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Basic Ionic Liquids. A Short Review

A.R. Hajipour[a,b,]* and F. Rafiee[b]
[a]*Department of Pharmacology, University of Wisconsin, Medical School, 1300 University Avenue, Madison, WI, 53706-1532 USA*
[b]*Pharmaceutical Research Laboratory, College of Chemistry, Isfahan University of Technology, Isfahan 84156, Islamic Republic of Iran*

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Basic ionic liquids as environmental-friendly solvents and catalysts with high activity and selectivity and easily recovered materials were used to replace traditional bases such as KOH, NaOH, K_2CO_3, $NaHCO_3$, NaOAc, triethylamine, or tetrabutylammonium acetate. Using the traditional bases generally suffered from disadvantages such as waste production, corrosion and environmental problems. Basic ionic liquids offering a new possibility for developing environmentally friendly basic catalysts due to the combination of the advantages of inorganic bases and ionic liquids. They are flexible, nonvolatile, noncorrosive, and immiscible with many organic solvents. Basic ionic liquids (BILs) have been used in base-catalyzed processes such as Michael addition, Markovnikov addition, Knoevenagel condensation, Henry reaction, Mannich reaction, oximation, Feist-Benary reaction and *etc*. In this short review, we wish to present an overview of the types, properties, synthesis and applications of basic ionic liquids.

Keywords: Basic ionic liquids, Task-specific ionic liquids, Lewis base ionic liquids, Condensation reactions

INTRODUCTION

Due to the increase in environmental consciousness in chemical research and industry, the challenge for a sustainable environment calls for clean procedures that avoid the use of harmful organic solvents. One of the most important principles of the green chemistry is the elimination of hazardous solvents in chemical synthesis and avoids using toxic solvent and the generation of waste. Ionic liquids have received considerable attention due to their interesting chemical and physical properties, such as wide liquid range with melting point around room temperature, good stability in air and moisture, high solubility including inorganic, organic, and even polymeric materials, and negligible vapor pressure [1].

The use of ionic liquids as reactions medium may offer a convenient solution to both the solvent emission and catalytic recycling problem [2]. Ionic liquids containing imidazolium cations can be used as powerful media in some catalytic organic reactions not only for the facilitation of catalyst recovery but also for the acceleration of the reaction rate and improvement of selectivity [3]. Ionic liquids have been widely vaunted as greener solvents, suitable for a range of organic reactions and providing possibilities such as control of product distribution, enhanced rate and reactivity, ease of product recovery, catalyst immobilization, and recycling [4].

Numerous chemical reactions, such as esterification reaction [5-9], cleavages of ethers [10], aldol condensation [11], protection of carbonyls [12-16], Koch carbonylation [17], polymerization [18], hydrogenation, regioselective alkylation and Friedel-Crafts reactions [19-22], dimerization

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*Corresponding author. E-mail: Haji@cc.iut.ac.ir

[23-24], Diels-Alder reactions [25-26], Mannich reaction [27-28], oximation [29], oxidation [30-32], Heck reaction [33], Knoevenagel reaction [34-36], Henry reactions [37], heterocyclic synthesis [38-41], cross-coupling reactions and some enzyme reactions can be carried out in ionic liquids.

These valuable solvents have also been referred to as designer solvents regards that their physical and chemical properties could be adjusted by a careful choice of cation and anion. Furthermore, they exhibit acidic or basic properties, therefore the combining of these unique properties emerging them as green reaction media [2].

Recently, the synthesis of functionalized ionic liquids or task-specific (TSILs) with special functions according to the requirement of a specific reaction has become an attractive field due to their tunable features for various targeted chemical tasks and the advantages as reusable homogenous supports, reagents, and catalysts with green credential. All these studies offered us the possibility of designing suitable catalysts for the appointed reaction. The tasks specific ionic liquids often serve the dual role of catalyst and reaction medium. Endowed with catalytically active groups, functional ionic liquids have been developed and successfully applied as catalyze in a number of chemical transformations. These kinds of ionic liquids still maintains the unique properties of ionic liquids, therefore can be easily recycled and reused as homogenous small molecular catalysts. Up to now, functionalized ionic liquids catalysis has been mainly focused on exploring acid or base mediated reactions. Considering the ‘designer’ properties of ionic liquids, there remains tremendous potential for FIL catalysis [42-45].

The acidity/basicity of the reaction media has a substantial influence on the efficiency of many reactive processes; therefore, a new class of acidic or basic ionic liquids is gaining special attention due to the possibility of increasing the efficiency of many processes by a wise manipulation of their properties. Acidic or basic ionic liquids (ILs) represent new classes of acids or bases. The study of the acidity/basicity of these task-specific ionic liquids is of great importance since the efficiency of many processes depends on the acidity/basicity of the media or can be controlled by it. These compounds aptness for the fine tuning of their properties through an endless combination of cations and anions, cataloging them as designer solvents, allow the design of solvents for the development of more efficient and sustainable processes and products [46].

The acidity or basicity of reactive ionic liquids is governed by the strength of the cation, the anion, or by the combination of the cation and anion. The most common ionic liquids comprise salts of tetraalkylphosphonium, tetraalkylammonium, N-alkylpyridinium or N,N′-dialkylimidazolium cations. Common cations contain $C_{1\text{-}18}$ alkyl groups, and include the ethyl, butyl and hexyl derivatives of N-alkyl-N′-methylimidazolium and N-alkylpyridinium. Other cations include pyrrolidinium, pyridazinium, pyrimidinium, pyrazinium, pyrazolium, triazolium, thiazolium and oxazolium. A wide of anions can be matched with the cation component of such ionic liquids for achieving a neutral ionic liquid or one that possesses Lewis basicity. Commonly used anions include carboxylates, fluorinated carboxylates, sulfonates, fluorinated sulfonates, imides, borates, phosphates, antimonates, halides, halometallates, *etc.* [47].

Room temperature ionic liquids include acidic, neutral and basic ionic liquids. The acidic and neutral ionic liquids have been well recognized and successfully applied in many organic reactions. However, the related report about the basic ionic liquids was rare [48].

The most popular acidic ILs including either protonated alkylimidazole salts or x-sulfonylalkylimidazolium salts are much less frequent basic ILs, for example 1,3-dialkylimidazolium hydroxide or monoalkylammonium salts of diamines which are prepared from tertiary diamines by mono-quaternization [49].

Basic ionic liquids (BILs) used in some base-catalyzed processes offering a new possibility for developing environmentally friendly basic catalysts due to the combination of the advantages of inorganic bases, stability in water and air, easy separation, high catalytic efficiency and reusability. These strong BILs exhibited great potential for the replacement of conventional basic catalysts because they are flexible, nonvolatile, noncorrosive, and immiscible with many organic solvents [1].

Some of the reactions such as condensation reactions, that catalyzed by a base, such as K_2CO_3, $NaHCO_3$, NaOAc, triethylamine, or tetrabutylammonium acetate, *etc.*, are of great importance for the synthesis of pharmaceutical and fine chemicals. Industrially, these reactions are indeed carried out in the homogeneous phase with KOH or NaOH. Using these bases, however, have numerous disadvantages such as waste production, corrosion and no catalyst recovery. Thus it is an exciting challenge to find new Brönsted-type basic catalysts with high activity and selectivity. Although the consumption of one equivalent of base is inevitable, a basic ionic liquid acting as both the solvent and base would make the procedure much easier to handle. This is essentially important for the reactions where normally a large excess of organic base, *e.g.* triethylamine, DBU, or piperidine, is required, which causes an additional environmental burden [50].

Basic ionic liquids have been successfully utilized to catalyze the Michael addition, Heck reaction and Markovnikov addition [51].

CLASSIFICATION OF IONIC LIQUIDS ACCORDING TO ACIDITY/ BASICITY

There is significant interest in the development of task specific ionic liquids, where the anion and/or cation is designed to impart specific properties to the ionic liquid, such as chirality, or improved extraction or separation capabilities.

The design and choice of ionic liquids commonly focuses on physical properties such as water-miscibility, conductivity, viscosity and solubility properties, although how the chemical structure of the ionic liquid affects these various characteristics is still poorly understood. However, there is another chemical property that imparts a variety of physical characteristics to the ionic liquids that has been little investigated; the relative acidity or basicity of the component ions. Lewis base anions can exhibit a base catalysis phenomenon, which can be utilized [52].

Neutral Anions

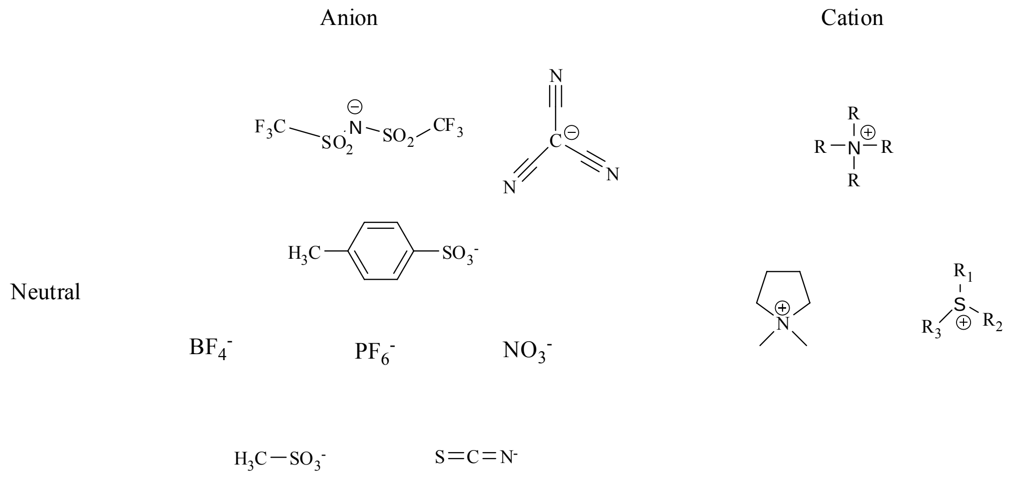
Typical ionic liquid anions are those that can be described as neutral in the acid/base sense or very weakly basic; these exhibit only weak electrostatic interactions with the cation and thus impart advantageously low melting points and viscosities. Included in this class are anions such as hexafluorophosphate, *bis*(trifluoromethanesulfonyl)amide (TFSA, also known as TFSI and $(Tf)_2N$, tetrafluoroborate, methanesulfonate (mesylate), thiocyanate, tricyanomethide and *p*-toluenesulfonate (tosylate) (Scheme 1). Ionic liquids formed from these anions typically exhibit good thermal and electrochemical stability and thus are often utilized as inert solvents in a wide range of applications [53-56].

Acidic Cations and Anions

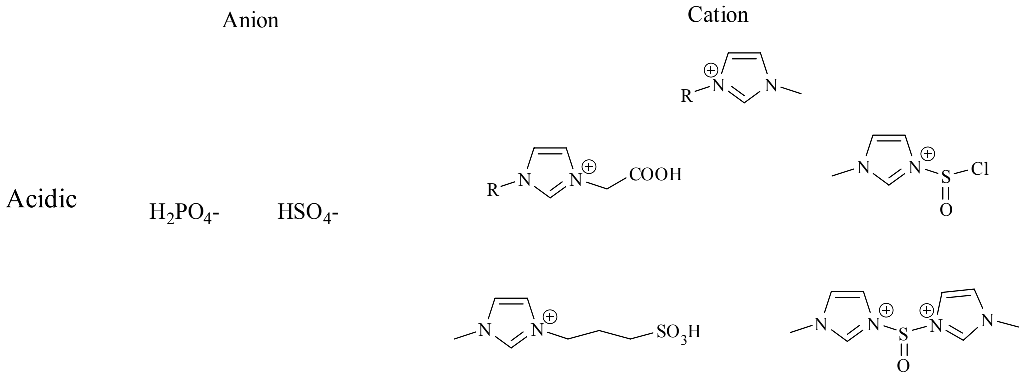
The simplest examples of slightly acidic ionic liquids are those based on the protic ammonium, pyrrolidinium and imidazolium ions, of which many are known. The well known $AlCl_3$ based ionic liquids are Lewis acidic when they contain an excess of $AlCl_3$ (Scheme 2) [57-67].

