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Chapter

Perspective Chapter: Applications of Novel Ionic Liquids as Catalyst

Ganesan Kilivelu

Abstract

Ionic liquids have much interesting attention in the area of biomedical and it's an alternative to traditional organic solvents owing to their unique chemical, physical properties and environmentally eco-friendly catalytic responses. Ionic liquids have distinct properties like tunability that allows their physical and chemical behaviors to be changed as desired by changing the organic cations with inorganic anions or inorganic cations with organic anions or both cation and anion from organic moieties. Most of the organic reactions are carried out with assistance of catalyst, usually commercially available catalyst are very expensive, more hydroscopic in nature, thermally unstable and very difficult to recycle them but ionic liquids are acted as potential Lewis acidic behaviors, thermally stable, easily recycle inexpensive compared to commercial catalyst and easy to prepare electrically neutral organic cation which are loosely bind with inorganic anions, and organic (pyridinium/imidazolium/piperidinium) cation could be easily accelerate (or) activate the functional group for most of the organic reactions. Hence, ionic liquids plays a vital role in modern organic synthetic field and may be inevitable in future research.

Keywords: substituted dimeric imidazolium cation, trimeric imidazolium salt, catalyst regenerations, pyrimidine derivative, one pot preparation

1. Introduction

Ionic liquids have attracted increasing interest from chemist in the last few decades because of their distinguishable properties including chemical stability, non-flammability, non-volatility and high thermal stability. Commercially available catalysts are very expensive, more hydroscopic in nature, thermally unstable and very difficult to recycle, whereas ionic liquids are thermally stable, easily recyclable, inexpensive compared to commercial catalyst, easy to prepare and have potential Lewis acidic behavior and so, nowadays it plays a vital role in catalysis. Ionic liquids are electrically neutral molecule consist of organic cations which are loosely bind with inorganic anions, hence organic pyridinium/imidazolium/piperidinium cation can easily accelerate (or) activate the functional group in most of the organic reactions. Most of the organic reactions are carried out with the assistance of catalyst [1, 2]. for example, in one pot preparation of 3,4-dihydro-3-substituted oxazine derivatives at room temperature, 1-ethylimidazolium sulphonate is used as a catalyst [3]. Acid based

bifunctional pyridinium salt used as a catalyst in Knoevenagel condensation reaction with and without solvent [4]. *N*-Methyl pyridinium bromide acted as highly efficient reagent for aliphatic nucleophilic substitution reaction of sulphate aryl substituted aliphatic ether [5]. 1,4-Diazobicyclo[2.2.2]octane based quarternary ammonium bromide which is recyclable, cheaper and environmentally friendly are used in the preparation of bisnaphtholmethane [6]. Chiral biaryl aluminate anion with imidazolium salt showed excellent catalytic response for asymmetric Baeyer-villiger oxidation with higher percentage of conversion [7]. Preparation of hydroxyl methyl substituted furfural in higher yield with shorter reaction time is achieved in the presence of chiral dimeric ionic liquids [8]. Bronsted acidic ionic liquid is used as a catalyst in the preparation of pyridylimidazopyridine [9].

Lewis acid accepts the pair of electrons to attain the octet electronic configuration. Acid is the electron deficient positive charged species that accepts the electrons to form a covalent bond. Base is the electron rich negative charged species that donates to electron deficient ions to form a covalent bond. Organic molecule containing electro positive nitrogen are acted as second-generation Lewis acid. Lewis acid such as $ZnCl_2$, BF_3 , $SnCl_3$, $AlCl_3$ and CH_3AlCl_2 catalyze the reaction between electron rich diene and electron deficient dienophile and also catalyze the inverse electron demand Diels Alder reaction. In most of the organic reactions like Aldol condensation reaction, Friedel craft alkylation and acylation, carbon- carbon (or) carbon-nitrogen/carbon-sulfur/carbon-oxygen bond formation can be catalyzed by Lewis acid. Most of the organic reactions are carried out with polar/non-polar organic solvents rather than water, because the reactants are insoluble/sparingly soluble or unstable/decompose in water. Now a days, despite few disadvantages, water plays a crucial role as a solvent for organic reactions due to its more polar nature, environment friendly, non-toxic, moderate boiling solvent, easily available and more abundant solvent in the earth. In recent years, Ionic liquids became a very interesting area of research in catalysis, drug delivery system and electro chemical aspects. ionic liquids are excellent alternate for the toxic organic solvents because of its low volatile nature, thermally stable and non-toxic nature. In this book chapter, we will discuss about the catalytic importance and plausible organic reaction mechanism of novel mono, di and trimeric imidazolium and pyridinium salts (ionic liquid) as a catalyst in Aldol condensation, Biginelli reaction, Erlenmeyer reaction, Mannich reaction and Pechmann reaction.

2. Novel 6,6'-(butane-1,4-diylbis(oxy))bis(methylene)bis(2,4-dimethyl-3-nitro-1-(4-nitrobenzyl)pyridinium) bromide used as a catalyst in Aldol condensation reaction

In Aldol condensation reaction, β -hydroxy derivatives are formed from α -hydrogen containing aldehyde (or) ketone in the presence of strong alkali. In this reaction, strong alkali abstracts the proton from α -hydrogen containing carbonyl compound and carbanion will attack another carbonyl group to form β -keto derivatives. There are two types of Aldol condensation reaction (simple and mixed Aldol condensation reactions). If both the reacting substrate are similar, then it is called simple Aldol reaction and if two different α -hydrogen containing carbon compounds are involved, then it is called mixed Aldol condensation reaction (**Figure 1**). α -Hydrogen containing aliphatic aldehydes are more reactive than the α -hydrogen containing ketones. In mixed Aldol condensation reaction, one α -hydrogen containing aliphatic aldehyde can react with or without α -hydrogen containing carbonyl compounds. The presence of

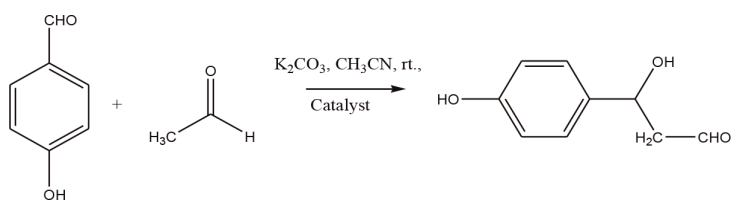


Figure 1.
 Mixed Aldol Condensation reaction.

Lewis acid enhances the carbanion attack with (or) without α -hydrogen carbonyl compound in Aldol condensation reaction.

