

Synthesis and Characterization of Methyl Substituted Imidazolium Dimeric Ionic Liquids and Their Activities

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Abstract— Novel dimeric ionic liquids are prepared from simple, environmental friendly solvents and easily available starting materials. We have tried catalytic activity for Mannich reaction from our ionic liquids gave higher yields and shorter the reaction time. We have observed that good responses from our synthesized ionic liquids for cyclic voltametric studies.

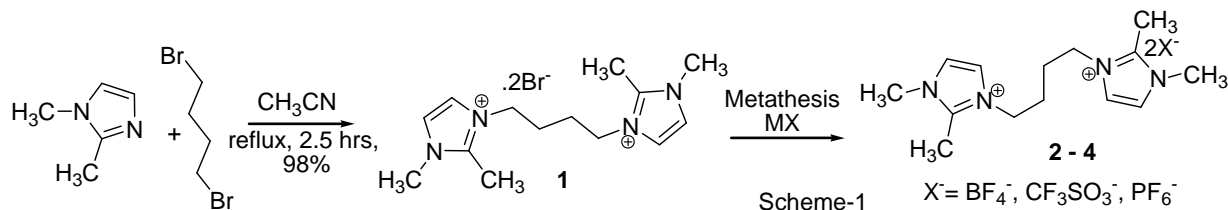
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I. INTRODUCTION

Ionic liquids are an important alternative to replace volatile, toxic organic solvents in Green chemistry¹⁻² due to very low vapor pressure, thermally and chemically stable, also show high polar, good catalytic, non-flammability and non-corrosive, good electrical conductive behaviors. The miscibility of ionic liquids with aqueous and non-aqueous solvents can be tuned by the selection of cations and anions³⁻⁵ often referred to as designer solvents. Crucial problems are posed to the chemical plant is to continuously deal with more toxic, hazardous and highly flammable solvents. If we want to conduct the organic reaction, solvents are required. Most of the time volatile organic solvents are expensive to purchase, difficult to reuse and dispose⁶⁻⁸ to overcome these problems ionic liquids are more suitable organic synthesis and catalysis organic reaction. Ionic liquid contains both the organic and inorganic segments are present so that resulting ionic liquids are do not crystallize therefore it's available in liquid form⁹. Imidazolium type ionic liquids are very good candidate for electro chemical behaviors, catalytic activity as well as also act as environment friendly solvent¹⁰. Herewith we have described that, the synthesis of some novel substituted imidazole in the form of dimeric ionic liquids; also characteristic behavior of catalytic activity and electro chemical screening are discussed.

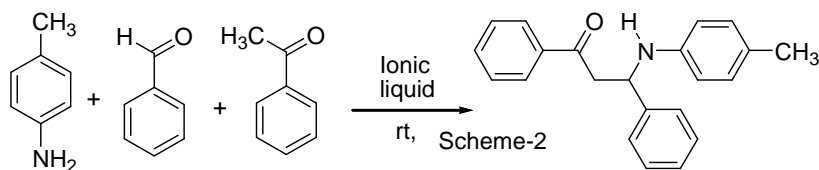
II. RESULT AND DISCUSSION

N-alkylation of 1,2- dimethyl imidazole (2.05 eq.) treatment with 1,4- dibromobutane (1.0 eq.) in the presence of CH₃CN at refluxing condition for about 2.5 hours to give dimeric imidazolium salt **1** in 98% yield is obtained after the purification. Quarternized dimeric imidazolium salt **1** followed by metathesis reaction with various counter anions in the presence of some inorganic salt such as NaBF₄, KPF₆, and LiCF₃SO₃ with 10 ml of deionized water (environmental friendly solvent) at room temperature for one hour gave counter ion exchanged products of ionic liquid **2-4**(Scheme -1). After complete the metathesis reaction; conventional work up is not suitable for separation because of both the ionic liquid and inorganic salt are soluble in water. Hence we have to use special setup like Soxhlet extraction with dry THF for separate ionic liquid from inorganic salt for about 1 hour extraction followed by concentrate will get inorganic salt free ionic liquid **2-4** with 95-99 % yield.



Catalytic Activity

Mannich reaction with some conventional reagent like proline¹¹⁻¹³, acetic acid¹⁴ and some Lewis acids¹⁵⁻¹⁶. If we use above mentioned conventional catalyst to conduct Mannich reaction will need more reaction time to complete, difficult to separate of product, more toxic solvent and also afford less amount of yield¹⁷.