Basic Cations and Anions

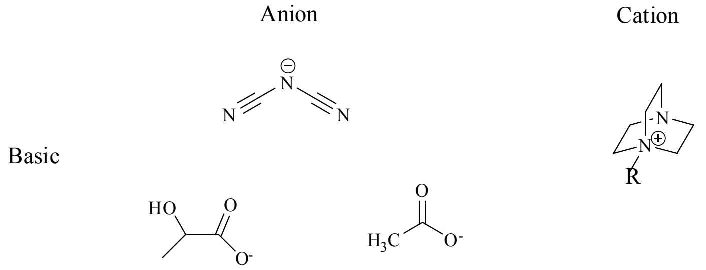
There are a number of ionic liquid forming anions that can class as basic. These include the lactate, formate, acetate (and carboxylates generally) and the dicyanamide (dca) anion. The



Scheme 1



Scheme 2



Scheme 3

dicyanamides, in particular, have become readily available because of their low viscosity, including as phosphonium salts. Since the basicity of these anions imparts different, advantageous properties to the ionic liquids, such as different solubilizing and catalytic properties, as discussed below, this category of ionic liquids is likely to grow considerably in the coming years.

An alternative to the design of ionic liquids utilizing a basic anion is to incorporate a basic site into the cation. This may afford more thermally stable ionic liquids than those containing basic anions, which frequently exhibit relatively low decomposition temperatures (Scheme 3) [52].

Amphoteric Anions

There are a small number of ionic liquid anions that fall into the interesting class of amphoteric anions, with the potential to both accept and donate protons depending on the other substances present. The hydrogen sulfate (HSO_4) and dihydrogen phosphate (H_2PO_4) anions are simple examples of such anions [52].

Lewis Base Aluminum Chloride Combined with Room Temperature Ionic Liquids

Aluminum chloride can be combined with certain organic salts to produce ionic liquids at room temperature. Familiar examples of such liquids are mixtures of aluminum chloride with 1-*n*-butylpyridinium chloride (BPC) or l-methyl-3-ethylimidazolium chloride (MEIC). Both systems have been found to be good solvents for electrochemistry and spectroscopy.

The Lewis acid-base properties of these ionic liquids can be varied by adjusting the ratio of $AlCl_3$, to organic salt. Melts in which the apparent mole fraction of $AlCl_3$ exceeds 0.5 are acidic, owing to the presence of the heptachloroaluminate ion, which is a chloride ion acceptor. Those melts with an $A1C1_3$ mole fraction less than 0.5 are basic, since they contain uncomplexed chloride ion [68-69].

BASICITY CHARACTERIZATION OF BASIC IONIC LIQUIDS AND SYNTHESIS OF BASIC IONIC LIQUIDS

Basicity Characterization

One of the important and very revealing properties of any solvent is the way that it responds to the presence of an acidic or basic solute. The state of an acid or base compound, such as acetic acid or ammonia, in an ionic liquid solvent is a strong function of the acidity/basicity of the ionic liquid itself.

In traditional solvents, acids and bases are categorized in terms of Brönsted acidity, which relates to the ability of the acid, HA, to donate a proton to a molecule of the solvent, S:

$$HA + S \rightleftharpoons A^- + HS^+$$

The equilibrium constant for this reaction, K_a, is a measure of the acidity of the acid, but it clearly also has a dependence on the basicity of the solvent, S. The more general Lewis definition of acidity and basicity involves simply the ability of the molecule to accept or donate electrons. The role of the solvent can be to act as the predominant base and thereby to form HS^+ (*e.g.*, H_3O^+ in water).

Some of the basic anions are more basic than water and therefore can be expected to act as stronger proton acceptors than water. An acid dissolved in an ionic liquid containing such an anion may then exhibit a higher degree of dissociation than in water. Thus the Brönsted acidity of a solute acid may be higher (K_a larger) in such ionic liquids than in water. The extent to which this is the case is a matter of the relative acceptor strength of the ionic liquid anion and the conjugate base of the solute acid. Such basic ionic liquids turn weak acids into stronger acids. This understanding can be investigated further by using acid solutes which have spectroscopic signatures that are sensitive to their state of protonation; the measurement of the basicity scale of these ionic liquids was conducted on UV-Vis spectrophotometer with an acidic indicator.

For example between ionic liquids contain acetate, dicyanamide (dca), tricyanomethide (tcm), nitrate, PF_6, TFSA and BF_4, emim acetate is able to act as a stronger acceptor for protons than water. In contrast to the neutral ionic liquids this ionic liquid can produce strongly dissociated solutions of the solute acid. The anions S^- in these ionic liquids thus act as Brönsted bases to promote the dissociation of the dissolved acid [52].

The state of a base will be altered by the presence of water in a neutral ionic liquid. Water will be at least partly dissociated, producing OH^- in a basic ionic liquid.

Preparation of 1-Butyl-3-methylimidazolium Hydroxide

Solid potassium hydroxide was added to a solution of [bmim]Br with equal molar amounts in dry methylene chloride, and the mixture was stirred vigorously at room temperature for 10 h. The precipitated KBr was filtered off, and the filtrate was evaporated to leave the crude [bmim]OH as a viscous liquid that was washed with ether and dried at 90 °C for 10 h to prepare the pure ionic liquid for use [70].

Also the basic ionic liquid [bmim]OH was prepared by anion change of [bmim]Cl using 1 mol equivalent KOH. The ionic liquid was dried under vacuum for 24 h and stored in a desiccator. This ionic liquid is highly stable under ambient conditions and can be used in reactions without any difficulty. The ionic liquid was firstly dried with anhydrous sodium sulfate, and the filtrate was then dried under vacuum at 90 °C for 24 h to eliminate the residual water [48].

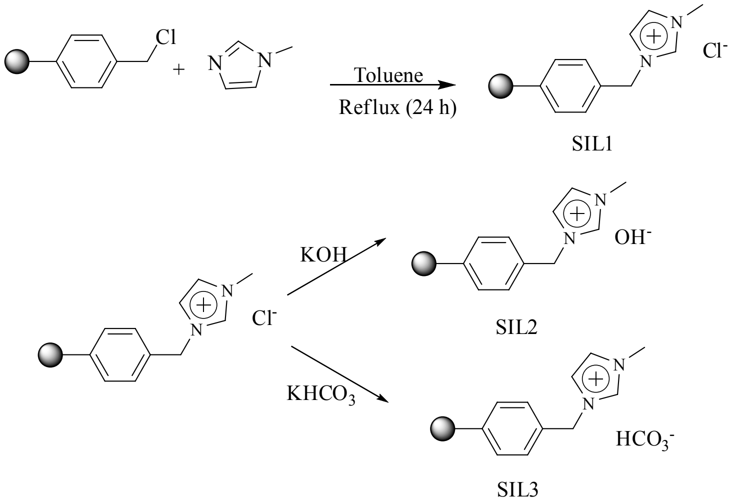
Preparation of Supported Basic Ionic Liquid

A mixture of polystyrene resin and 1-methylimidazole in toluene was refluxed for 24 h. After cooling to room temperature, the reaction mixture was filtered, and the supported ionic liquid 1 (SIL 1) was washed with toluene, HCl, water and methanol, followed by drying under reduced pressure to give SIL 1 (Scheme 4).

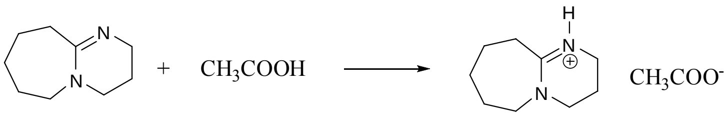
For preparation of supported basic ionic liquid 2 and 3 solid potassium hydroxide or potassium hydrogen carbonate and SIL 1 (10.0 g) were added to water and the mixture was stirred vigorously at room temperature for 24 h. Then the mixture was filtrated and washed with water until neutral, followed by drying under reduced pressure to give the supported basic ionic liquid 2 (SBIL 2) and supported basic ionic liquid 3 (SBIL 3) (Scheme 4) [51].

Synthesis of (3-Amino-propyl)-tributyl-phosphonium Glycine ($[3a\text{-}C_3P(C_4)_3][Gly]$)

Equal molar amounts of tri-*n*-butylphosphine and 3-bromopropylamine hydrobromate were added to a round-bottom flask containing acetonitrile as solvent. The mixture was vigorously stirred for 8 h at 60 ºC, and then 48 h at 80 ºC. The solvent acetonitrile was removed by vacuum evaporation at 70 ºC. Then, n-hexane was added to the flask to dissolve the remaining material with thorough stirring. After standing for 30 min, two phases were formed. The top phase, containing unreacted starting material and n-hexane, was decanted. The bottom phase was the product fraction. This washing process was repeated until no starting material exited in the top phase.



Scheme 4



Scheme 5

The obtained product, [3a-$C_3P(C_4)_3$]Br, was dried in a vacuum oven at 70 ºC for 24 h. Then [3a-$C_3P(C_4)_3$]Br was dissolved in deionic water, and the solution was added to the pretreated ionic exchange resin column, resulting in the transformation of Br^- into OH^-. The obtained solution of [3a-$C_3P(C_4)_3$][OH] was evaporated to remove most of the water. Equal molar amount of glycine was added to the solution of [3a-$C_3P(C_4)_3$][OH] with stirring for 24 h at room temperature. Then, water was removed by vacuum evaporation. The final product [3a-$C_3P(C_4)_3$][Gly] was dried in a vacuum oven at 70 ºC for 48 h [71].

Synthesis of (3-Amino-propyl)-tributyl-phosphonium Alanine ([3a-$C_3P(C_4)_3$][Ala])

This synthesis followed the same procedure as for [3a-$C_3P(C_4)_3$][Gly] described above, although alanine was used instead of glycine [71].

Task-Specific Ionic Liquid, 1,8-Diazabicyclo[5.4.0]-undec-7-en-8-ium Acetate

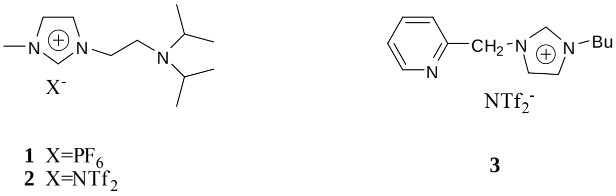
Basic task-specified ionic liquid, 1,8-diazabicyclo[5.4.0]-undec-7-en-8-ium acetate ([DBU][Ac]) through the neutralization reaction of equal molar amounts of DBU and acetic acid. To a three necked flask was added DBU. Acetic acid was then added dropwise at the temperature of 65 ºC cooled by ice bath. After dropwise addition, the ice bath was removed and the reaction mixture was stirred at room temperature for 24 h. The oil residue was dried in vacuum at 60 ºC for 24 h to afford [DBU][Ac] as a light yellow, viscous liquid (Scheme 5) [72].

1-(2'-Diisopropylamino)ethyl-3-methylimidazolium Hexafluorophosphate (1) or *Bis* (trifluoromethane-sulfonyl)amide (2)

N-Methylimidazole was added to a solution of 2-(diisopropylamino)ethyl chloride hydrochloride in ethanol, and the mixture was heated at reflux for 12 h. After the reaction was complete, the solvent was removed under reduced pressure, and the residue was washed with THF to leave a white powder. The solid was dissolved in water and NaOH was added. After stirring for 15 min, dichloromethane and KPF_6 were added, stirred for a further 30 min, and the aqueous phase was extracted with CH_2Cl_2. The combined organic layer was dried with Na_2SO_4. After evaporation of the solvent, the desired product was obtained (Scheme 6) [50].

1-Butyl-3-(2-pyridinylmethyl)imidazolium Bis(trifluoromethanesulfonyl) Amide (3)

To 2-(bromomethyl) pyridine hydrobromide dissolved in methanol was added sodium hydrogen carbonate (1 equiv.) to neutralize hydrobromide. After stirring for 30 min at room temperature, 1-butylimidazole was added, and the solution was stirred at 25 °C for 12 h. Methanol was then evaporated under reduced pressure, and the residue was dissolved in water and extracted several times with ether. To the aqueous phase was added $LiNTf_2$. The resulting oily product was washed with water and dried in vacuum (Scheme 6) [50].