In the above reaction, a very expensive chiral catalysts are used to prepare α -hydroxy derivatives. Simple Aldol condensation reaction is more advantageous than the mixed Aldol condensation [10, 11].

Lewis acid facilitates the carbonyl compound to attack enolate nucleophile. Hongxin Liu and co-workers used very expensive catalyst which consumes longer reaction time and lesser β -hydroxy derivatives [12]. The literature shows that catalyst such as TiCl_4 , AlCl_3 , BF_3 , AlCl_3 or ZnCl_2 are used in Aldol condensation reaction. These catalysts activate only one carbonyl compound to facilitate the enolate attack (**Figure 2**) whereas, dimeric pyridinium salt in a very low concentration i.e. one equivalence of pyridinium salt activates two equivalence of carbonyl compounds (**Figure 3**). After completion of inter (or) intra-molecular Aldol condensation reaction, the catalyst is easily recovered, recycled and used upto four cycles [13].

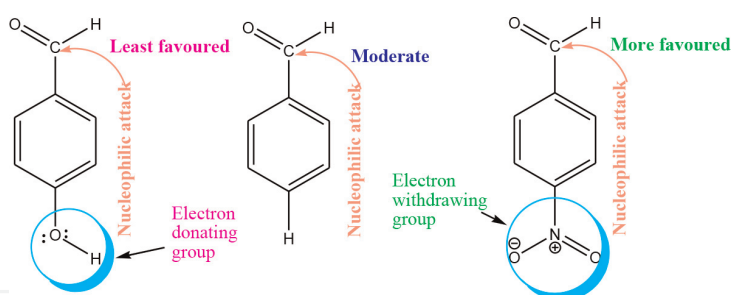


Figure 2.
 Feasibility of nucleophilic attack.

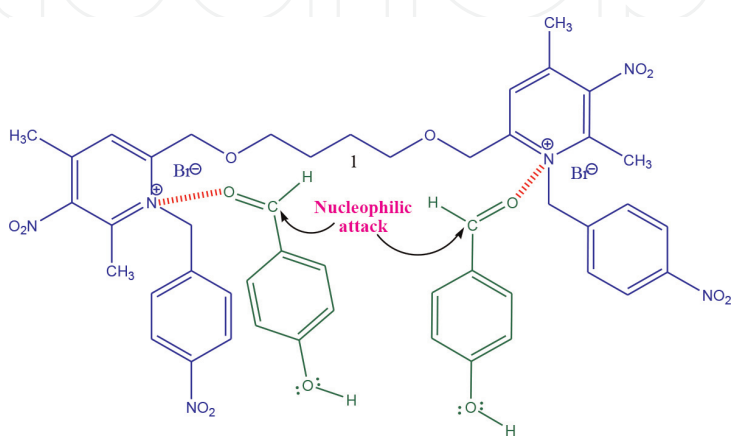


Figure 3.
 Aldol condensation catalyzed by dimeric ionic liquid 1.

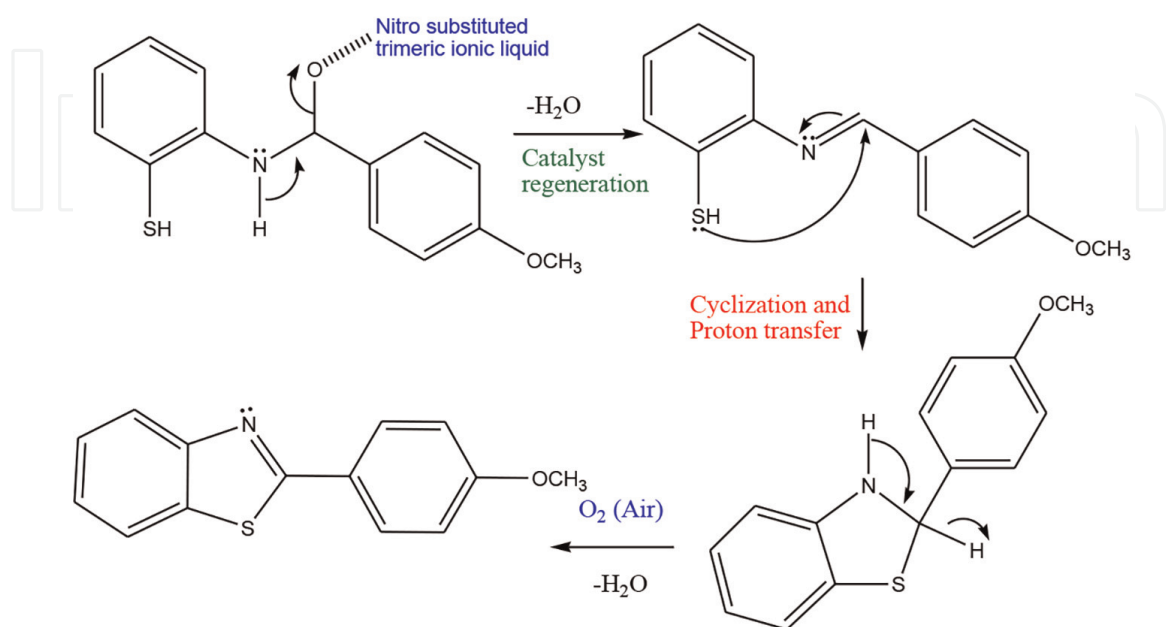
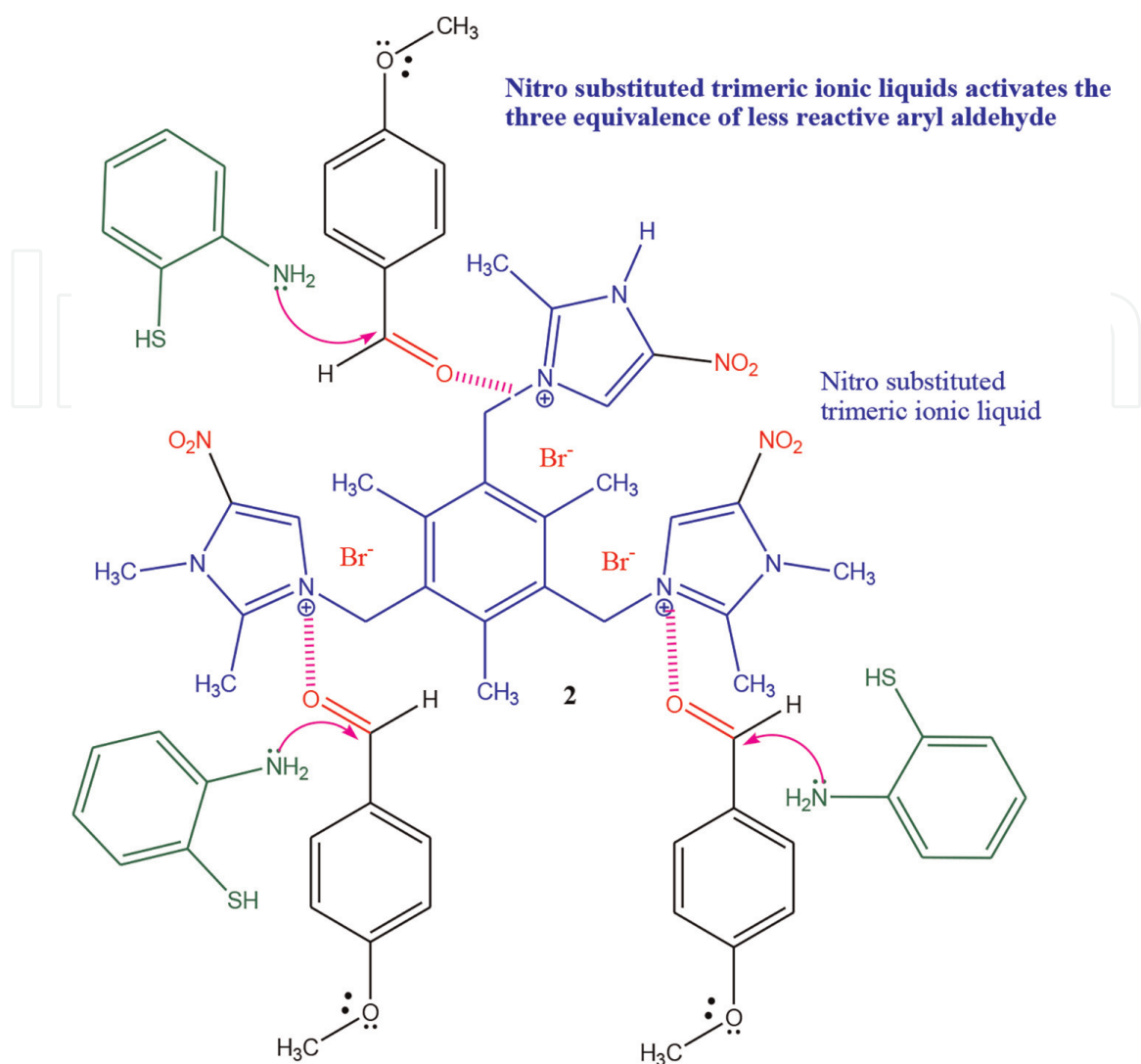


