92	98
18					KPF_6	94	97

[a] Time (18 h), temperature (80 °C) in toluene.
[b] Time (15 min), temperature (80 °C), power (240 W), pressure (40 Psi).
[c] Time (3 h), temperature (80 °C).
[d] Time (10 min), temperature (70 °C), power (300 W), pressure (40 Psi).
* Higher temperatures and longer reaction times are required in CP.

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