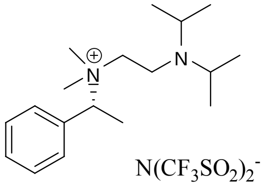
1 X=PF_6
2 X=NTf_2

3

Scheme 6

(R)-(1-Phenylethyl)[2-diisopropylamino)ethyl] dimethylammoniumbis(trifluoromethanesulfonyl) imide

2-(Diisopropylamino)ethyl chloride was added to (R)-N,N-dimethyl-1-phenylethanamine. The flask was flushed with nitrogen, closed with a septum, and the mixture was stirred at 60 ºC for 4 days. A light-orange precipitate could be seen in the solution. After cooling to room temperature n-hexane was added. The supernatant solution was decanted and the solid was washed twice with n-hexane. The crude light-yellow crystals were dried at room temperature at high vacuum to give the corresponding chloride. This was dissolved in distilled water and the solution was washed with CH_2Cl_2. To the water solution was then added, under stirring, in small portions, a solution of $LiN(SO_2CF_3)_2$ in distilled water. The mixture was stirred at room temperature for 3 h, and the upper water layer was separated and washed with CH_2Cl_2. To the bottom (ionic liquid) layer was added CH_2Cl_2, and the solution was washed with distilled water. CH_2Cl_2 solutions were combined and dried over $MgSO_4$. After filtration to remove the $MgSO_4$, CH_2Cl_2 was evaporated. Product was obtained as light-yellow oil (Scheme 7) [49].



Scheme 7

2-(2-(Diisopropylamino)ethoxy)-N-ethyl-N,N-dimethylethanammonium(S)pyrrolidine-2-carboxylate

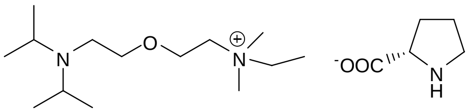
Reaction was started by preparation of Annex AT in OH mode. An Annex AT 0806 column was washed with distilled water, which is five times the volume of Annex AT, then with NaOH solution and finally again with distilled water until the pH of the washing water was neutral. A saturated solution of 2-[2-(dimethylamino) ethoxy]ethyl-N,N-diisopropyl-ammonium bromide in distilled H_2O was than applied to the top of the column, which was then washed with distilled water. The pH of the fractions was monitored and those with basic pH were collected. Into this basic solution was added, under stirring, a solution of L-proline in distilled water. The resulting mixture was then stirred at room temperature for 20 h. Water was evaporated using a rotary evaporator and the residue was dried under high vacuum to obtain ionic liquid as a light brown very viscous liquid (Scheme 8) [49].

Synthesis of Choline Hydroxide

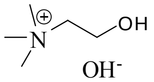
Methanol, choline chloride and KOH in term of molar ratio of 1:1 were charged in a three-neck flask fixed with a condenser and magnetic stirrer. The reactor was then heated to 60 ºC in water bath under stirring strongly for 12 h. After cooling to room temperature, the mixture reaction solution was filtered to remove solid KCl and choline hydroxide solution was obtained (Scheme 9) [73].

Synthesis of 1-Ethyl-4-aza-1-azoniabicyclo[2.2.2] octane Iodide ([C$_2$dabco]I)

1,4-Diazabicyclo[2.2.2]octane (dabco) was reacted with less than equimolar amount of iodoethane in ethyl acetate for 2



Scheme 8



Scheme 9

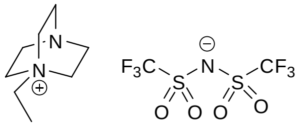
h at room temperature. The white precipitate was collected by filtration, and was then dried in vacuum. The filtrate was recrystallized from isopropanol to give the compound as a brilliant white powder [74].

Synthesis of 1-Ethyl-4-aza-1-azoniabicyclo[2.2.2] octane bis(trifluoromethane sulfonyl)amide ([C$_2$dabco]TFSA)

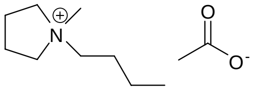
The iodide derivative was dissolved in distilled water and slightly excess LiTFSA aqueous solution was added. Since the TFSA derivative is water soluble, the desired material was extracted from aqueous solution by means of dichloromethane and the solvent was evaporated in vacuum. Acetone and activated charcoal were added to the residue and the solution was stirred with charcoal at room temperature for 2 h. The mixture was filtered through an activated alumina column. The solvent was removed by rotary evaporator and the residue was dried in vacuum for 2 days at 90 ºC (Scheme 10) [74].

N-Butyl-N-methylpyrrolidinium Acetate

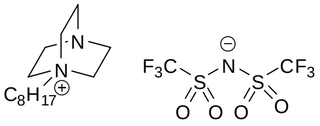
N-*n*-Butyl-N-methylpyrrolidinium iodide was dissolved in distilled water and added to a column loaded with acetate anions. (The first step in the use of the ion exchange resin involves loading with the desired anion. A 20 wt% NaOAc solution was flushed through a column containing 1 kg of resin. The above solution was required to achieve complete substitution of the chloride ions. Then, flushing the column with an aqueous solution of the iodide salt of the desired cation resulted in rapid displacement of the target anion by the iodide. After the reaction was complete, the aqueous solution containing the new IL was concentrated and the IL isolated and dried (Scheme 11) [75].



Scheme 10



Scheme 11



Scheme 12

1-Octyl-4-aza-1-azonia-bicyclo[2.2.2]octane Bis(trifluoromethanesulfonyl)amide ([C$_8$dabco]TFSA)

The bromide salt and LiTFSA in molar ratio of 1:1 yielded [C$_8$dabco]TFSA as a colorless oil [75] (Scheme 12).

APPLICATION OF BASIC IONIC LIQUIDS IN ORGANIC REACTIONS

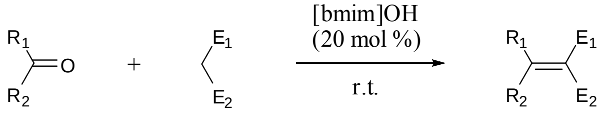
Knoevenagel Condensation

Within the family of base catalyzed reactions for fine chemical synthesis, the Knoevenagel condensation is widely employed to synthesize intermediates of fine chemicals. The Knoevenagel condensation is a very useful reaction and has been widely employed for carbon-carbon bond formation in organic synthesis from carbonyl compounds and active methylene groups. This reaction is usually catalyzed by a base, an acid, or a heterogeneous neutral support. A wide range of bases can be employed for this condensation; however, alkali metal hydroxides and pyridine as well as other amines such as ethylenediamine and piperidine are the most studied. A wide range of solid catalysts and solid-supported catalysts have also been applied to this reaction such as anion-exchange resins, KF, magnesium and aluminum oxides, alkali-exchanged and alkali-encapsulated zeolites, hydrotalcites, amino group-immobilized silica materials, clays, alkali and alkaline earth carbonates, nitridated aluminosilicates and aluminophosphates, and porous silicate quaternary ammonium composites [76-79].

The basic ionic liquid 1-butyl-3-methylimidazolium hydroxide, [bmim]OH, efficiently catalyzed Knoevenagel condensation without requirement of any organic solvent. A wide range of aliphatic and aromatic aldehydes and ketones easily undergo condensations with diethyl malonate, malononitrile, ethyl cyanoacetate, malonic acid and ethyl acetoacetate (Scheme 13). The reactions proceed at room temperature and are very fast. The significant advantages offered by this methodology were: (a) general applicability to a large number of substrates with very facile reaction of aliphatic aldehydes with diethyl malonate, which was difficult to achieve by other methods, (b) mild reaction conditions (room temperature), (c) clean and fast (7-40 min) reaction, (d) high isolated yields of products and (e) reusability of catalyst and cost-effectiveness. Another attractive feature of this methodology was the use of ionic liquid as catalyst as well as reaction medium primarily avoiding hazardous organic solvent in the whole procedure in contrast to the reported procedures using ionic liquids together with additional catalysts and organic solvents in the process [80].

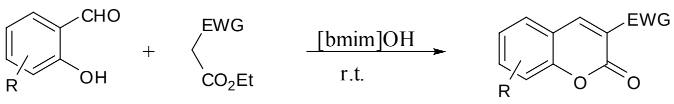
When an aromatic *o*-hydroxy aldehyde was condensed with diethyl malonate or ethyl acetoacetate by this procedure, the corresponding coumarin was obtained in one pot in very high yields (Scheme 14) [80].

Task specific basic ionic liquids had been shown to facilitate the Knoevenagel condensation reaction of a range of carbonyl molecules with methylene nucleophiles (Scheme 15). Using the basic ionic liquid without solvent produced a homogeneous reaction system and showed high initial activity and overall conversion. However, on recycle, degradation of the IL was observed and it was difficult to remove the entire product by solvent extraction due to the reaction mixture solidifying which results in loss of activity on subsequent reactions. Supporting the basic ionic liquid in an immiscible solvent or on a silica support reduces the initial activity, in general; however, in both cases, excellent recyclability was found with the reaction repeated over five times without leaching of the ionic liquid into the extractant phase or reduction in activity [81].

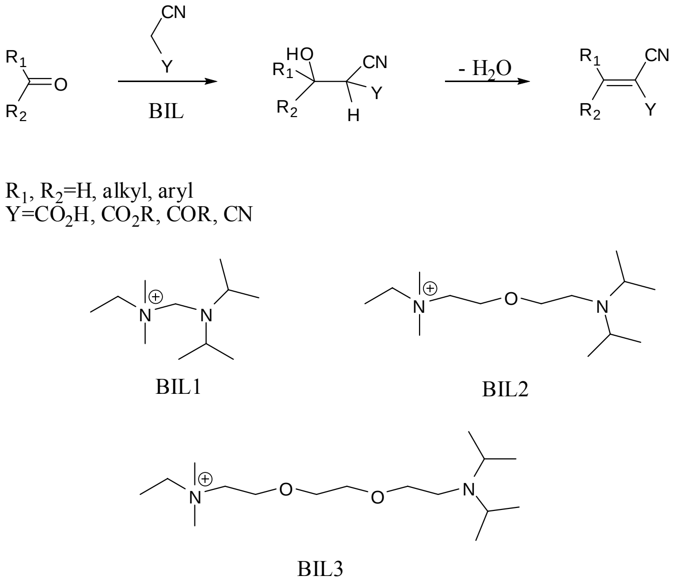


R_1, R_2= alkyl, aryl, H
E_1, E_2= CN, COMe, COOMe, COOEt, COOH

Scheme 13



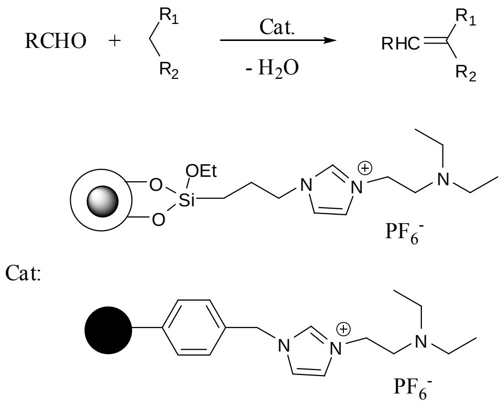
Scheme 14



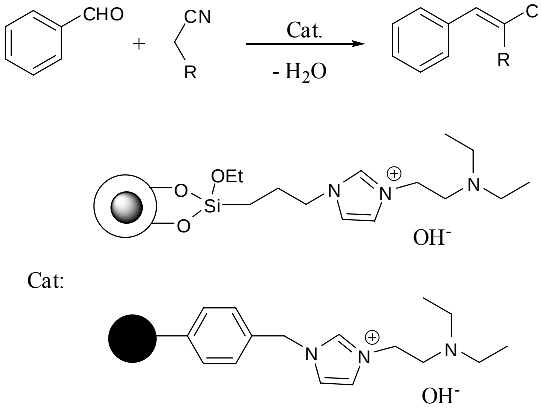
R_1, R_2=H, alkyl, aryl
Y=CO_2H, CO_2R, COR, CN

Scheme 15

Hydroxyapatite-encapsulated γ-Fe_2O_3 nanoparticles functionalized with aliphatic amine basic ionic liquids leaded to creation of surface basic sites as well as increase of magnetism. The basic magnetic nanoparticles were used as efficient heterogeneous catalysts for the Knoevenagel condensation reaction of several aldehydes with malononitrile under mild conditions (Scheme 16). The cooperation between the basic magnetic nanoparticles carrier and supported basic ionic liquids resulted in a significant rise of catalytic activity. The basic magnetic catalyst could be facilely isolated from the reaction mixture by simple magnetic decantation using a permanent magnet and it could be reused four times without significant degradation in activity [82].



Scheme 16



Scheme 17

A series of basic ionic liquids functionalized hydroxyapatite-encapsulated γ-Fe_2O_3 magnetic nanoparticles were used as efficient heterogeneous catalysts for aqueous Knoevenagel condensation under mild condition and excellent results for extended substrates were obtained (Scheme 17). In comparison with the control experiments, the high activity isascribed to the cooperatives between the base sites generated by framework hydroxyapatite and supported basic ionic liquids. Separation of the catalyst from the reaction mixture was readily achieved by simple magnetic decantation and the catalyst could be easily recycled without appreciable loss of catalytic activity [83].