Figure 4. Plausible mechanism for benzoxazole formation with trimeric imidazolium salt 2.

2.1 Novel 3,3'-(2,4,6-trimethyl-5-((2-methyl-5-nitro-1H-imidazol-1-ium-3-yl)methyl)-1,3-phenylene)bis(methylene)bis(1,2-dimethyl-5-nitro-1H-imidazol-3-ium) bromide as a catalyst in the preparation of benzoxazole

Synthesis of dimeric and trimeric substituted imidazolium cation with different anion is carried out using easily available starting materials under conventional as well as solvent free solid supported method [14]. Benzoxazole and its derivatives are prepared using very low concentration of catalyst (dimeric/trimeric substituted imidazolium salts). Trimeric imidazolium salt showed excellent catalytic response than the dimeric substituted imidazolium salts. 0.33 equivalent of trimeric substituted imidazolium salt is sufficient to accelerate the benzoxazole formation where as other catalyst requires equal molar ratio. Benzoxazole and its derivatives are prepared by reaction between substituted aryl aldehyde and *o*-amino phenol (or) *o*-amino thiol in the presence/absence of solvents. With the required equivalence of starting materials, in the absence of catalyst for 10 hours gives only 48% of yield whereas addition of catalyst {trimeric imidazolium salt (2.2458×10^{-4} mmol)} in CH₃CN solvent under refluxing condition for 30 min. gives 89% of benzoxazole derivatives. From the above reaction, trimeric substituted imidazolium salts activate three equivalence of substituted aryl aldehyde and then *o*-phenol is more facile for cyclization (**Figure 4**). Same benzoxazole and its derivatives are prepared using trimeric substituted imidazolium salts in the absence of solvent and reaction is completed in shorter reaction time with the higher yield and with the easy purification process. It is environment friendly due to the absence of solvent. Benzoxazole is prepared with optimum concentration of trimeric substituted imidazolium salts in the presence of polar and moderately polar solvents such as CHCl₃, THF, Acetone, C₂H₅OH and DMSO. Among these solvents, DMSO showed higher percentage of benzoxazole formation in shorter reaction time [15].

2.2 Biginelli reaction catalyzed by novel 2,2'-(butane-1,4-diylbis(oxy))bis(1-(4-nitrobenzyl)pyridinium) bromide

Preparation of pyrimidone derivatives from one pot multi component reaction using ethyl acetoacetate, diamide and simple/substituted aryl aldehyde with the assistance of Lewis acid. The literature shows that, the Biginelli reaction required longer reaction time, expensive catalyst and gives very low percentage of yield [16–19].

Preparation of pyrimidine derivatives from conventional method [6] takes 24 hours to complete the reaction, whereas flexible dimeric pyridinium cation as catalyst showed excellent catalytic activity even at very low concentration by

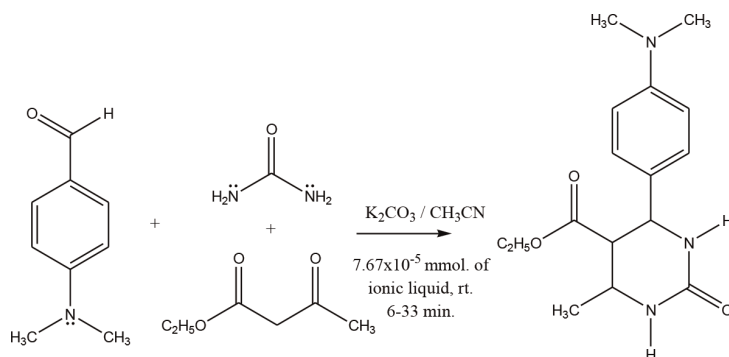


Figure 5.
Pyrimidone formation under Biginelli reaction.

