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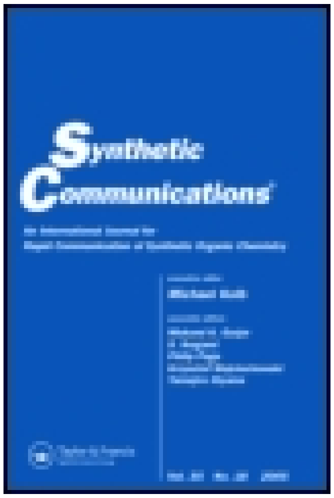

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Synthesis and Characterization of 1,2-Dimethyl Imidazolium Type of Ionic Liquids and Its Catalytic Activities

Ganapathi Pandurangan[a] & Ganesan Kilivelu[a]
[a] PG & Research Department of Chemistry, Presidency College (Autonomous), Chennai, India

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SYNTHESIS AND CHARACTERIZATION OF 1,2-DIMETHYL IMIDAZOLIUM TYPE OF IONIC LIQUIDS AND ITS CATALYTIC ACTIVITIES

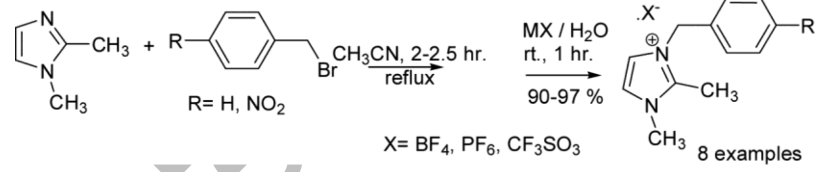
Ganapathi Pandurangan[1], Ganesan Kilivelu[1]

[1]PG & Research Department of Chemistry, Presidency College (Autonomous), Chennai, India

Address correspondence to Ganesan Kilivelu, PG & Research, Department of Chemistry,
Presidency College, Chennai 600 005, India.
E-mail: kiliveluganesan@yahoo.co.in

Abstract

The synthesis of substituted imidazolium type ionic liquids via a simple method is described. Our synthesized ionic liquids are more useful in the catalytic behavior of Mannich reaction.



KEYWORDS: Ionic liquids, metathesis, Mannich reaction, recyclable

INTRODUCTION

Salts in their liquid state at room temperature are called room temperature ionic liquids (RTIL) which has a variety of applications such as energy storage devices [1], solvent for nanoparticle stabilization [2] and electrode position [3]. Combining a larger organic segment with charge diffuse anion [4] is the possible method to prepare IL at room temperature. IL's are safer solvents due to non – toxic ions and insignificant vapor pressure. Significant properties of IL's are heat capacity and viscosity which are easily controllable by selection of cation and anion segments [5]. The equal molar ratio of H_2SO_4 and IL are used as effective chlorinating agent [6], compared with powerful, environmental damaging solvent and more toxic chlorinating reagents like $COCl_2$, PCl_3, and $SOCl_2$ etc. [7] IL's are acted as product controller to improve the stereo selectivity for Diels – Alder reaction [8-9]. Some of IL's acted as both solvent and catalyst for Friedel – Craft reaction with effective response [10-11]. Essawy and coworkers reported that Michael Adducts of α-phenyl chalcone with various ketones are showed variety of medicinal activities[12]. IL's are more suitable solvent for oxidation reaction due to its stability even under oxidizing condition and its inertness [13-19]. Most of the IL's has dual function [20] some of imidazolium salts are acted as mild antioxidative and reducing species [21]. The solubility property of IL's with hydrophobic (or) hydrophilic solvent can be tuned by altering the cations and anions [22-24]. Ionic liquids acted as electrolytes with number of merits when compared to conventional materials due to its high ionic conductivity and non-volatile nature [25-27]. Room temperature ionic liquids are considered as environmental friendly solvent for industrial actinide extraction [28]. Convenient synthesis of bulky groups containing imidazolium / pyridinium type of ionic liquids has been reported[29]. Herein, we wish to report the synthesis and catalytic activity of dimethyl imidazolium type of ionic liquids.

RESULTS AND DISCUSSION

1, 2 – Dimethylimidazole (1.0 equi; $1.04\text{x}10^{-2}$) is treated with benzylbromide / 4 - nitrobenzylbromide (1.05 equi; $1.092\text{x}10^{-2}$) in the presence of dry CH_3CN

under refluxing condition for 2 to 2.5 hours to give (**1a-b**) in 95 - 97 % yield. After *N* – alkylation, anion exchange reaction is carried out with various inorganic salts in the presence of minimum amount of deionized water, which is used as a solvent, for about 1 hour to give anion exchanged products.