A novel basic ionic liquid paired by 1-butyl-3-methylimidazolium cation and imidazolide anion ([bmim]Im) was synthesized and its basicity was investigated. The basicity of [bmim]Im approaches to that of [bmim]OH and is much stronger than that of [bmim]OAc. In aqueous solution at room temperature, 2% of [bmim]Im showed good catalytic properties for Knoevenagel condensations between aromatic aldehyde and active methylene compounds with 86%-95% yield and 100% selectivity for ylidenemalononitriles. This kind of imidazolide ionic liquid also has better recycle ability [84].

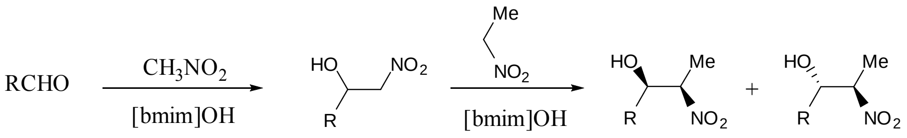
Henry Reaction

The Henry reaction is one of the most useful carbon-carbon bond forming reactions and has wide synthetic applications in organic synthesis by which 2-nitroalcohols are formed on treatment of nitroalkanes and carbonyl derivatives with a basic catalyst. Nitroalcohols are useful intermediates in the preparation of nitroalkenes, α-nitroketones, and β-aminoalcohols derivatives, such as ephedrine and norephedrine. Henry reactions can be catalyzed by organic and inorganic bases. For example 1,1,3,3-tetramethyl guanidine (TMG) and its cyclic analogs were utilized as efficient catalysts [37].

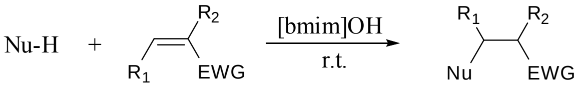
An efficient protocol for Henry reaction using basic ionic liquid [bmim]OH as catalyst and reaction medium was reported (Scheme 18) [85].

Michael Reaction

N-Substituted imidazoles, triazoles, pyrazoles, pyrimidines, purines and their derivatives obtained through Michael addition are usually pharmacologically active and may be applied as potential therapeutic alternatives. Generally these reactions require strong bases or Lewis acids to activate nucleophiles or Michael acceptors. These would lead to environmentally hazardous residues and undesirable side-products. To avoid typical disadvantages resulting from the presence of such a catalyst, a large number of alternative strategies have been developed in the past few years using basic clays, KF/Al_2O_3, guanidine, microwave irradiation and enzyme. Unfortunately, many of these procedures require long reaction times (several days), rigorous reaction conditions or highly dangerous chemicals. Moreover, the use of solvents such as DMSO or DMF is inevitable for some N-heterocycles such as pyrimidines and purines. Generally the catalyst could not be recycled. Thus, development of a fast and facile protocol that could be performed at ambient temperature for the Michael addition of N-heterocycles to α,β-unsaturated

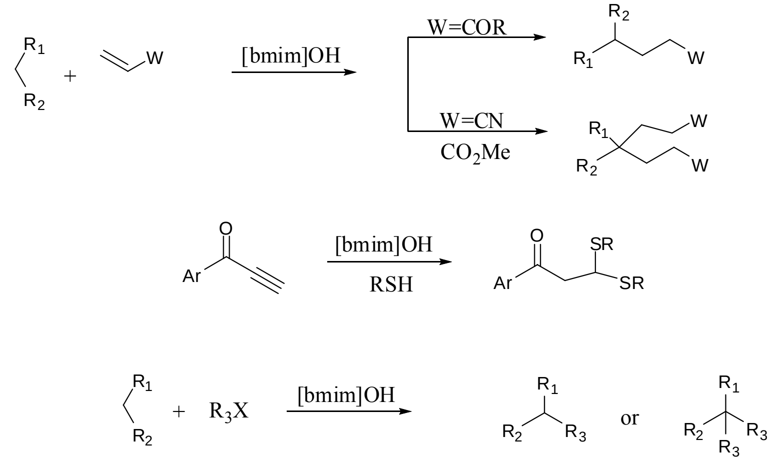


Scheme 18



EWG = CN, COMe, CO_2Me

Scheme 19



Scheme 20

compounds becomes particularly fascinating and remains a great challenge [48].

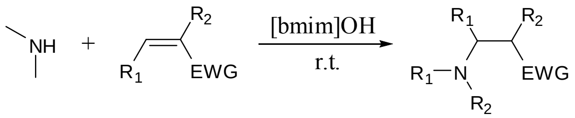
A fast and green protocol for the Michael addition of N-heterocycles to α,β-unsaturated compounds at room temperature was developed using a basic ionic liquid, 1-methyl-3-butylimidazolium hydroxide, [bmim]OH, as a catalyst and a reaction medium (Scheme 19). The reactions were performed at room temperature with good yields in short reaction times (0.5-3 h). This strategy is quite general and it works with a broad range of N-heterocycles, including five-membered N-heterocycles, pyrimidines and purines. The recovered ionic liquid could be reused for several cycles with consistent activity.

The basic ionic liquid 1-methyl-3-butylimidazolium hydroxide, [bmim]OH, catalyzed the Michael addition of active methylene compounds to conjugated ketones, carboxylic esters and nitriles. It further catalyzes the addition of thiols to α,β-acetylenic ketones and alkylation of 1,3-dicarbonyl and -dicyano compounds (Scheme 20). The Michael addition to α,β-unsaturated ketones proceeded in the usual way, giving the monoaddition products, whereas addition to α,β-unsaturated esters and nitriles leaded exclusively to the bis-addition products. The α,β-acetylenic ketones undergo double conjugate addition with thiols produced β-keto 1,3-dithio-derivatives. In the alkylation reaction the acyclic 1,3-diketones were monoalkylated, whereas cyclic ketones undergo dialkylation under identical conditions. This method offered marked improvements with regard to operational simplicity, reaction time, high isolated yields of products, greenness of the procedure, avoiding hazardous organic solvents and toxic catalysts. The ionic liquid was also recycled [86].

The aza-Michael reaction is an important reaction in organic chemistry, especially for the synthesis of C-N heterocycles containing the β-aminocarbonyl functionality, which not only constitutes a component of biologically active natural products but also serves as an essential intermediate in the synthesis of β-amino ketones, β-amino acids and β-lactam antibiotics. Such aza-Michael reactions have generally been promoted by harsh bases or strong acids, which give rise to environmentally hazardous residues and undesirable by-products. With the goal of avoiding the typical disadvantages resulting from the presence of such catalysts, a large number of alternative procedures have been developed in the past few years. Unfortunately, though, many of these procedures require long reaction times, rigorous reaction conditions, large excesses of reagents, and/or highly damaging chemicals. In many cases the catalyst and excess reagents have not been recoverable, which has strongly limited industrial applications. The development of an environmentally benign and simple procedure for aza-Michael addition has thus become particularly fascinating and remains a great challenge.

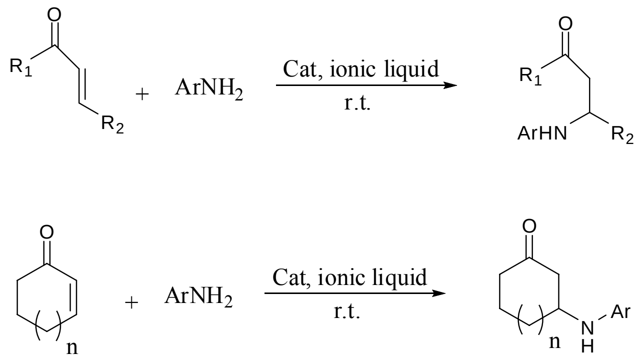
The basic ionic liquid [bmim]OH provided a convenient, clean, efficient, and recyclable catalytic medium for Michael addition reactions between various amines and α,β-unsaturated compounds, thus substituting for volatile organic solvents and toxic catalysts (Scheme 21). Furthermore, the products were distilled directly from the ionic liquid in large-scale reactions, thus totally avoiding the use of any organic solvent. The ionic liquid was reused for at least eight runs without loss of activity, thanks to which it exhibited industrial potential. Furthermore, the ionic liquid was stable during the reaction process [87].

A task-specific ionic liquid, 1,8-diazabicyclo[5.4.0]-undec-7-en-8-ium acetate had been successfully used as a catalyst for aza-conjugate addition of aliphatic or aromatic amines to various electron deficient alkenes under solvent-free conditions and at room temperature (Scheme 22). The catalyst was reused for six times without noticeable loss of activity [72].



EWG=CN, COMe, CO_2Me

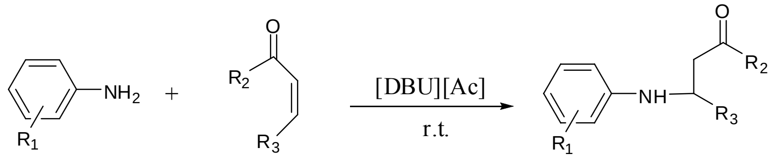
Scheme 21



Scheme 23

A highly efficient [bmim]OH catalyzed the aza-Michael reaction of aromatic amines and N-heterocycles to α,β-unsaturated cyclic and acyclic ketones under solvent-free conditions to produce the desired Michael adducts smoothly (Scheme 23). The process was simple and generated a diverse range of aromatic amino carbonyl derivatives in excellent yields. Furthermore, it was remarkable that the use of an easily accessible and recyclable basic ionic liquid make this procedure as a quite simple, more convenient and environmentally benign [88].

By performing density functional theory calculations, the Michael addition of acetylacetone to methyl vinyl ketone in the absence and presence of the ionic liquid 1-butyl-3-methylimidazolium hydroxide ([bmim]OH) had investigated. In the absence of ionic liquids, acetylacetone was firstly tautomerized to enol form and then take place Michael addition to methyl vinyl ketone. As in the catalyzed Michael addition reaction, a $[bmim]^+OH^-$ ion pair was introduced into

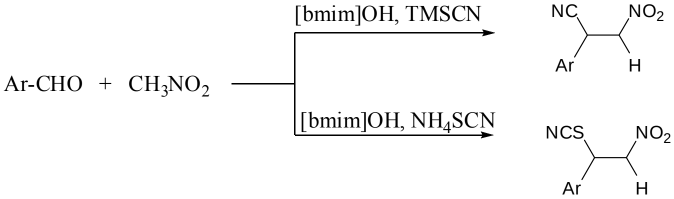


Scheme 22

the reaction system to model the effect of the ionic liquid environment on the reactivity. The calculated results showed that the anion enhanced nucleophilic ability of acetylacetone since the OH^- anion captures a proton to form an acetylacetone anion-H_2O complex, and the cation improved the electrophilic ability of methyl vinyl ketone by forming intermolecular hydrogen-bonds. Both the remarkable effects of the cation and anion on the reactivity of reactants promoted this reaction, which take place more easily compared with uncatalyzed reaction. The calculated results showed that the main product of the Michael addition was in its ketone form [89].

Modern synthetic design demands high efficiency in terms of minimization of synthetic steps together with maximization of complexity. One of the ways to fulfill these goals is the development and use of multicomponent reactions (MCRs) which consist of several simultaneous bond-forming reactions and allow a highly efficient synthesis of complex molecules starting from simple substrates in a one-pot procedure.

The importance of nitroalkanes in organic synthesis is tied up to their propensity to undergo facile a-alkylation reactions and interconversions to other important organic functional groups. Aliphatic nitro compounds have proven to be valuable intermediates, and are powerful synthetic tools because they facilitate the carbon-carbon bond-forming processes. Most importantly, the nitro group can be converted to a carbonyl compound using the Nef reaction. An efficient nitroalkane-mediated cyclopropanation is a key step in the synthesis of β-amino acid analogues of Pregabalin and Gabapentin that target the α_2-σ protein. Hydrocyanation or hydrothiocyanation of nitroalkenes affords straightforward access to nitroalkanes bearing a nitrile or thiocyanate functionality of considerable synthetic utility. The diverse transformations in which nitriles participate place them among the most versatile intermediates in organic chemistry. Furthermore, organic thiocyanates have gained considerable importance in various areas of organosulfur chemistry and are useful scaffolds for the synthesis of various heterocycles, some of which are associated with herbicidal and other important biological activity. Moreover, the thiocyanato group occurs as an important functionality in certain anticancer natural products formed by deglycosylation of glucosinolates derived from cruciferous vegetables.