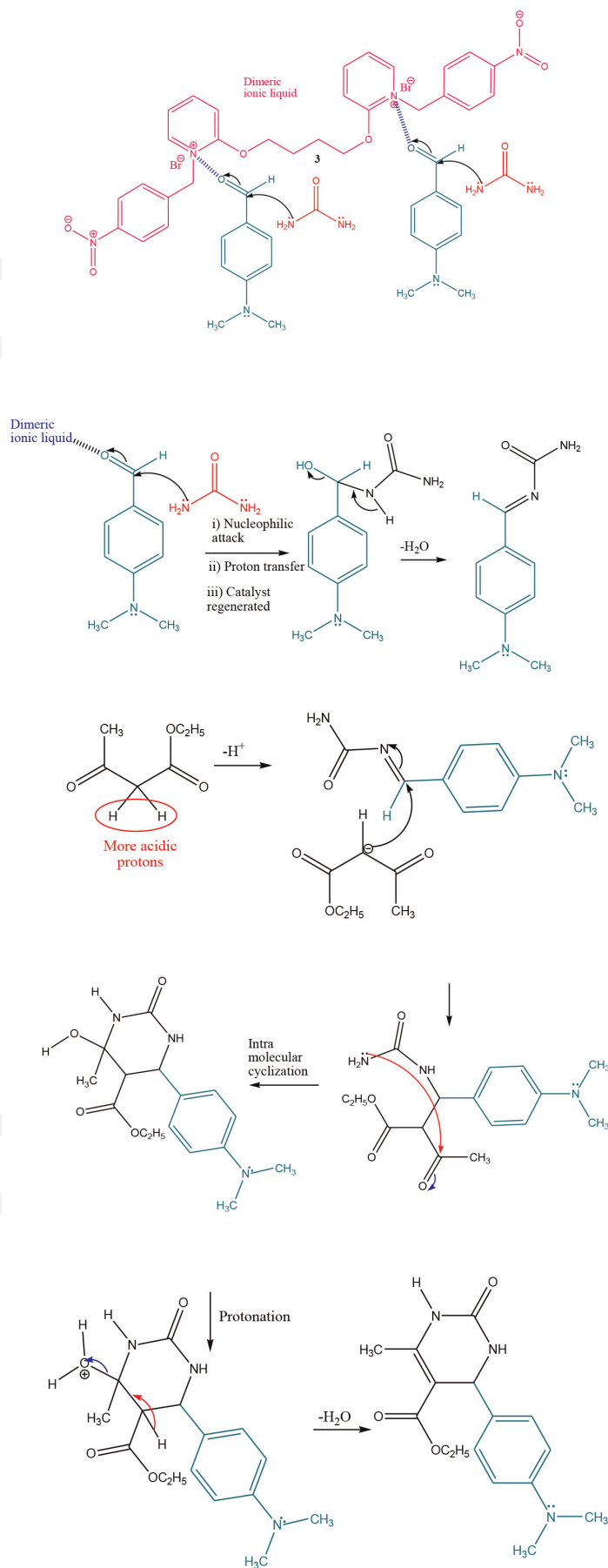


Figure 6. Plausible mechanism for formation Pyrimidone catalyzed by flexible dimeric pyridinium ionic liquid **3**.

activating the substituted benzaldehyde even in half the equivalence of dimeric pyridinium salts (**Figure 5**). In this reaction (**Figure 6**), various counter anions such as Br, BF_4^- , PF_6^- and CF_3SO_3^- are used. Among these, bromide counter anion containing flexible dimeric pyridinium cation showed effective catalysis. Here, the size of the counter anion plays a crucial role in catalytic response. Bromide counter anion containing dimeric pyridinium cations are freely available, which in turn easily activate the simple/substituted aryl aldehyde when compared with other counter anions [20].

2.3 Novel 1,1',1''-(2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene)tris(4-(4-nitrophenyl)pyridinium) bromide as a catalyst Erlenmeyer reaction

Preparation of benzylidene oxazolone by Erlenmeyer reaction is carried out between aryl aldehyde and hippuric acid in the presence of anhydrous K_2CO_3 and acetic acid without any catalyst at room temperature for 5 hours. There is no interesting findings are observed. Some of the recent report states that, benzylidene oxazolone derivatives are also prepared using special reaction setup with higher concentration of ionic liquids (20%) at high temperature using expensive catalyst [21–23]. Hence, 4-Nitro benzyl substituted monomeric, dimeric and trimeric pyridinium bromides are tried as a catalyst for Erlenmeyer reaction. 4-Nitro benzyl substituted pyridinium salts showed excellent catalytic response and suitable for Erlenmeyer reaction when compared with other literature catalyst due to inexpensive starting material and stability. 5.7×10^{-5} mmol. concentration of 4-nitro benzyl substituted pyridinium salt is sufficient to complete Erlenmeyer reaction in short time at room temperature with higher yield. 4-Nitro benzyl substituted trimeric pyridinium cation showed excellent catalytic activity than the 4-nitro benzyl substituted dimeric pyridinium salt. Dimeric pyridinium salt showed good catalytic response than the monomeric substituted pyridinium salt. One equivalence of 4 nitro benzyl substituted pyridinium cation will activate three equivalence of carbonyl compounds (**Figure 7**), hence 0.33 equivalence of 4-nitro substituted trimeric pyridinium cation is sufficient for Erlenmeyer reaction [24].

2.4 Novel 1-benzyl-2-methoxypyridinium bromide and 1-benzyl-2,6-dimethoxypyridinium bromide as a catalyst in Mannich reaction

Aliphatic triaryl amine is one of the most important functional groups in the active pharmaceutical ingredients because of its interaction *via* H-bond donor/acceptor with the target binding site. Hence, β -amino carbonyl compound containing triaryl amine plays a crucial role in medicinal chemistry. One pot preparation of oxirane derivatives from easily available aryl amine, phenol and paraformaldehyde (**Figure 8**).

2-Methoxy benzyl substituted pyridinium salts showed excellent catalytic properties than the 2, 6-dimethoxy benzyl substituted pyridinium salts. In the catalyst, methoxy group acted as an electron donating group. If electron withdrawing group is more in the Lewis acid, then the activation of carbonyl group may be less or inactive. So, 2, 6-dimethoxy benzyl substituted pyridinium salts catalytic activity is lesser than the 2-methoxy benzyl substituted pyridinium salts. Different inorganic counter anions such as Br^- , BF_4^- , PF_6^- and CF_3SO_3^- containing 2-methoxy benzyl substituted pyridinium salts plays a crucial role in the activation of carbonyl group because of its bulkier (or) less electro negative nature. The pyridinium carbon is freely