The anion exchanged product undergoes Soxhlet extraction in the presence of dry THF for about 1 hour to remove the metal bromide to give pure form of imidazolium salts (**2a-f**) in 90 - 93 % yield. Reaction between 1, 2 - dimethylimidazole with 4 - nitrobenzylbromide is much faster than benzyl bromide due to nitro benzyl C - Br bond which is weaker than simple benzyl bromide. The same reaction is repeated with DMSO and observed that the reaction is much faster than CH_3CN, but work up is not easier due to water soluble nature of both solvent and imidazolium bromide, therefore CH_3CN is the more suitable solvent for *N*-alkylation.

CATALYTIC ACTIVITIES

One pot multi component organic reactions are gaining more importance because of quicker diversity and efficiency[30]. Mannich product (substituted oxazine) has more features in the area of biologically important natural residues [31, 32]. Some of the substituted oxazine and its derivatives are reported in literature [33-35]. Multicomponent preparation of some of the naphthol heterocyclic substituted compounds in the presence of ionic liquids needs more reaction time to complete with insignificant yield [36]. Deepak and coworkers reported that one pot three components condensation reaction between aldehyde, ketone and aromatic amine in the presence of mixed oxides MgO/ZrO_2 in the ratio of 1:3 needs 16 hours to complete the reaction with poor yield [37]. But our synthesized ionic liquids for Mannich reaction afforded appreciable observation (Table – 1 & 2). We have tried with different concentration of ionic liquids such as $7.299x10^{-5}$, $1.497x10^{-4}$, $2.245x10^{-4}$ and $2.994x10^{-4}$ concentrations. Among these concentrations, we have observed that $2.245x10^{-4}$ concentration is the optimum concentration to complete the reaction with less reaction time with higher conversion. In Mannich reaction, we have used two types of aromatic amines (*m*/*p*-nitro aniline). From that we observed that *m*-nitro aniline is two times faster than *p*-nitro aniline with higher yields (Table-1). *m*-Nitroaniline shows better nucleophilic activity than para isomer. Mannich products are thoroughly characterized by spectral and analytical data which are closely matching with literature [38].

So our synthesized ionic liquids are potential candidates to accelerate the Mannich reaction as quicker with higher yield. Our synthesized ionic liquids are recycled upon four cycles and used for Mannich reaction with same reaction condition. Even after fourth recycle, the product obtained was same as we observed in the fresh use shown in the Table- 3.

CONCLUSION

We have used simple synthetic methodology to prepare imidazolium type of ionic liquids. Our synthesized ionic liquids are more useful for catalytic behavior in Mannich reaction to reduce the reaction time and improve the percentage of yield. We have examined the catalytic activity of synthesized ionic liquids. Among the eight ionic liquids, **1a** & **1b** showed better catalytic activity than the others due to better Lewis character. We have tried the catalytic activities with different concentrations ($7.299x10^{-5}$mol/L, $1.497x10^{-4}$mol/L, $2.245x10^{-4}$mol/L and $2.994x10^{-4}$mol/L concentration) of our synthesized ionic liquids. From the result, we have concluded that $2.245X10^{-4}$ concentration is the optimum concentration to complete the Mannich reaction with higher yield and lesser reaction time. The same reaction is repeated with our recycle IL's showed good catalytic activity with higher yield.

EXPERIMENTAL

Procedure For *N*-Alkylation

1, 2- dimethylimidazole ($1.040x10^{-2}$mol/L; 1.0 equi.) is treated with benzylbromide ($1.092x10^{-2}$ mol/L; 1.05 equi.) in the presence of 30 mL of dry CH_3CN under refluxing condition for about 2 hours afforded the *N*-alkylated quaternary ammonium bromide **1a** in 95% yield after the purification.

1,2-Dimethyl(3-Methylene Benzene)-Imidazolium Bromide 1a

2.75g; 95% Semisolid; ^1H NMR (D_2O); δ: 2.45(s, 3H); 3.66(s, 3H); 5.22(s, 2H); 7.20(d, *J*=1.8 H_Z, 2H) 7.24 (s, 2H) 7.33(t, *J*=7.2 H_Z, 3H); ^{13}C NMR δ: 9.19, 34.75, 51.42, 121.10, 122.37, 127.76, 129.26, 133.73, 144.58; MS:267; Elemental analysis:- Molecular Formula ($C_{12}H_{15}N_2Br$); Calculated: C: 53.93; H: 5.61; N: 10.48; Found C: 53.86; H: 5.52; N: 10.40.

Procedure For Anion Exchange Reaction

N-Alkylated quaternary ammonium bromide (1.0 equi.) is treated with $NaBF_4$ (1.05 equi.) in the presence of 10 mL deionized water at room temperature with stirring for about 1 hour afforded the anion exchanged ionic liquid. After the anion exchanged reaction, we have used Soxhlet extraction for separation using dry THF for about 1 hour followed by concentration will give ionic liquid **2a** in 93% yield.