Scheme 24

A novel and convenient three-component coupling reaction of nitromethane, aromatic aldehydes and trimethylsilyl cyanide (TMSCN) or ammonium thiocyanate had been developed for an expeditious synthesis of β-nitrocarbonitriles or β-nitrothiocyanates, respectively, *via* C-C and C-S bond-forming reactions (Scheme 24). The synthetic protocol strategically involved a one-pot sequential Henry reaction and a Michael addition efficiently promoted by the same ionic liquid [bmim]OH. The main advantages of the present approach included the use of inexpensive simple substrates and an ionic liquid as an efficient reaction promoter for the mild synthesis in a one-pot procedure [90].

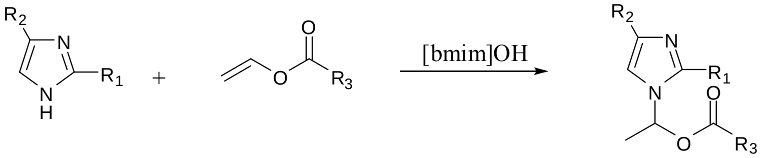
Markovnikov Addition

Markovnikov-type addition is among the most useful carbon-carbon, oxygen-carbon, or nitrogen-carbon bond-forming reactions. It is especially important to synthesize bioactive N-heterocycles derivatives with a nitrogen-carbon linkage, which could be achieved by an addition reaction. This reaction was traditionally promoted by harsh bases, strong acid, or high temperature, which would lead to environmentally hazardous residues and unwanted byproducts. A lot of effort has been made in view of green synthesis [91].

The basic ionic liquid 1-butyl-3-methyl imidazolium hydroxide ([bmim]OH) provided an efficient and convenient protocol for Markovnikov addition of N-heterocycles to vinyl esters without the requirement of any other catalyst and organic solvent (Scheme 25). This strategy was quite general and it worked with a broad range of N-heterocycles as addition substrates, including five-membered N-heterocycles, pyrimidines, and purines. Furthermore, this method exhibited a simple and green procedure, mild conditions, and general applicability and avoids hazardous organic solvent and toxic catalysts [92].

Mannich-Type Reaction

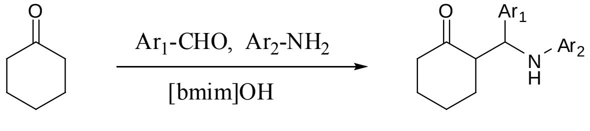
The Mannich-type reactions are very important carbon-



Scheme 25

carbon bond-forming reactions in organic synthesis and have been one of the most basic and useful methods for the preparation of β-amino carbonyl compounds for its use in various pharmaceuticals, natural products, and versatile synthetic intermediates. Mannich reactions have gained popularity in synthetic chemistry over the past decades. The most frequently used promoters like Lewis acid catalysts, Brönsted acid catalysts, Lewis base catalysts, rare metal salt catalysts, and organo catalysts have been reported to catalyze the Mannich reaction. Most of these methods suffer from severe drawbacks including the use of large amount of catalysts, expensive reagents or catalysts, harsh reaction conditions and difficulty in product separation, sometimes long reaction time, and low yield, *etc.* Hence, there is high interest in developing new convenient methods for the synthesis of β-amino carbonyl compounds [93-95].

The basic ionic liquid [bmim]OH catalyzed one-pot Mannich-type reaction for three-component synthesis of β-amino carbonyl compounds (Scheme 26). The ionic liquid, which was environmentally friendly, was recycled at least 5 times without significant loss of activity [95].



Scheme 26

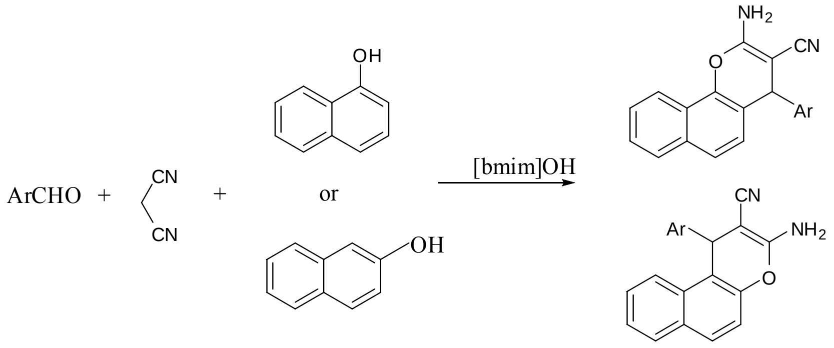
Synthesis of Substituted 2-Amino-2-chromenes

2-Amino-2-chromenes are an important class of compounds found as the main components of many naturally occurring products employed as cosmetics and pigments and utilized as potential biodegradable agrochemicals. Thus the synthesis of 2-amino-2-chromenes is of much importance to organic chemists. These compounds are generally prepared by reacting aldehydes, activated methylene compounds and activated phenols in organic solvents (*i.e.*, ethanol, acetonitrile) and in the presence of organic bases like piperidine, which are frequently utilized in stoichiometric amounts.

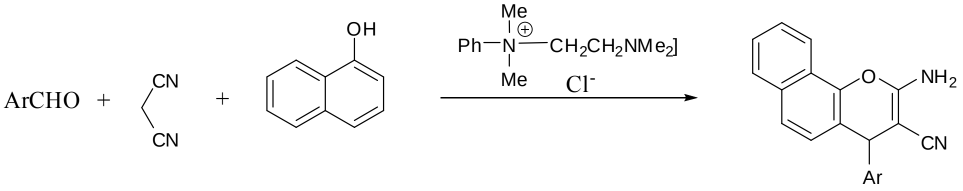
Recently, relatively benign catalysts such as cetyltrimethylammonium chloride (CTACl), montmorillonite KSF clay, KF/Al_2O_3, $TiCl_4$, triethylamine, basic alumina, MgO and NaOH have been used in this reaction. However, the application of some of these methods is limited due to the moderate yields of the products, longer reaction time and laborious workup procedure. Furthermore, some of these catalysts such as MgO can only catalyze the condensation reaction of aromatic aldehydes, malononitrile and α-naphtol not β-naphtol. The development of an environmentally benign and simple procedure for synthesis of 2-amino-2-chromenes has thus become particularly fascinating and remains a great challenge [96-98].

The basic ionic liquid 1-butyl-3-methyl imidazolium hydroxide ([bmim]OH), catalyzed three-component condensation reaction of aromatic aldehydes, malononitrile and α- or β-naphthol proceeded rapidly in water at reflux to afford corresponding 2-amino-2-chromenes in high yields (Scheme 27). The attractive features of this protocol were simple procedure, short reaction time, use of cheap and benign solvent, the reuse of the aqueous media, and its adaptability for synthesis of a diverse set of 2-amino-2-chromenes [2].

A simple, clean, and environmentally benign three-component process to the synthesis of 2-amino-4Hchromenes using N,N-dimethylaminoethylbenzyldimethyl ammonium chloride, $[PhCH_2Me_2N^+CH_2CH_2NMe_2]Cl^-$, as an efficient catalyst under solvent-free condition was described (Scheme 28). A wide range of aromatic aldehydes easily undergo condensations with α-naphthol and malononitrile under solvent-free condition to afford the desired products of good purity in excellent yields. This procedure offered several advantages including mild reaction conditions, cleaner reaction, and satisfactory yields of products, as well as a simple experimental and isolated procedure, which make it a useful and attractive protocol for the synthesis of these compounds [99].



Scheme 27

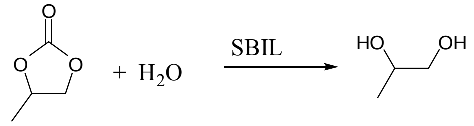


Scheme 28

Hydrolysis of Propylene Carbonate to 1,2-Propylene Glycol

1,2-Propylene glycol is chemicals of acknowledge commercial importance. It can be used in many applications areas such as antifreeze agents, brake fluids, intermediates in the production of pharmaceuticals and fine chemicals, the diol component in the manufacture of polyurethanes and the starting point for the manufacture of poly(propylene glycol)s. Therefore, a number of routes leading to the manufacture of 1,2-propylene glycol, such as the addition of water to 1,2-propylene oxide, the preparation from propene *via* 1,2-diacetoxypropane followed by saponification thereof, the single-stage hydrogenolysis of dihyfroxyacetone, the hydrogenolysis of glycerol and the hydrolysis of propylene carbonate. However, currently all these methods suffered from low selectivity and/or yield of 1,2-propylene glycol, and high pressure and high temperature are required. Development of a method for the manufacture of 1,2-propylene glycol with high selectivity and yield under mild conditions still remains a challenge [100-104].

Hydrolysis of propylene carbonate to 1,2-propylene glycol was performed by using a supported basic ionic liquid (SBIL) catalyst (Scheme 29).

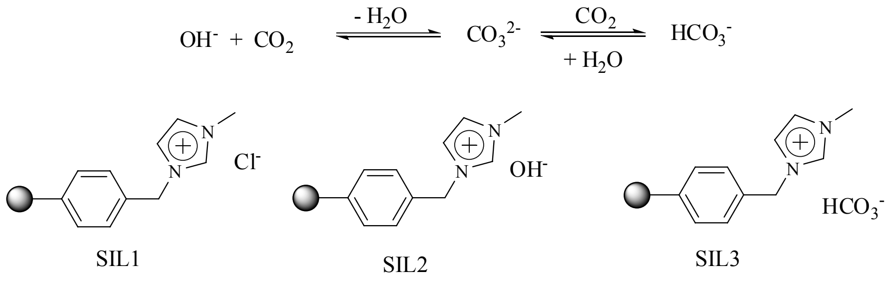


Scheme 29

The activities of different supported ionic liquid were tested for the hydrolysis of propylene carbonate to produce 1,2-propylene glycol. The results show that the SBIL3 exhibits the highest activity. Excellent selectivity (>99%) and yield (>99%) of 1,2-propylene glycol was obtained in the presence of SBIL 3. The activity of SBIL 3 is higher than that of SBIL 2 and a simple hydroxide containing ion exchange resin was probably due to the reaction of OH$^-$, CO_2 and H_2O (Scheme 30) [51].

Synthesis of Oximes

Numerous functional group transformations of oximes make them very important in synthetic organic chemistry. Among other synthesis applications, these compounds were successfully transformed into nitriles, amides, nitro compounds amines, *etc*. Therefore, synthetic organic chemists are interested in a facilitation of oxime synthesis. The classical method for preparing oximes is the reaction of an aldehyde or ketone with hydroxylamine hydrochloride in an alcoholic solution, under reflux temperature, and in the presence of sodium acetate or pyridine. The latter method is the most used, especially for the oximation of hardly soluble ketones and



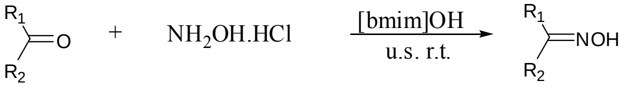
Scheme 30

steroidal ketones. However, pyridine presents some limitations since this base is highly flammable, and harmful by inhalation and in contact with skin. To avoid typical disadvantages resulting from the presence of such a catalyst, a large number of alternative strategies have been developed in the past few years using alumina, silica gel coupled with microwave irradiation, TiO_2/SO_4^{2-} without solvent, supported-POM and Na_2SO_4. These methods all have their own merits and shortcomings. Some methods are not very satisfactory due to drawbacks such as low yields, high reaction temperature, long reaction time and effluent pollution. Recently, high yield of hydroxyiminocycloalkanes could be achieved by treatment of the corresponding ketones with hydroxylamine or its salts in ionic liquids and in the presence of additives, such as sodium acetate. However, the substrate is limited on cyclohexanone only [105-108].

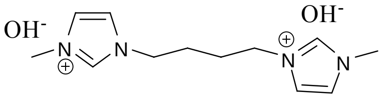
The basic ionic liquid 1-butyl-3-methylimidazolium hydroxide, [bmIm]OH, efficiently catalyzed the condensation reaction of aldehydes and ketones with hydroxylamine hydrochloride under ultrasound irradiation (Scheme 31). Compared with conventional methods, the main advantages of the present procedure were milder conditions, shorter reaction time and higher yields [109].