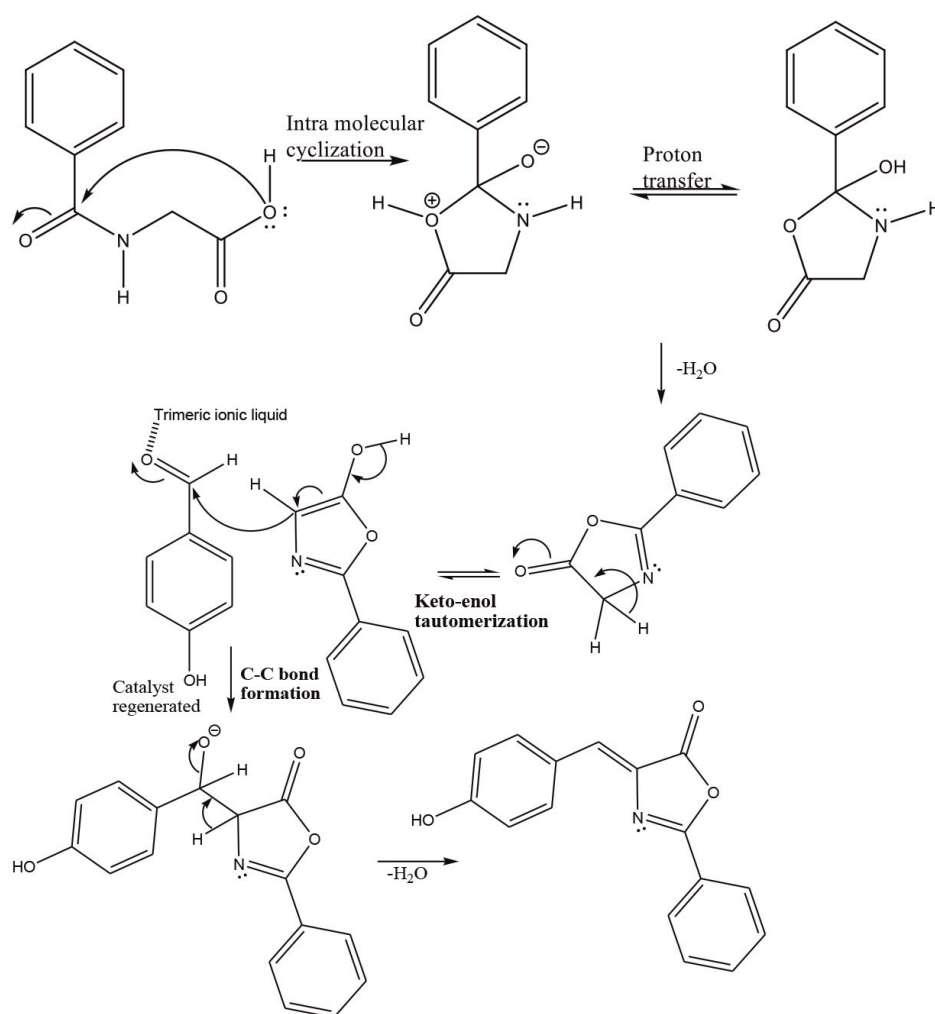
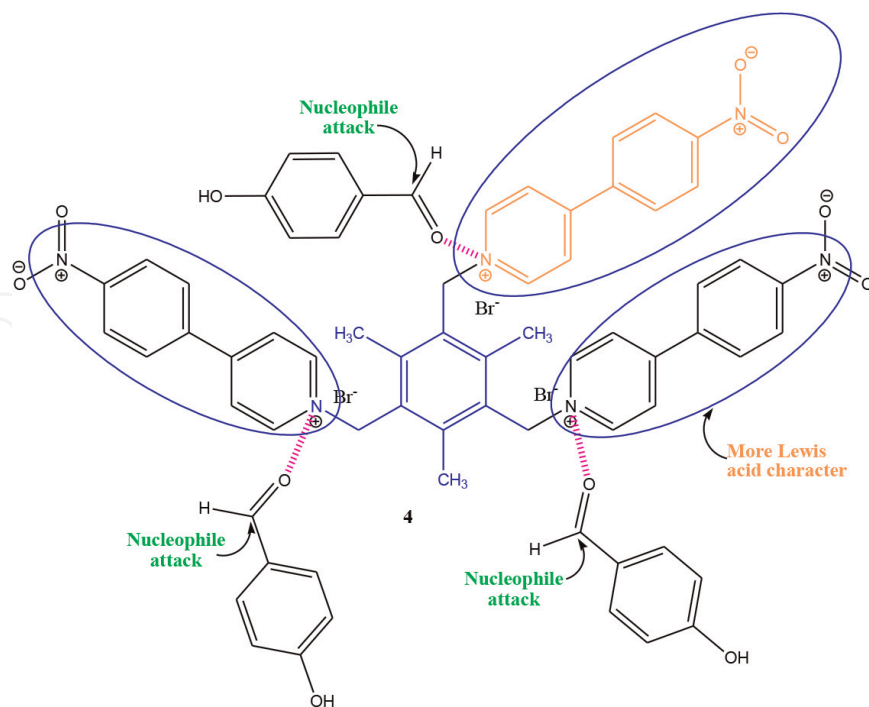


Figure 7.
Plausible mechanism for Erlenmeyer reaction.

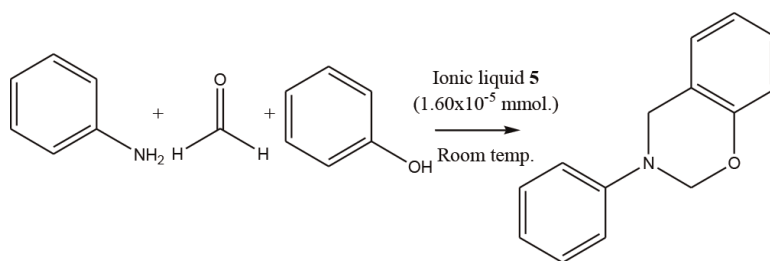


Figure 8.
Mannich reaction catalyzed by monomeric pyridinium ionic liquid 4.