To overcome these problems; we have demonstrated Mannich reaction (scheme-2) with our synthesized ionic liquids **1-4**. Equal molar concentrations of benzaldehyde, acetophenone and p-toluidine to conduct the Mannich reaction in the presence of different concentration of our synthesized ionic liquids at room temperature afforded the condensed product of 3-(N-tolylamino)-1,3-diphenylpropan-1-one was characterized by spectral and analytical data. Mannich reaction in the presence of ionic liquid at with different concentration ionic liquids are summarized in the table-I. Mannich reaction carried out absence of catalyst under room temperature takes 13 percentage of yield. Under these circumstances we have tried with our synthesized ionic liquids under ambient condition; we have received appreciable observation as listed in table-I.hours to complete the reaction with just 68% of yield. So we have to reduce the reaction time and improve the

Table – I: Catalytic activity for Mannich reaction with different normal Concentration

Ionic liquids	Concentration of ionic liquids							
	$4.16 \times 10^{-5} \text{ mmol}$		$8.33 \times 10^{-5} \text{ mmol}$		$1.25 \times 10^{-4} \text{ mmol}$		$1.66 \times 10^{-4} \text{ mmol}$	
	Time (h)	Yield %	Time (h)	Yield %	Time (min)	Yield %	Time (min)	Yield %
Compound 1	4.30	82	1.50	84	40	87	40	89
Compound 2	4.30	78	1.50	79	40	85	40	86
Compound 3	4.30	80	1.50	82	40	85	40	87
Compound 4	4.30	80	1.50	81	40	85	40	85

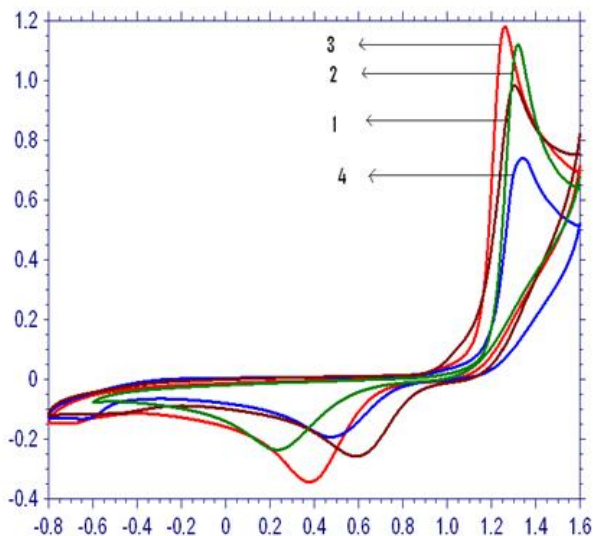
So our synthesized ionic liquids are potential candidates to accelerate the Mannich reaction as quicker with higher yield. Our ionic liquids are recycled upon four cycles and used for Mannich reaction with same reaction condition. Even after fourth recycle product was obtained same as we observed in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

Table – II: Efficiency of ionic liquids

S. No	Compound	Cycle	% of yield
1	IL with Br ⁻	Fresh to 4 th cycles	88-90
2	IL with BF ₄ ⁻	Fresh to 4 th cycles	84-86
3	IL with PF ₆ ⁻	Fresh to 4 th cycles	88-90
4	IL with CF ₃ SO ₃ ⁻	Fresh to 4 th cycles	85-87

Cyclic voltammetry studies

Cyclic Voltammetric studies of dimeric ionic liquids ($1.225 \times 10^{-4} \text{ mmol}$) were conducted in the presence of water containing 0.1 M solution of KNO₃ act as supporting electrolyte with potential difference between from -0.5V to + 1.5V against Ag/AgCl. The cyclic voltogram of dimeric ionic liquid with bromide as a counter ion **1** shows highest reversible reduction wave in the cathodic potential region at $E_{pc} = + 0.5837 \text{ V}$. Ionic liquid with PF₆⁻ anion shows reversible reduction wave in the cathodic potential is $E_{pc} = + 0.4736 \text{ V}$ whereas in the case of ionic liquids with CF₃SO₃⁻ and BF₄⁻ anions were shows lower cathodic reduction potential $E_{pc} = + 0.3757 \text{ V}$ and 0.2404 V respectively; this is may be due size of the anions. Bigger size anions containing ionic liquids are showed reduction potential is very easier than smaller anions. So our synthesized ionic liquids shows the following order of reduction potential Br⁻ > PF₆⁻ > CF₃SO₃⁻ > BF₄⁻.



1=IL with Br⁻, 2=IL with BF₄⁻, 3=IL with CF₃SO₃⁻, 4=IL with PF₆⁻

III. EXPERIMENTAL RESULT

Synthesis of dimeric imidazolium salt 1

1.830g of 1,2- dimethyl imidazole (2.05 eq.) react with 2.0g of 1,4- dibromobutane (1.0 eq.) in presence of 30 mL of CH₃CN under the refluxing condition for about 2.5 hours afforded the dimeric imidazolium salt **1** in 98% yield after the purification. ¹H NMR (300 MHz; D₂O): δ: 1.85 (q, 4H); 2.64 (s, 6H); 3.95 (t, 4H); 4.04 (s, 6H); 7.42 (s, 2H); 7.44 (s, 2H); ¹³C NMR δ: 30.5, 31.2, 36.9, 123.4, 129.8, 142.2 and 144.6; MS: *m/e*: 408; Elemental analysis:- Molecular Formula (C₁₄H₂₄N₄Br₂): Calculated: C: 41.20; H= 5.93; N=13.73; found C: 41.15; H= 5.80; N=13.68.