Synthesis of Flower-Like ZnO

ILs can act as morphology templates for the synthesis of inorganic materials with novel or improved properties. Various nano- or micro-structured materials, such as Bi_2S_3 nanostructures, Bi_2Se_3 nanosheets, and hollow TiO_2 micro-spheres have been recently synthesized in ILs. There have been few reports on the preparation of ZnO micro-flower in ILs. ZnO, a wide band gap semiconductor with large excitation binding energy, possesses unique properties. The size and morphology of ZnO nano-particles have great influences on their performances. Because the properties of nano-materials depend on their size and shape, new synthetic strategies in which the size and shape of nanostructures can be easily tailored are important. Wurtzite-type ZnO crystals are used for a wide variety of industrial applications, such as varistors, semiconductors, catalysts, room-temperature UV lasers, light-emitting diodes, solar cells, and sensors. Several techniques are used for preparation of Wurtzite-type ZnO crystals. Among them, hydrothermal synthesis is becoming popular for environmental reasons [110-111].



Scheme 31



Scheme 32

Flower-like ZnO morphology, with different shapes, had been successfully synthesized via a novel and environment-friendly hydrothermal method using zinc acetate and a task specific dicationic dibasic ionic liquid, $[mmpim]_2[OH]_2$ (Scheme 32), which played an important role in fabrication of ZnO structure [112].

Synthesis of Quinazoline-2,4(1H,3H)-diones

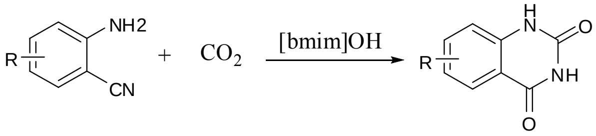
Quinazoline-2,4(1H,3H)-diones are important intermediates in the pharmaceutical industry as a key building blocks in the synthesis of FK 366 (Zenarestat) and KF 31327 molecules. FK 366 (Zenarestat), which functions as an aldose reductase inhibitor and also useful as a remedy for complication of diabetes mellitus. KF 31327 was developed as a remedial drug for heart disease and as an impotence medicine.

The 6,7-dimethoxyquinazoline-2,4(1H,3H)-dione derivatives are useful building blocks in the synthesis of alpha adrenergic receptor antagonists such as Prazosin (Minipress1), Bunazosin (Detantol1) and Doxazosin (Cardenalin1) and are also useful as anti-hypertensive. Several synthetic methodologies exists for the preparation of quinazoline-2,4(1H,3H)-diones, *i.e. via* reaction of anthranilic acid with urea, anthranilamide with phosgene and anthranilic acid with potassium cyanate or chlorosulfonyl isocyanate. However, the scope of these methodologies for the preparation of quinazoline-2,4(1H,3H)-diones are often limited by the requirement for specialized reagents, and operational complexity due to the use of either toxic or cumbersome reagents like-phosgene.

Few efforts were made to replace toxic reagents using incorporation of CO_2 into quinazoline-2,4(1H,3H)-diones derivatives. However, most of these reports have drawbacks like the high catalyst loading, lower substrate compatibility, use of organic solvents and the use of non-recyclable homogeneous base, which limits their application. There was sufficient scope for the development of an active and recyclable base catalyst for this transformation (Scheme 33). Hence, considering the economical value of the quinazoline-2,4(1H,3H)-diones derivatives still there was need to develop a truly catalytic and environmentally viable protocol which can minimizes the number of unit operations and waste streams [113].

Feist-Benary Reaction

The Feist-Benary (FB) reaction is a very useful reaction for the construction of highly substituted furan derivatives *via* condensation of β-dicarbonyl compounds with α-haloketones in the presence of a base. If this reaction is stopped at the hydroxydihydrofuran stage using a milder base, it is called the ‘Interrupted Feist-Benary’ (IFB) reaction. The IFB reaction is important for an easy access to substituted dihydrofurans which are constituents of many natural products arising from plants and marine organisms with promising biological activities. However, only a limited number of methods are available for FB and IFB reactions [114-115].

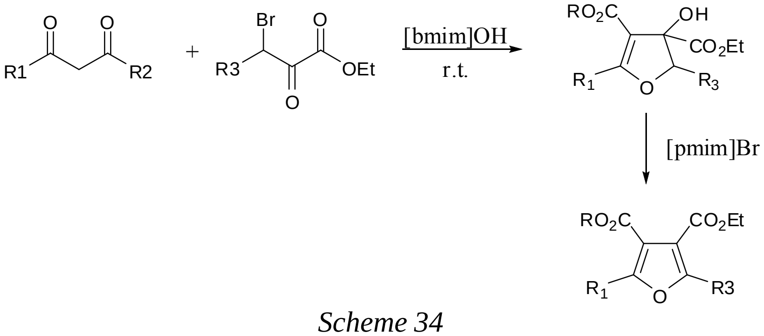


Scheme 33

The basic ionic liquid, 1-butyl-3-methylimidazolium hydroxide promoted the interrupted Feist-Benary reaction at room temperature under organic solvent-free conditions to produce a variety of substituted hydroxydihydrofurans. The hydroxydihydrofurans were converted to furans (Feist-Benary products) using the ionic liquid, 1-methyl-3-pentylimidazolium bromide at 70-75 ºC (Scheme 34). The significant advantages offered by this procedure were room temperature operation, considerably fast reaction, high yields and excellent cis stereoselectivity for the IFB products [116].

Glycolysis of Poly(ethylene terephthalate)

Poly(ethylene terephthalate) (PET) is a thermoplastic polyester with excellent tensile and impact strength, chemical resistance, clarity, processability, transparency, and appropriate thermal stability. Tremendous quantities of this material are consumed in the manufacture of video and audio tapes, X-ray films, food packaging, and especially of soft-drink bottles. With the widespread use and increasing consumption of PET, the amount of waste PET is growing rapidly. Although this kind of polyester does not create a direct hazard to the environment, it does not decompose



Scheme 34

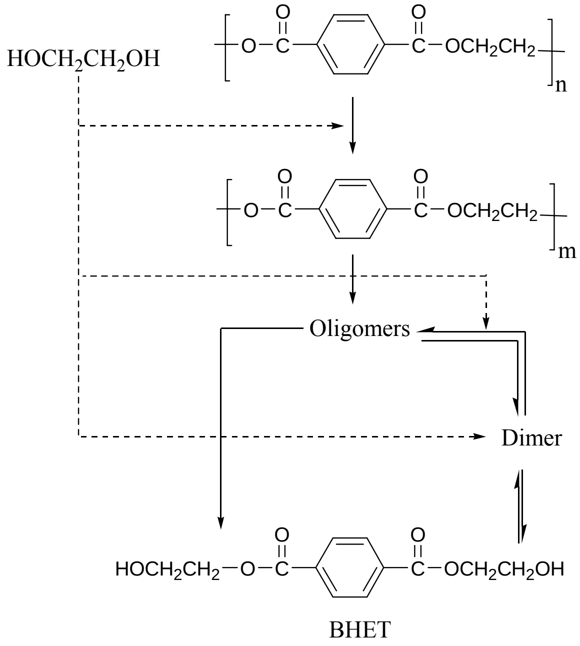
readily in nature. Thus, the effective recycling of PET wastes for the preservation of resources and protection of the environment has received considerable attention. PET wastes can be converted by mechanical methods into extruded or molded articles, whose properties are inferior to those of the original. PET decomposition and its conversion into reusable chemical products becomes one of the important recycling strategies for this material.

Several processes for PET depolymerization have been put forward, such as alcoholysis process with methanol, glycolysis with ethylene glycol or other glycol, and hydrolysis under the promotion of acidic or basic conditions. Alcoholysis to dimethyl terephthalate (DMT) with liquid or gaseous methanol has the obvious disadvantage of volatilization of methanol. The glycolysis process involves the insertion of a diol into PET chains to give bis(hydroxyethyl) terephthalate (BHET), which is easily integrated into conventional PET products. The main drawback of this process is that the reaction products are not discrete chemicals but BHET along with higher oligomers, which are difficult to purify with conventional methods [117-118].

Hydrolysis of PET under acidic or basic conditions gives terephthalic acid (TPA), along with corrosion and pollution problems. Since glycolysis of PET can produce the BHET monomer, which has been widely used in the production of unsaturated polyesters and rigid or flexible polyurethanes.

Various kinds of catalysts, such as titanium-phosphate, metal acetate, and solid super acids are required to facilitate the process. Although these catalysts are effective in the glycolysis of PET, it is difficult to separate the catalysts from the products, as illustrated in the literature. Thus, the catalysts could not be recycled and reused, and the purity as well as application fields of the depolymerization products will be seriously threatened.

The glycolysis of PET was catalyzed by different kinds of ionic liquids at atmospheric pressure (Scheme 35). Results showed that basic ionic liquids (3-amino-propyl)-tributyl phosphonium glycine ([3a-$C_3P(C_4)_3$][Gly], (3-amino-propyl)-tributyl-phosphonium alanine [3a-$C_3P(C_4)_3$][Ala]) and neutral ionic liquids 1-butyl-3-methylimidazolium chloride ([bmim]Cl, 1-butyl-3-methylimidazolium bromine [bmim]Br) accelerated the glycolysis process. But when acidic ionic liquids ([bmim]H_2PO_4, [bmim]HSO_4) were used the conversion of PET was diminished. The catalytic effect of basic ionic liquids was desirable and the conversion of PET could reach 100%. However, this kind of ionic liquids was quite complex to synthesize and price of the materials was very high. Neutral ionic liquids, which also had good catalytic effects and appropriate price, became the alternative [71].



Scheme 35

Synthesis of Hydrofluoroether

Hydrofluoroethers (HFEs) have been considered as the most promising candidates for refrigerants, cleaning solvents, and blowing agents to replace chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), due to their zero ozone depleting potential, low global warming potential, and favorable physical and chemical properties including low surface tension, nonflammability, and excellent solvating ability. HFEs have also been regarded as an important class of fluorinated organic compounds for many potential applications: heat transfermedia, particulate removal and carrier fluids, buffing abrasive agents, displacement drying agents, power cycle working fluids, and clinical usages [119-120].

Numerous methods have been reported to produce HFEs including the fluorination of ether with F_2 or metal fluoride,

$$\underset{1}{CF_3CH_2OH} + \underset{2}{CF_3CF{=}CF_2} \longrightarrow CF_3CH_2OCF_2CHFCF_3 \quad 3$$

$$+$$

$$CF_3CH_2OCF{=}CFCF_3 \quad 4, 5 \text{ (cis and trans)}$$

$$+$$

$$CF_3CH_2OCF_2CF{=}CF_2 \quad 6$$

$$4, 5 + CF_3CH_2OH \longrightarrow CF_3CH_2OCF_2CHFCF_2OCH_2CF_3 \quad 7$$

$$6 + CF_3CH_2OH \longrightarrow (CF_3CH_2O)_2CFCHFCF_3 \quad 8$$

Scheme 36

the electrochemical fluorination of ether, and the alkylation of acyl halides using a sulfonic acid ester as an alkylating agent in the presence of anhydrous KF. However, these methods suffer from either the low product selectivity or the difficulty in handling the hazardous and reactive raw materials. HFEs can also be obtained from the hydroalkoxylation reaction of commercially available fluorinated olefins (tetrafluoroethylene and hexafluoropropylene) in the presence of a base catalyst or free radical initiator, but these methods either require long reaction time or produce relatively large amounts of unsaturated HFEs were always co-produced, which are difficult to remove by distillation due to the closeness in boiling points between saturated and unsaturated HFEs.

Ionic liquids such as 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF_4) and 1-ethyl-3-methylimidazolium hexafluorophosphate ([Emim]PF_6) were also employed as catalysts and reaction media for the hydroalkoxylation of fluoroolefins, but the yields of HFEs were not high even at elevated temperatures and long reaction time, possibly due to the lack of basicity of [Emim]BF_4 and [Emim]PF_6. Since base catalysts such as NaOH and KF are known to be highly active for the hydroalkoxylation of fluoroolefins, it is easily conceivable that a basic ionic liquid could proceed the hydroalkoxylation more effectively than the neutral ionic liquids, [Emim]BF_4 and [Emim]PF_6. It is also expected that the unique properties of ionic liquids could suppress the formation of olefinic side products.

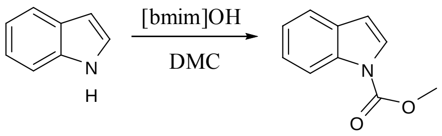
A hydrofluoroether, one of the third generation chlorofluorocarbon (CFC) alternatives, $CF_3CH_2OCF_2CHFCF_3$ was obtained in high yield and selectivity from the hydroalkoxylation reaction of hexafluoropropylene and 2,2,2-trifluoroethanol conducted in the presence of an imidazolium-based ionic liquid catalyst such as 1-butyl-3-methylimidazolium acetate, 1-butyl-3-methylimidazolium bicarbonate, or 1-butyl-3-methylimidazolium carbonate. Structures of the products from the hydroalkoxylation of HFP with TFE are shown in (Scheme 36) [121].