available and its easily bind and activate the carbonyl compounds. The Mannich reaction is tried with 2-methoxy benzyl substituted pyridinium cation with Br^- , BF_4^- , PF_6^- and CF_3SO_3^- . Among the catalyst, bromide counter anion containing catalyst showed excellent catalytic response than the BF_4^- , PF_6^- and CF_3SO_3^- . The catalytic efficiency depends on electron deficient and freely available pyridinium cation [25]. One pot multi component Mannich reaction is carried out with the assistance of flexible longer alkyl chain containing substituted dimeric imidazolium cation with various counter anions (Br^- , BF_4^- , PF_6^- and CF_3SO_3^-). Flexible dimeric substituted imidazolium cation acted as a potential catalyst when compared with 2-methoxy benzyl substituted pyridinium cation. One equivalence of flexible dimeric substituted imidazolium cation catalyst activates two equivalences of carbonyl compound. The catalytic efficiency of flexible dimeric substituted imidazolium cation with bromide anion showed excellent catalytic response than the others. 1.66×10^{-4} mmol. (optimum concentration) of catalyst is sufficient to form Mannich product with shorter reaction time. Reuse of flexible dimeric substituted imidazolium salts showed same efficiency even after fourth cycle [26]. Substituted oxazine derivatives are acted as an important candidate in the area of medicinal industries [27, 28]. One pot multi component preparation of oxazine derivative of naphtho heterocyclic substituted compounds using various Lewis acids and Ionic liquids showed poor yield and longer reaction time [29–31]. 1,2-Dimethyl benzyl substituted imidazolium salt is used as a third generation Lewis catalyst for the preparation of naphtho heterocyclic substituted oxazine derivatives instead of expensive/inexpensive catalyst which gives poor yield with longer reaction time. 1,2-Dimethyl benzyl substituted imidazolium cation showed shorter reaction time and higher yield due to its effective activation of carbonyl compound (Figure 9). The efficiency of the recycled catalyst is also the same even after the fourth cycle [32].

2.5 Novel 5-methyl-2-nitro-3-(4-nitrobenzyl)-1H-imidazol-3-ium bromide as a catalyst in Pechmann reaction

2-Methyl-5-nitro substituted imidazolium salts are prepared by conventional and solid supported muffle furnace method. Quaternization of 2-methyl-5-nitro imidazole with benzyl bromide/4-nitro benzyl bromide under refluxing condition requires 13 hours for completion, whereas solvent free Muffle furnace method requires only 1/4th of reaction period. Electron Donating/electron withdrawing substituent containing phenol (Figure 10) is treated with ethyl acetoacetate in the presence of optimum concentration of 2.0128×10^{-4} mmol. afforded substituted chromenone derivatives. 4-chloro phenol is treated with ethyl acetate along with 2.0128×10^{-4} mmol. of

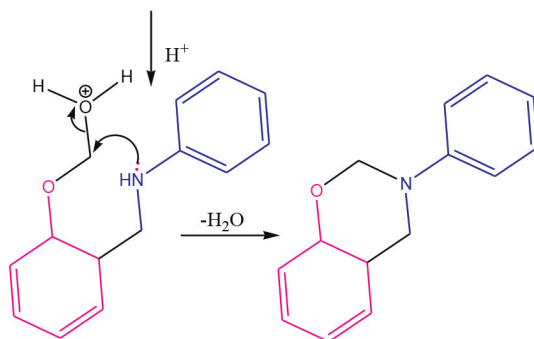
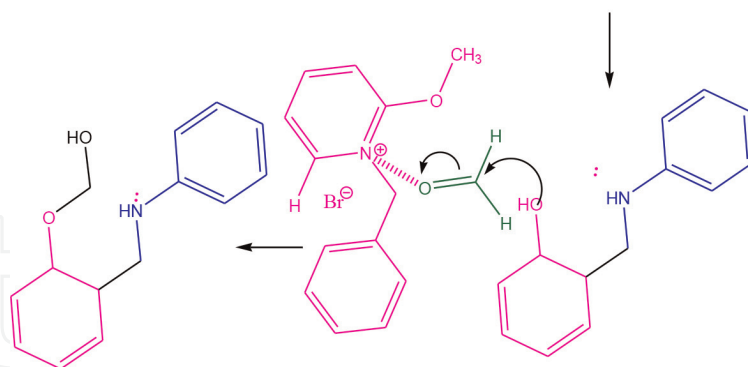
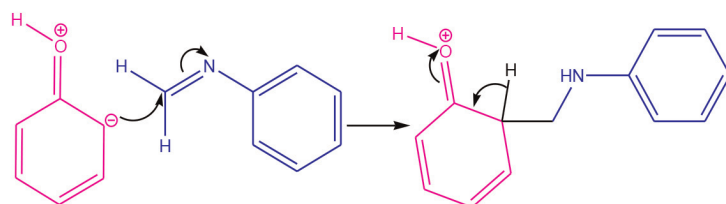
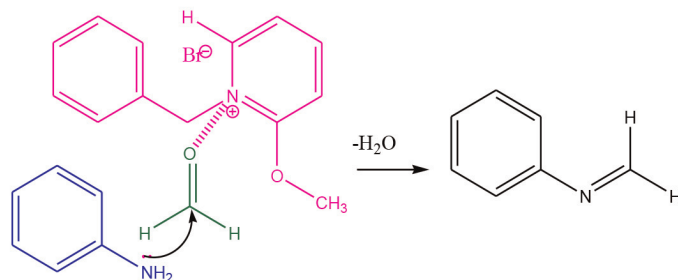
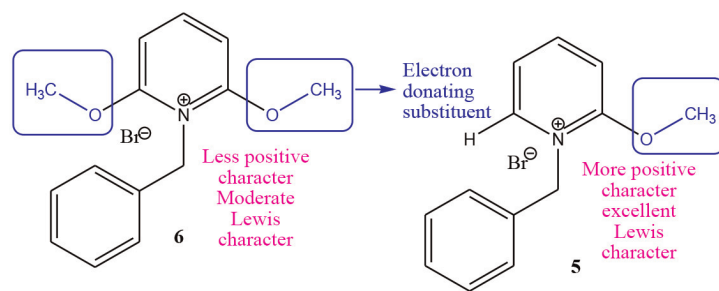


Figure 9. Plausible mechanism for Mannich reaction catalyzed by mono meric pyridinium ionic liquid 5&6.

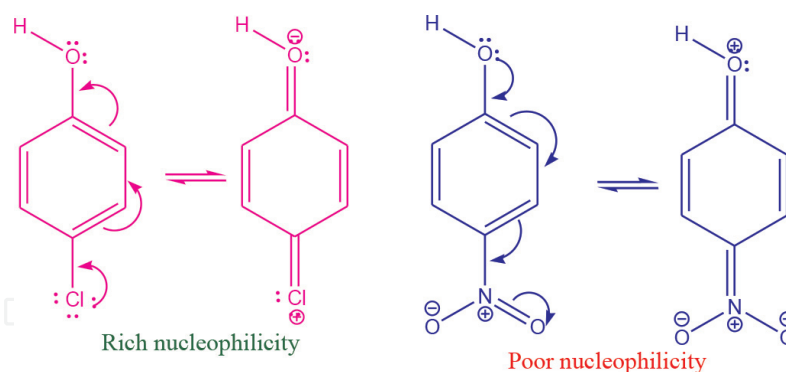


Figure 10.
Reactive probability of substituted phenols.

