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ORIGINAL ARTICLE

A novel L-amino acid ionic liquid for quick and highly efficient synthesis of oxime derivatives – An environmental benign approach

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L-Amino acid-ionic liquid;
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Abstract A mild, efficient, and eco-friendly procedure for the conversion of aliphatic, alicyclic and aromatic carbonyl compounds into the corresponding oximes, was catalyzed by a novel imidazolium based ionic liquid coupled with amino acid (asparagine) (L-AAIL, L-Amino acid functionalized ionic liquid) catalytic system. The quantitative conversion of aryl and alkyl carbonyl compounds into the corresponding oximes was achieved by simply grinding at ambient temperature using 0.05 mmol of catalyst in 50 s. In addition, this L-AAIL catalyst exhibited good reusability for five consecutive trials without significant loss of its catalytic activity.

1. Introduction

In synthetic organic chemistry, oximes are vital intermediate for many functional group transformations. These compounds were successfully transformed into amides (Owston et al., 2007), amines (Li et al., 2009), hydroxylamine (Mamani et al., 2011), hydroxylamine O-ethers (Miyabe et al., 2009), nitroalkanes (Kudyba et al., 2005), quinoxaline derivatives (Dong et al., 2008), etc. It is well-known intermediate for Beckmann rearrangement (Meng et al., 2011). Therefore, synthetic organic chemists are interested in the facilitation of oxime synthesis.

Although alternative methods exist (Liang et al., 2010), reaction of carbonyl compounds with hydroxylamine hydrochloride remains still the most important route. Many improvements of this methodology have been convoluted. Hean Luo described the treatment of ketones with hydroxylamine hydrochloride in the presence of an ion-exchange resin as the catalyst in ethanol gave oxime in high yields at room temperature and with a simple work-up procedure (You et al., 2008).

In the literature, there were reports on, irradiation of carbonyl compounds and hydroxylamine hydrochloride impreg-

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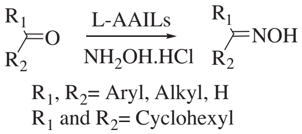

Scheme 1 Synthesis of oximes in the presence of L-AAILs.

nated on wet basic Al_2O_3, or grinding them with molecular sieves gave the corresponding oximes (Kad et al., 2001). High yields of hydroxyiminocycloalkanes could also be achieved by treatment of the corresponding ketone with hydroxylamine or its salts in ionic liquid and the presence of additives, such as sodium acetate.

We required extensive amount of several oxime of carbonyl compound as starting material in a more comprehensive synthesis project through an environmentally benign process. In last 10 years, Ren et al. (2001) reported environmental friendly and economical method for the preparation of cyclic ketoximes using aqueous hydroxylamine in ionic liquid. Damljanovic et al. (2006) reported a synthesis of oximes by grinding carbonyl compounds and hydroxylamine hydrochloride in the presence of sodium hydroxide/silica gel as a catalyst, in the absence of solvent. Song et al. (2007) achieved highly selective synthesis of methyl ethyl ketone oxime through amino oximation over Ti-MWW catalyst. Zang et al. (2009) reported ultrasound-promoted synthesis of oximes catalyzed by a basic ionic liquid [bmim]OH. Recently, it has been reported that $BF_3{\cdot}OEt_2$ in methanol using microwave irradiation could successfully achieve this condensation without any base (Sridhar et al., 2011).

This encouraged us to study the possibility of the condensation reaction of various carbonyl compounds with hydroxylamine hydrochloride in the presence of L-AAIL at room temperature. To our best knowledge, there is no report of using the ionic liquid L-AAIL, as catalyst for the preparation of oximes by grinding method. Herein, we desire to report a quick, facile synthesis of oximes in the presence of L-AAIL without solvent (Scheme 1).

Among the numerous methods for the synthesis of oximes, involved the use of some bases/catalysts which were not entirely environment friendly (Table 1). Ionic liquids play a vital role as dual catalyst and green solvent having enormous applications in synthetic organic chemistry due to their peculiar chemical and physical properties, such as wide liquid range with melting point around room temperature, good recyclability and stability in air and moisture, high solubility including inorganic, organic and even polymeric materials and negligible vapor pressure (Bica and Gaertner, 2006). The main goal of the present work is to design novel green catalyst (L-AAIL) by coupling L-asparagine with 1-(2-aminoethyl)-3-methyl-imidazolium bromide.

2. Experimental

2.1. Materials

Melting points were recorded on a Buchi B-545 apparatus in open capillary tubes and reported uncorrected. ^1H NMR spectra were recorded on Bruker (500 MHz) and mass spectra were recorded on JEOL GC MATE II HRMS (EI) spectrometer. FTIR was recorded on AVATRA 330 Spectrometer with DTGS detector. All solvents and chemicals were commercially available and used without further purification unless otherwise stated. *N*-Methyl imidazole, L-asparagine, aromatic aldehydes and ketones were purchased from SD Fine (Chennai). 3-Bromopropionic acid and acetophenone were obtained from spectrochem (Bengaluru).

2.2. Preparation of L-amino acid functionalized ionic liquid [L-AAIL-2]

The catalyst [L-AAIL-2] was synthesized according to the literature (Yang et al., 2007). It is a colorless viscous liquid, yield:

Table 1 Comparison of the reported methods for synthesis of oxime with the present method.

S. No.	Catalyst used	Conditions (*T*, °C/time)	Yield (%)	Ref.
1	[bmim] OH	Ultrasonic (RT/5–10 min)	93	Zang et al. (2009)
2	NaOH	Grinding (RT/30–120 min)	93	Damljanovic et al. (2006)
3	L-Amino acid containing ionic liquid	Grinding (RT/50 s)	96	Present work

Table 2 Optimization reaction of the acetophenone to acetophenoximes in various catalyst and condition.[a]

Entry	Catalyst	Conc. of catalyst (mmol)	Temp. (°C)	Grinding time (s)	Yield (%)
1	No catalyst	–	RT	21,600	–
2	NaOH/CH_3COONa	1–10%	25–60	180–7200	60
3	Glycine	0.1–1	RT	3600	–
4	Asparagine	0.1–1 g	RT	3600	13
5	L-Proline	0.1–1 g	RT	3000	18
6	[Cemim] Br	0.1–1	RT	3000	35
7	[Aemim] Br	0.1–1	RT	360	45
8	L-AAIL-1	0.1	RT	180	68
9	L-AAIL-2[b]	0.05	RT	50	96

RT – room temperature.
L-AAIL-1 was reported in Yang et al. (2007).
[a] Reaction conditions: acetophenone and hydroxylamine hydro chloride (1/1.2 mmol); grinding in mortar and pestle at room temperature.
[b] Catalyst with basic amino acid shows high catalytic activity.

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