N-Heterocyclic Carbomethoxylation

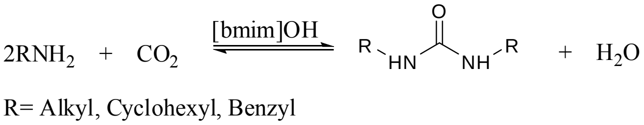
Carbamates are very important materials in the fields of medicine and agriculture. They are also frequently used as protecting groups in organic synthesis. Conventionally, carbamates are mostly synthesized using phosgene or its derivatives and catalyzed by stoichiometric strong bases. However, phosgene or its derivatives are extremely toxic reagents. Obviously, these procedures are not environmentally benign. On the other hand, strong bases restrict the use of substrates containing certain functional groups, and are difficult to be recycled. To avoid these drawbacks, numerous studies on carbamates synthesis have been investigated [122].

Many efforts are currently being turned to the utilization of dimethyl carbonate (DMC) as a carbomethoxylating reagent DMC is considered as a safe, nontoxic and eco-friendly reagent. DMC molecule contains several active basic groups, such as CH_3-, CH_3O-CO-, -CO- group; therefore, it has been used in carbonylation, carbomethoxylation and methylation reactions to substitute phosgene, methyl halides, *etc.* [123-126].

A procedure for the synthesis of N-heterocyclic carbamates from N-heterocycles and dimethyl carbonate catalyzed by ionic liquids was investigated (Scheme 37). These ionic liquids had high catalytic activities under mild reaction conditions. Furthermore, ionic liquids was recycled by simple extraction and reused at least four times without any loss of activity. The activation of carbonyl group of DMC taken by the hydrogen bond interaction between imidazolium cation and the carbonyl oxygen played a dominating role in



Scheme 37



Scheme 38

catalyzing the reaction of indole and DMC [127].

Synthesis of Substituted Ureas

The synthesis of disubstituted ureas from amines and CO_2 were carried out using a basic ionic liquid (IL) 1-n-butyl-3-methyl imidazolium hydroxide ([bmim]OH) as the catalyst (Scheme 38). The effects of reaction time, amount of [bmim]OH, reaction temperature, pressure, and solvent on yields of the products were investigated. The results indicated that aliphatic amines, cyclohexylamine, and benzylamine were converted to the corresponding ureas selectively in moderate yields under solvent-free conditions without using any dehydrating regent. The ionic liquid was reused after a simple separation procedure [128].

Syntheses of Heterocyclic Compounds and Tetra-substituted Pyrroles

Pyrrole is one of the most important heterocyclic compounds, having become increasingly important in medicinal chemistry and organic synthesis. Consequently, numerous procedures have been developed for the construction of pyrroles. However, some of these methods often suffer from certain drawbacks such as hazardous organic solvents, high cost, long reaction time, use of stoichiometric and even excess amounts of acids because they can be trapped by amine in this condensation, and drastic reaction conditions. Therefore, the development of facile and environmentally benign methods for synthesis of pyrroles is a necessary part of organic synthesis [129-130].

Synthesis of tetrasubstituted pyrroles by the three component condensation reaction of acid chlorides, dialkyl acetylenedicarboxylates, and amino acids in the presence of various room-temperature ionic liquids (RTILs) as catalysts in water was reported. Among the ionic liquids used, the basic functionalized ionic liquid, butyl methyl imidazolium hydroxide [bmim]OH, was the most effective catalyst. The [bmim]OH/H_2O catalyst system was reused for at least five recycles without appreciable loss of efficiency. The attractive features of this protocol were: simple procedure, short reaction time, use of cheap and environmentally benign solvent, and reuse of the aqueous media [131].

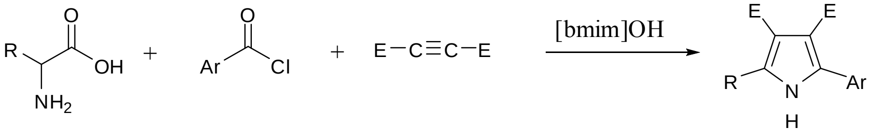
Synthesis of Highly Functionalized Pyrroles

Task-specific basic ionic liquid was used as a reusable and green catalyst for one-pot synthesis of highly functionalized pyrroles in aqueous media (Scheme 39) [132].

Synthesis of 4*H*-Benzo[*b*]pyran

In recent years, 4H-benzo[b]pyran compounds have attracted much attention due to their wide range of biological and pharmacological activities. It has been reported that benzo[b]pyran derivatives have diverse pharmacological activities such as anticoagulant, anticancer, spasmolytic, antiancaphylactia, *etc*. In addition, 4H-benzo[b]pyrans also constitute the structural unit of a series of natural products.

Considering the importance of these compounds, many methods for the synthesis of 4Hbenzo[b]pyran derivatives have been reported successively. The conventional synthesis involves the condensation of 5,5-dimethylcyclohexane-1,3-dione (dimedone) with aromatic aldehyde and malononitrile under refluxing DMF or acetic acid. However, these solvents make the workup procedure complicated, lead to poor yields of products, and pollute the environment. The use of microwave and ultrasound irradiation is also reported for the



Scheme 39

synthesis of pyrans.

Recently, many methods had been reported for the preparation of 4H-benzo-[b]pyrans through two-component or three-component condensation including the use of 4-dodecylbenzenesulfonic acid, rare earth perfluorooctanoate (RE(PFO)$_3$), $(NH_4)_2HPO_4$, NaBr, tetramethyl ammonium hydroxide N-methylimidazole, (S)-proline, *etc*., as catalysts had been introduced for the synthesis of 4Hbenzo[b]pyrans. In spite of the merits of these procedures, each of them suffered at least from one of the following limitations: low yields, unavailability of the reagents, long reaction times, effluent pollution, harsh reaction conditions, and tedious workup procedures [133-134].

A simple, clean, and environmentally benign three-component process for the synthesis of 4H-benzo[b]pyran derivatives using basic ionic liquid N,N-dimethyl aminoethylbenzyldimethylammonium chloride ($[PhCH_2Me_2N^+CH_2CH_2NMe_2]Cl^-$) as an efficient catalyst under solvent-free condition was described (Scheme 40). A wide range of aromatic aldehydes easily undergoes condensation with malononitrile and 5,5-dimethylcyclohexane-1,3-dione (dimedone) under solvent-free condition to afford the desired products of good purity in excellent yields. Taking into account environmental and economical considerations, the protocol presented here had the merits of environmentally benign, simple operation, convenient workup, and good yields [135].

Synthesis of Tetrahydrobenzo[b]pyran Derivatives

The task specific basic ionic liquid, [bmim]OH promoted efficient, green and one-pot synthesis of tetrahydro-benzo[b]pyran derivatives (Scheme 41). The ionic liquid acted both as catalyst and reaction medium and was reusable up to five times without loss of activity [136].

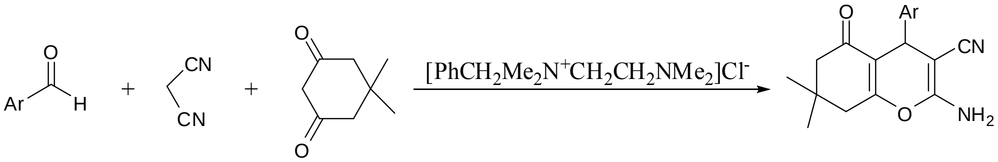
Hydrogen-Transfer Reduction

Asymmetric transfer hydrogenation of prochiral ketones and imines is an effective method for preparation of optically active alcohols or amines. The most famous catalysts for asymmetric hydrogen-transfer reaction are Ru(arene)(diamine) complexes with chiral ligands. In particular, a ruthenium catalyst with a chiral ligand such as mono N-tosylated diphenylethylenediamine (TsDPEN; Noyori's catalyst) has been well studied on a variety of substrates [137-139].

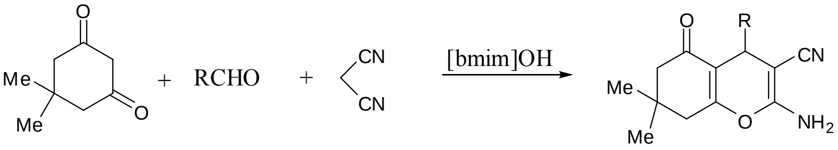
Attempts to improve the handling and separation of the catalyst from the reaction product, and its recycling, have led to immobilization of this catalytic system on a variety of supports, either inorganic or organic. Noyori's catalyst has been immobilized on supports such as dendritic polymers, silica, polystyrene, or, with hydrophilic function, for biphasic catalysis. Noyori's ligand can be immobilized on an ionic liquid moiety by introduction of imidazolium tags either at the complexed arene or at the tosyl group.

Although application of ILs in organic synthesis and catalysis is a very active area of chemistry, few papers report use of ILs for hydrogen-transfer reactions.

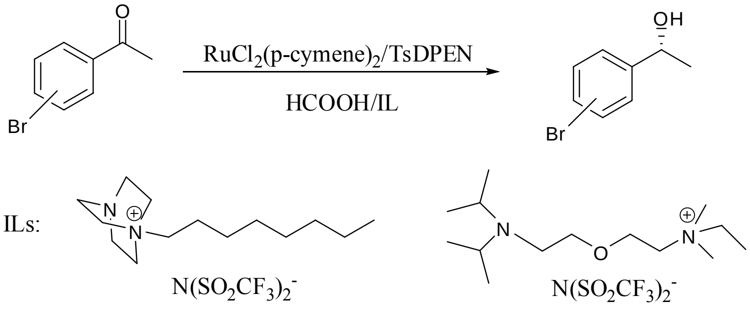
Several achiral and chiral basic ionic liquids (ILs) were prepared and tested as the medium for Ru-catalyzed hydrogen-transfer reduction of different aromatic ketones (Scheme 42). Hydrogen-transfer reduction of ketones proceeded well in achiral basic ILs using chiral catalysts. The interesting observation was made that raising the reaction temperature did



Scheme 40



Scheme 41



Scheme 42

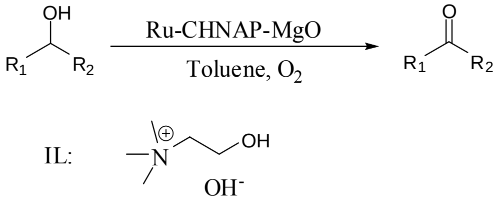
not have a negative effect on enantioselectivity of the reaction. On the other hand no reaction was observed in chiral ILs. Hydrogen-transfer reductions of acetophenones in basic ILs proceed with comparable enantioselectivity as in neutral or acidic ILs, but with lower reaction rate. This means the only advantage of basic ILs as the reaction medium in this reaction was that no external base had to be used, which was beneficial environmentally [49].

Oxidation

The selective oxidation of alcohols to carbonyl compounds is the foundation of many important industrial and fine-chemical processes. Many stoichiometric oxidants are known for the oxidation of alcohols such as chromates, hypochlorites, permanganates, and others, however many of these oxidants are toxicand produce large amounts of wastes [140-141]. Much attention is being directed to newer and selective methods of oxidations. Catalytic oxidation with molecular oxygen or air is particularly attractive from economical and environmental points of view.

The design of nanobuilding units consisting of functional metals generates a new class of high performance materials with potential applications in the electronics, space, chemical and energy sectors.

The selective oxidation of various alcohols into their corresponding aldehydes and ketones was achieved by ruthenium species stabilized on the nanocrystalline magnesium oxide (NAP-MgO) by the incorporation of choline hydroxide, a basic ionic liquid, in excellent yields (Scheme 43). The procedure was simple, efficient and environmentally benign. The catalyst was used for four cycles with almost consistent activity [142].

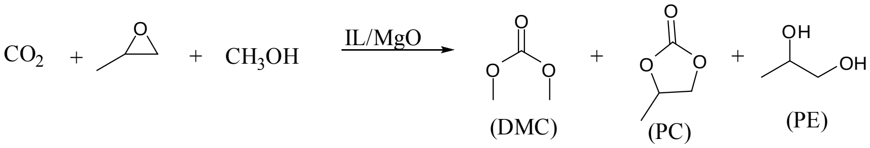


Scheme 43

Synthesis of Dimethyl Carbonate

Dimethyl carbonate (DMC) is a green chemical that has been paid too much attention in recent years. It can be effectively used as an environmentally benign substitute for highly toxic phosgene and dimethyl sulfate in carbonylation and methylation reaction, as monomer for several types of polymers and an intermediate in the synthesis of pharmaceutical and agricultural chemicals. Also, DMC can be used as a promising octane booster due to its high oxygen content. Currently, DMC is produced by phosgene and non-phosgene route, but phosgene route is limited for the use of toxic phosgene. For the non-phosgene route, DMC is mainly prepared by the oxidative carbonylation of methanol and the two-step transesterification from epoxide, methanol and CO_2 in the bulk production. However, the oxidative carbonylation of methanol suffers from the low production rate, the need for corrosion resistant reactors, the toxicity and potential explosion of carbon monoxide.