2-methyl-5-nitro substituted imidazolium type of ionic liquids as a catalyst and gives 6-chloro-4-methylchromenone derivative in 80% of yield in 30 minutes. Whereas, same optimized concentration of 2-methyl-5-nitro substituted imidazolium type of ionic liquid is used in the reaction between 4-nitro phenol and ethyl acetoacetate and afforded 75% of Pechmann product (**Figure 11**) in longer reaction time [33].

Pechmann reaction is tried with various concentrations such as 8.385×10^{-5} mmol, 1.3418×10^{-4} mmol, 2.012×10^{-4} mmol, and 2.683×10^{-4} mmol. Among these concentrations, 2.012×10^{-4} mmol of catalyst showed higher percentage of conversion with shorter reaction time. There is no appreciable progress in both reaction time and percentage of yield, when increasing the concentration of the catalyst to 2.683×10^{-4} mmol. so the optimum concentration of the catalyst is 2.012×10^{-4} mmol. for Pechmann reaction. Preparation of 6-chloro-4-methyl chromonone derivative from required equivalence of starting materials in various solvents such as THF, acetone, ethanol, methanol and DMSO. Among these solvents, DMSO showed higher yield with shorter reaction time compared with other solvents.

2.6 Preparation of Xanthene and its derivatives using novel 3,3',3''-(2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene)tris(1,2-dimethyl-1H-imidazol-3-ium) as a catalyst

Xanthene and its derivatives play a crucial role in pharmaceutical applications as analgesic, antiviral, antibacterial and anti-inflammatory drugs [34–36]. One pot preparation of benzoxanthene and its derivatives in the presence of various expensive and nano-particle supported catalyst [37–41]; and it has some limitations such as very high toxic halogenated solvents, high reaction temperature, tedious purification procedure and very low percentage of conversion. 2:1 ratio of β -naphthol and simple/substituted benzaldehyde with or without catalyst in the presence or absence of solvent afforded aryl substituted benzoxanthene and its derivatives [34–36]. The reaction is tried with electron donating/electron withdrawing substituted containing aryl aldehyde with two equivalence of β -naphthol. In these reactions, the electron withdrawing substituent containing aryl aldehyde reacts faster than the electron donating substituent because of the carbanion in β -naphthol which easily attack more electro positive carbonyl carbon of aryl aldehyde. The β -naphthol carbanion is much more facile to attack, if the catalyst is trimeric substituted imidazolium salts. In benzoxanthene and its derivatives preparation, various polar and non-polar solvents are tried under conventional method. Dimethyl sulphoxide (DMSO) solvent showed excellent response,

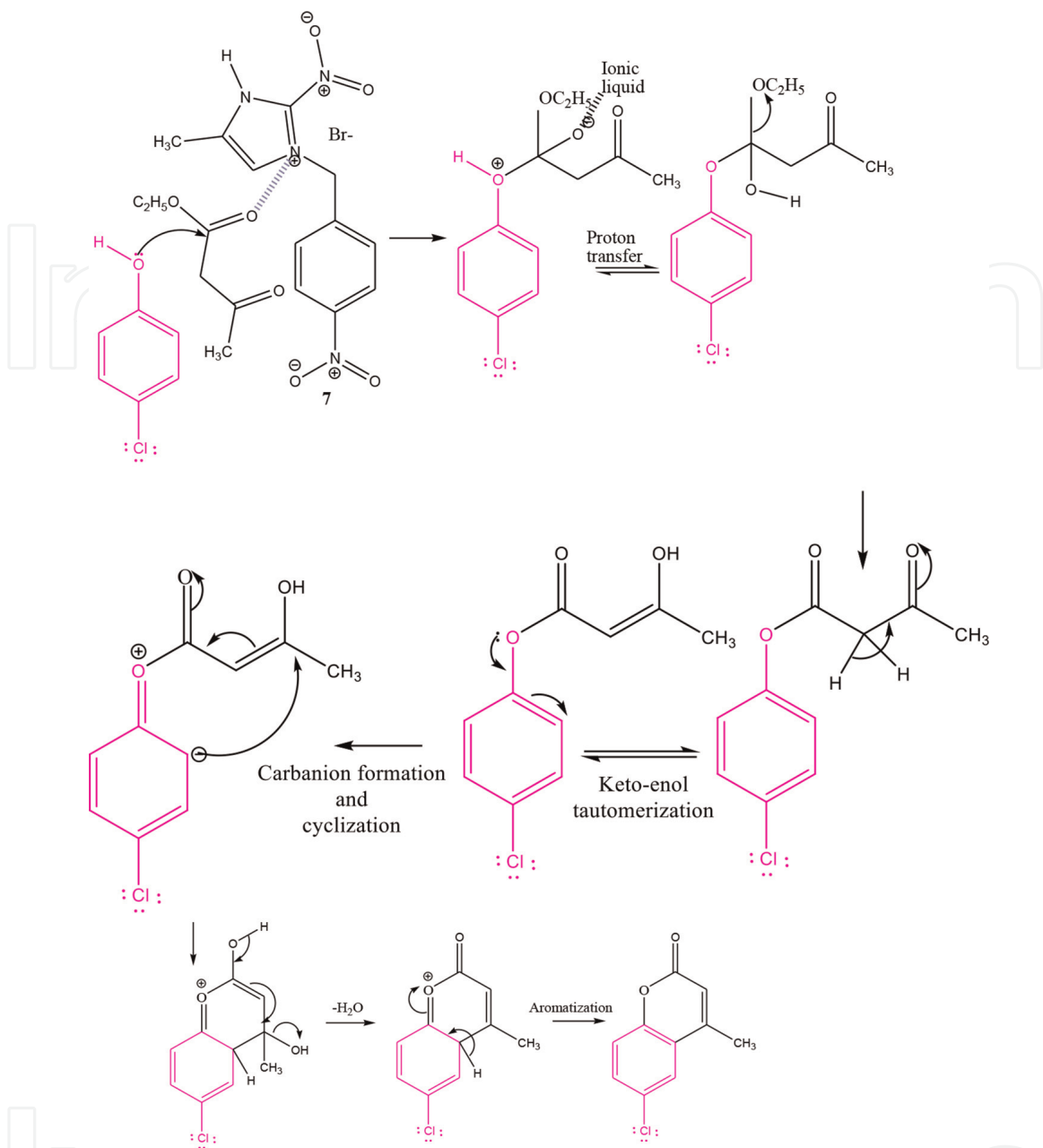


Figure 11.
Plausible mechanism for Pechmann reaction.