General procedure for metathesis reaction:

Dimeric imidazolium salt **1** (1.0 equi.) with varies anion containing inorganic salt (2.05 equi.) in the presence of 10 mL of deionized water at room temperature stirring for 1 hour afforded the dimeric ionic liquids **2-4**. After complete the metathesis reaction; we have used Soxhlet extraction with dry THF as a solvent for separation of ionic liquid from inorganic salt for about one hour extraction followed by concentrate will get inorganic salt free ionic liquid **2-4** with 95-99% yield.

Ionic Liquid 2: ¹H NMR (300 MHz; D₂O):δ 1.88 (q, 4H); 2.67 (s, 6H); 3.91 (t, 4H); 4.10 (s, 6H); 7.38 (s, 2H); 7.48 (s, 2H); ¹³C NMR δ: 31.0, 32.1, 37.2, 123.9, 131.1, 142.9, 144.9. MS: *m/e*: 420; Elemental analysis: C₁₄H₂₄B₂F₈N₄:- Calculated: C: 39.85; H: 5.73; N: 13.28; found C: 39.71; H: 5.76; N: 13.38.

Ionic Liquid 3: ¹H NMR (300 MHz; D₂O) δ: 1.82 (q, 4H); 2.61 (s, 6H); 3.90 (t, 4H); 4.02 (s, 6H); 7.44 (s, 2H); 7.42 (s, 2H); ¹³C NMR δ: 30.3, 31.0, 37.1, 123.1, 129.5, 142.1, 144.2. MS: *m/e*: 538; Elemental analysis: C₁₄H₂₄P₂F₁₂N₄:- Calculated: C: 31.24; H: 4.49; N: 10.41; Found C: 31.19; H: 4.43; N: 10.39.

Ionic Liquid 4: ¹H NMR (300 MHz; D₂O): δ: 1.78 (q, 4H); 2.57 (s, 6H); 3.86 (t, 4H); 3.98 (s, 6H); 7.41 (s, 2H); 7.46 (s, 2H); ¹³C NMR δ: 30.0, 31.3, 36.8, 122.8, 129.1, 141.8, 144.0. MS: *m/e*: 546; Elemental analysis: C₁₆H₂₄F₆O₆S₂N₄:- Calculated: C: 35.16; H: 4.43; N: 10.25; Found C: 35.09; H: 4.39; N: 10.21.

Synthesis of 3-(*N*-tolylamino)-1, 3-diphenyl-propan-1-one from Mannich reaction:

Equal molar concentration of benzaldehyde (176 mg; 1.664 × 10⁻³ mmol), acetophenone (200 mg; 1.664 × 10⁻³ mmol) and *p* - toluidine (178 mg; 1.664 × 10⁻³ mmol) are mixed with different concentration ionic liquid (4.16 × 10⁻⁵ mmol; 8.33 × 10⁻⁵ mmol; 1.25 × 10⁻⁴ mmol and 1.66 × 10⁻⁴ mmol) at room temperature afforded the condensed product of 3-(*N*-tolylamino)-1,3-diphenyl-propan-1-one in 80 - 85 % yield.

3-(*N*-tolylamino)-1, 3-diphenyl-propan-1-one: ¹H NMR (300 MHz; CDCl₃): 2.49 (s, 3H), 3.41(2H, d), 4.93 (1H, m), 6.48 - 7.85 (m, 15H; IR (cm⁻¹): 3399 and 1672; MS: *m/e*: 315; Elemental analysis: C₂₂H₂₁NO:- Calculated: C: 83.78; H: 6.71; N: 4.44; Found C: 83.62; H: 6.58; N: 4.30.

IV. CONCLUSION

We have used a simple synthetic methodology to prepare dimeric imidazolium salt containing various anions. Our synthesized ionic liquids are more useful due to catalytic behavior of shorter reaction time and higher percentage of yield for Mannich reaction. Among the four ionic liquids; bromide containing imidazolium salt shows better catalytic activity due to better Lewis acid than others. We have tried with four different concentrations (4.16×10^{-5} , 8.33×10^{-5} , 1.25×10^{-4} and 1.66×10^{-4} mmol) of our synthesized ionic liquids for catalytic behaviors of Mannich reaction. Among the four different concentrations; we have observed that 1.25×10^{-4} mmol concentration is optimum concentration and their after while increase the ionic liquids concentration there is no appreciable observation (reaction time and percentage of yield) were made. From the result we could conclude that for catalytic activity of ionic liquid best concentration is 1.225×10^{-4} mmol enough to complete the Mannich reaction in higher yield and shorter reaction period. Another interesting observation that for our ionic liquids from cyclic voltammetric studies shows that dimeric imidazolium bromide shows higher reversible reduction potential than three ionic liquids. Based on dimeric imidazolium salts are observed that dimeric imidazolium bromide shows good response for both catalytic and cyclic voltammetric studies.

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