1,2-Dimethyl(3-Methylene Benzene)-Imidazolium Tetrafluoroborate 2a

0.67g; 93%; Semisolid; ^{1}H NMR (D_2O); δ: 2.43(s, 3H); 3.68(s, 3H); 5.26(s, 2H); 7.18(d, *J*=1.9 H_Z, 2H) 7.21 (s, 2H) 7.4 (t, *J*=7.4 H_Z, 3H); ^{13}C NMR δ: 9.17, 34.78, 51.44, 121.08, 122.35, 127.74, 129.27, 133.71, 144.55; MS:274; Elemental analysis:- Molecular Formula ($C_{12}H_{15}BF_4N_2$); Calculated: C: 52.55; H: 5.47; N: 10.22; Found C: 52.48; H: 5.32; N: 10.14.

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SUPPORTING INFORMATION

Experimental procedure, $^{\mathbf{1}}$H and C^{13} NMR spectrum of new compounds for this article can be accessed on the publisher’s website.

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Table 1 One pot synthesis of *m*-nitrooxazine derivatives

S. No	**IL**	**Time**	**Yield (%)**
1	Absence of catalyst	8 hours	40
2	**1a**	1.5 min.	90
3	**2a**	1.5 min.	85
4	**2b**	1.5 min.	90
5	**2c**	1.5 min.	88
6	**1b**	1.5 min.	87
7	**2d**	1.5 min.	80
8	**2e**	1.5 min.	87
9	**2f**	1.5 min.	84

Reagents and conditions: α – Naphthol (200mg;1.387 x10^{-3} mol/L); paraformaldehyde (85mg; 2.843x10^{-3} mol/L);

m -nitroaniline (0.148g; 1.387x10^{-3} mol/L); CH_3CN (10 mL); IL (2.245x10^{-4} mol/L); rt.

Table 2 One pot synthesis of *p*-nitrooxazine derivatives

S. No	**IL**	**Time**	**Yield (%)**
1	Absence of catalyst	10 hr.	30
2	**1a**	2 min.	82
3	**2a**	2 min.	78
4	**2b**	2 min.	81
5	**2c**	2 min.	81
6	**1b**	2 min.	77
7	**2d**	2 min.	72
8	**2e**	2 min.	75
9	**2f**	2 min.	75

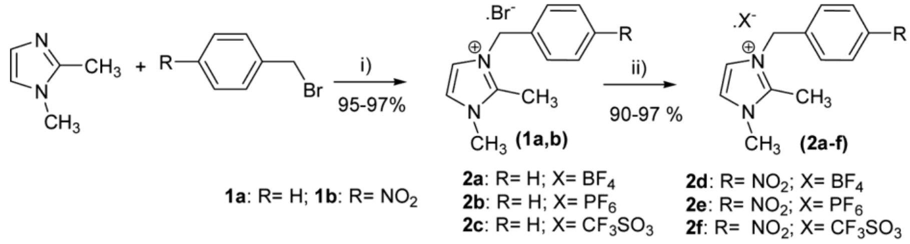
Reagents & conditions:- α – Naphthol (200mg;1.387 x10^{-3} mol/L); paraformaldehyde (85mg; 2.843x10^{-3} mol/L);

p -nitroaniline (0.148g; 1.387x10^{-3} mol/L); CH_3CN (10 mL); IL (2.245x10^{-4} mol/L) ; rt.

Table 3 One pot synthesis of oxazine by using 4th cycle recycled IL's

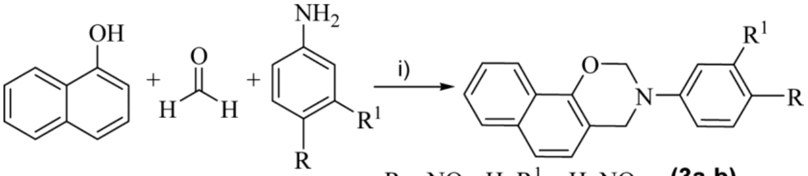
S. No	**IL**	**Yield (%)**
1	**1a**	72 - 85
2	**2a**	70 - 80
3	**2b**	74 - 82
4	**2c**	70 - 75
5	**1b**	70 - 76
6	**2d**	66 - 70
7	**2e**	68 -73
8	**2f**	65 - 70

Scheme 1. Synthesis of substituted imidazolium type of ionic liguids



Reagent and conditions: i) MeCN,reflux, 2 - 2.5 hr., ; ii) MX / H_2O; 1 hr.

Scheme 2. One pot preparation of oxazine using imidazolium type of ionic liquid



$R = NO_2, H; R^1 = H, NO_2$ **(3a,b)**

Reagent and conditions:- i) $2.245X10^{-4}$ mol/L of IL, rt, 1.5 - 2 min.