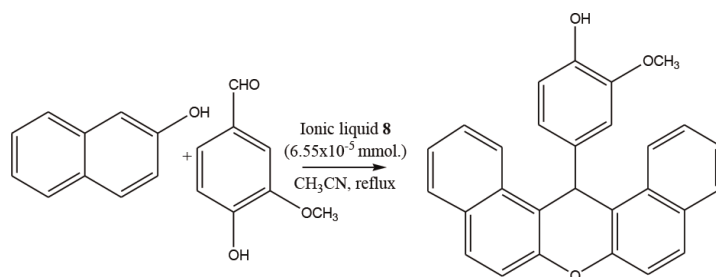


Figure 12.
Xanthene derivative formation catalyzed by trimeric imidazolium salt **8**.

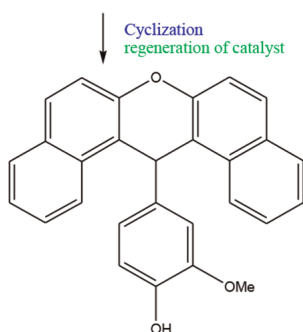
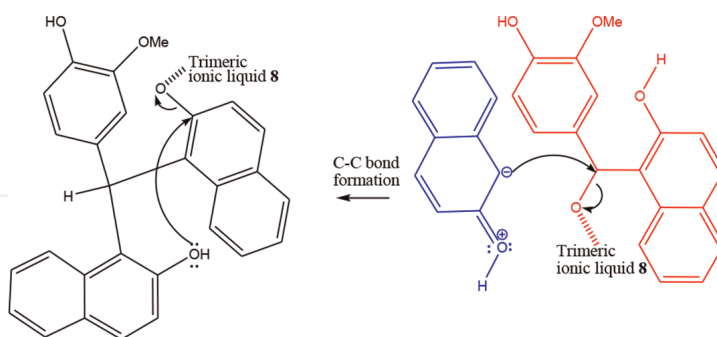
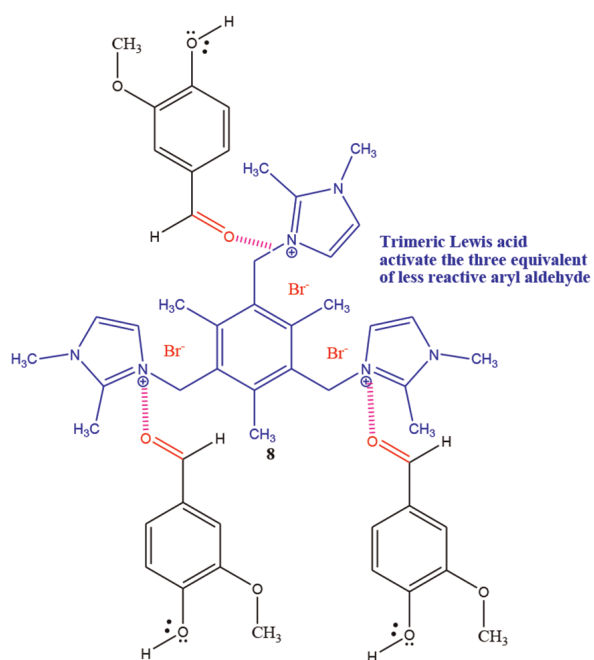
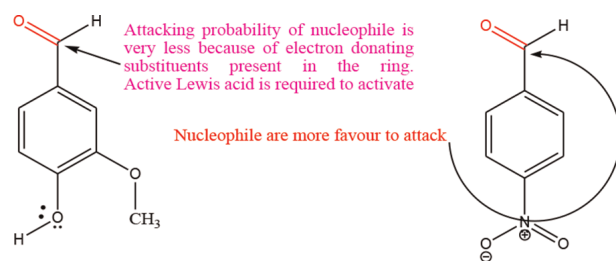


Figure 13.
Plausible mechanism for formation of xanthene catalyzed by trimeric ionic liquid 8.

such as higher yield in shorter reaction time when compared with other solvents such as THF, ethyl alcohol, chloroform and acetone [32]. In β -naphthol, hydroxy group is an electron donating group, hence, it is acted as *o* and *p*-directing group for aromatic electrophilic substitution reaction. In this regard, *para* position is already substituted, only two possible positions are available to make C-C bond formation with aryl aldehyde. The C-C bond formation is mostly at the first position of β -naphthol (Figures 12 and 13).

3. Conclusions

Mono, di and trimeric imidazolium and pyridinium salts are more useful in catalysis to prepare biologically important intermediate and target molecules from novel synthetic methodology. We have synthesized novel mono, di and trimeric imidazolium and pyridinium salts (ionic liquids) and used these ionic liquids as a catalyst in the following reactions. Oxazolone derivatives which has antibacterial, anti-inflammatory, anti-fungal and immunomodulatory properties are prepared by Erlennmeyer reaction with the assistance of trimeric nitro substituted pyridinium salts as catalyst with higher yields. Inexpensive flexible dimeric nitro substituted dimeric pyridinium salts are used in the preparation of biologically active β -hydroxy substituted alkanal in excellent yield. In one pot multi component reaction, oxirane and its derivatives are prepared by Mannich reaction in the presence of very low concentration of recyclable 2-methoxy benzyl substituted pyridinium salts under normal reaction condition. In general, Biginelli reaction requires longer reaction time and gives moderate yield even in the presence of expensive catalyst. Whereas, inexpensive, recyclable flexible longer alkyl chain linked dimeric pyridinium bromide gives excellent response. Flexible longer alkyl chain linked methyl substituted imidazolium bromide acted as an excellent Lewis catalyst for Mannich reaction in the formation of xanthene and its derivatives. 1/3rd of 2.245×10^{-4} mmol. concentration of trimeric mesityl core connected imidazolium bromide is sufficient to prepare benzoxazole and its derivatives. In Pechmann reaction, minimum concentration of monomeric, dimeric and trimeric substituted imidazolium/pyridinium salts showed excellent catalytic response.

Acknowledgements

Author thanks Mrs. Revathi Ganesan, Dr. P. Ganapathi, Dr. C. Manikandan, Dr. R. Tamilarasan, Dr. R. Sundaram, Dr. N. Arunagirinathan, Dr. N. Vijayakanth, Dr. A. Aravind, Mr. R. Naveenkumar, Mrs. R. Rajalakshmi, Mr. Senthilnathan Govindaraj, Mr. Sadaiyan Govindaraj for their great support, hard work and co-operation.

Conflict of interest

“The authors declare no conflict of interest.”

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