Several catalysts, such as inorganic base composites and/or basic metal oxide, $Re(CO)_5Cl/K_2CO_3$, KOH/4A molecular sieve, $n\text{-}Bu_4NBr/n\text{-}Bu_3N$, $[bmim]/BF_4$, Mg containing. Smectite, heterogeneous anion exchange resins and inorganic base/phosphonium halide functionalized polyethylene glycol *etc*. have been employed for the one-pot synthesis of DMC.



Scheme 44

But, most of these systems suffer from several drawbacks such as lower activity and selectivity to DMC, difficult recycle of these catalysts and rigorous reaction conditions from a practical point of view.

The basic ionic liquid choline hydroxide, supported on MgO to form Choline hydroxide/MgO material used as a catalyst in one-pot synthesis of dimethyl carbonate from propylene oxide, methanol and carbon dioxide (Scheme 44). A good catalytic performance was obtained with 98% conversion of epoxide and selectivity of above 90% to DMC + PC over the composite catalyst. However, the catalyst was reused three times without a significant change in its catalytic activity [73].

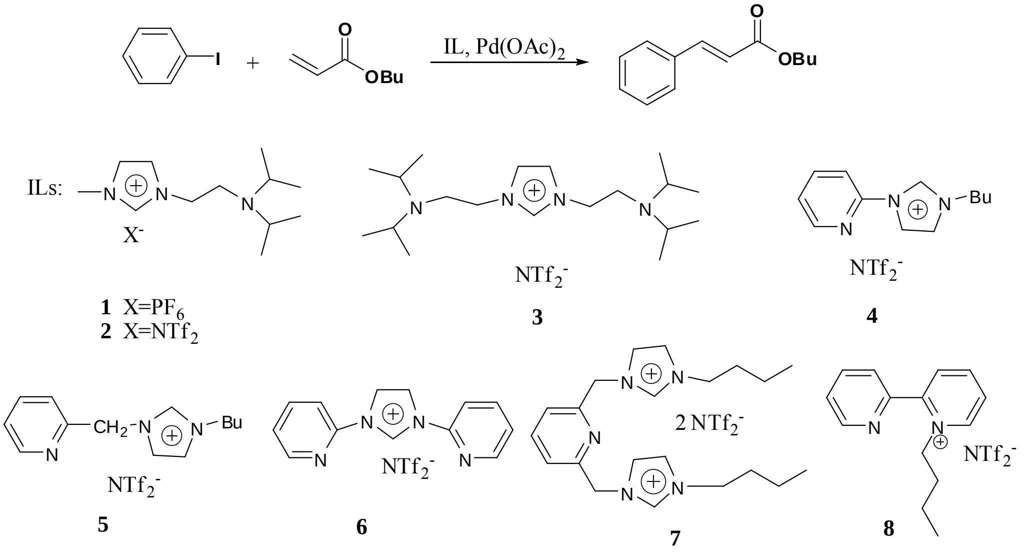
Carbon-Carbon Bond Formation Reactions

The Heck reaction has been studied extensively in ionic liquids, where Pd^{II} complexes or Pd^0 nanoparticles act as catalysts. Catalytic cycle of palladium colloids described in Heck reactions: a palladium precursor can act as a reservoir for a catalytically active Pd^0 species (Pd colloids or highly active forms of low coordinated Pd^0 species) that undergoes oxidative addition of the aryl halide on the surface with subsequent detachment to generate a homogeneous Pd^{II} species. The main catalytic cycle is initiated by oxidative addition of iodobenzene to the Pd^0 species, which is followed by the reversible coordination of the olefin to the oxidative addition product. The Pd^0 formed in the main catalytic cycle, after β hydride and reductive elimination steps, can either continue in the catalytic cycle or fall back to the nanoparticles reservoir [143].

In these cases, a base, such as K_2CO_3, $NaHCO_3$, NaOAc, triethylamine, or tetrabutylammonium acetate, *etc.*, must be added. Although the consumption of one equivalent of base is inevitable, a basic ionic liquid acting as both the solvent and base would make the procedure much easier to handle. This is essentially important for Sonogashira reactions where normally a large excess of organic base, *e.g.* triethylamine, DBU, or piperidine, is required, which causes an additional environmental burden. Moreover, ionic liquids have been proven to be excellent media for syntheses of nanoparticles, nanorods, and nanowires, whose preparation include chemical reduction of transition-metal salts with various reagents, *e.g.*, hydrogen, hydrazine, borohydrides, or alcohols, in the presence of stabilizers, such as special ligands, polymers, or surfactants of the type $R_4N^+X^-$. There are few reports where amines are used as reducing agents.

Basic ionic liquid serve as both the solvent and base for Heck, “copper-free” Sonogashira reactions, and for homocoupling reactions of terminal alkynes. The ionic liquids with tertiary aliphatic amines are effective solvents for these reactions. Under reflux conditions, eight equivalent basic ionic liquids and $Pd(OAc)_2$ in THF or acetone produced palladium colloids with diameters of (2.6 ± 0.3) or (3.7 ± 0.5) nm, respectively.

The Heck reaction of iodobenzene and butyl acrylate was conducted in ionic liquids **1-8** at 110 °C with the use of 1 mol-% palladium acetate as the catalyst (Scheme 45). After eight hours, almost quantitative conversions and selectivity were found when ionic liquids **1**, **2**, and **3** were used as solvents. The reaction became much slower with the use of **5** or **7**, whereas no reaction occurred in **4**, **6**, or **8**, where the nitrogen base was weaker. These results indicated that for Heck reactions the ionic liquids having aliphatic tertiary amine pendants were superior to the ones substituted with pyridine functionality. The catalytic system described above was readily recovered for further use simply by washing with a $NaHCO_3$ solution. After five recycles, no obvious loss in catalytic activity was observed. By using **3** and **5**, owing to their strong affinity for the product, a lengthy procedure was required to extract the product totally from the ionic liquid phase. Because **2** was a liquid with low viscosity at room temperature, it was chosen as the solvent for C-C bond formation reactions, *e.g.* Heck and Sonogashira reactions, and



Scheme 45

Knoevenagel condensations [50].

Decontamination Reactions

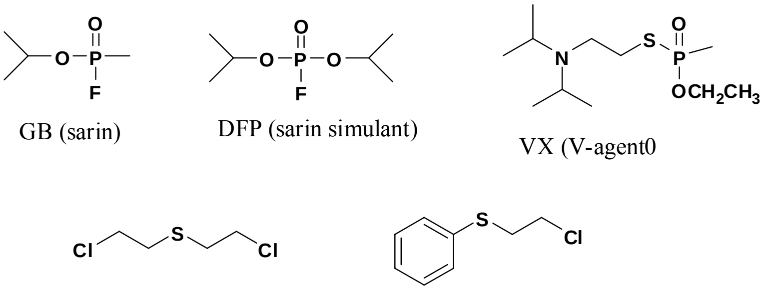
Despite the greatly reduced threat of Cold War superpower confrontation, the threat of chemical, biological, radiological, and nuclear attack remains serious and credible. There is now renewed interest to develop biological and chemical reaction systems to neutralize a variety of chemical warfare agents (CWAs). These interests center on establishing rapid and reliable decontamination processes for the nerve agents Sarin (GD) and VX and for the blister agent sulfur mustard (HD). Established criteria asserted that, for a decontamination/neutralization process to be effective, it must be rapid, generate nontoxic reaction products, and be contained in a medium that is environmentally safe [144].

Increased acts of international terrorism called for the development of rapid and reliable chemical agent decontamination reactions to minimize human exposure and material loss. Even though many chemical reaction processes had been reported, most remain unattractive for various reasons. The chemical warfare agent simulants diisopropylfluorophosphate (DFP), bis(2-ethylhexyl) phosphate (BEHP), and CEPS were readily decontaminated in a single reaction matrix comprising a binary ionic liquid solvent composed of 1,2-dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl) amide and a tetraalkylammonium hydroxide hydrate and an alcohol. Chemical warfare agents and simulants show in Scheme 46.

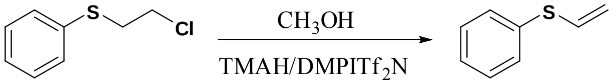
The decontamination reactions occurred rapidly resulting in alcoholysis, hydrolysis, and dehydrohalogenation processes. These preliminary results suggested that alcoholic solutions of tetraalkylammonium hydroxide hydrates in ionic liquids was provide a multipurpose chemical warfare agent decontamination reaction matrix that was very effective, did not involve aqueous systems, and produced reaction products that was isolated from the environmental Base-catalyzed dehydrohalogenation of CEPS show in Scheme 47 [145].

O-Acetylation of Alcohols and Carbohydrates

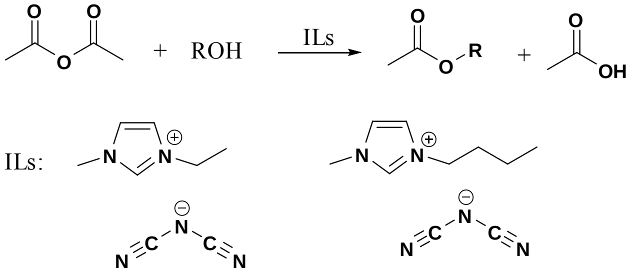
Hydroxy group O-acetylation is used extensively in carbohydrate chemistry as a protection strategy, and for the isolation and identification of sugars. The standard O-acetylation reaction uses acetic anhydride as the primary reagent and a wide range of solvents and catalysts. Pyridine is the most widely used solvent/catalyst for the acetylation of saccharides even though it is known to have acute toxicity. Derivatives of pyridine such as 4-(dimethylamino)pyridine and 4-(1-pyrrolidino)pyridine also catalyze the acetylation, in some cases faster than pyridine. Sodium acetate is also commonly used as a catalyst in the acetylation of D-glucose it yields exclusively the diacetylated product. Other reagents that have been shown to catalyze acetylation of saccharides by



Scheme 46



Scheme 47



Scheme 48

acetic anhydride include: Lewis/Brönsted acids such as $ZnCl_2$, $HClO_4$, $FeCl_3$, H_2SO_4, iodine, heterogeneous catalysts such as tetrabutylammonium bromide-NaOH, anionic surfactants, Montmorillonite K-10, H-beta zeolite, zirconium sulfophenyl phosphonate and enzyme catalysts such as lipases. A variety of other reagents used to catalyze O-acetylation of alcohols are also known [146].

Basic ionic liquids used as catalysts in the context of the base catalyzed acetylation of alcohols including glucose. This was a widely used means of protecting alcohol groups which is conventionally performed using acetic anhydride and a base catalyst in a traditional solvent. There were a wide range of solvents and catalysts commonly utilized for the O-acetylation reaction of carbohydrates; for example pyridine was a commonly used solvent/catalyst, despite considerable safety concerns.

Dicyanamide-based ionic liquids behaved as effective solvents and also as active base catalysts in the O-acetylation reactions of alcohols and carbohydrates using acetic anhydride (Ac_2O), with no additional base catalyst in some cases (Scheme 48). They were low-viscosity solvents that dissolve a wider range of inorganic and organic compounds including unprotected saccharides as compared to other imidazolium ionic liquids with bis(trifluoromethanesulphonyl)amide [Tfsa], Cl^-, PF_6^- and BF_4^- anions.

A number of simple alcohols such as 2-naphthol and t-butyl alcohol were readily acetylated using a dicyanamide ionic liquid and acetic anhydride, even in the absence of any other catalyst. Polyhydroxylated compounds such as N-acetylneuraminic acid, sucrose and raffinose were also completely acetylated within 24 h at room temperature. An increase in the reaction temperature is expected to speed up the reaction rate for the complex saccharides by increasing their solubility in the ionic liquids [52].

Absorption of Sour Gases

From the wide range of applications envisioned for ionic liquids, such as catalysts for acid-catalyzed organic reactions, hydrosilation processes, lubricants, performance additives, media for metal-catalyzed reactions, their use as CO_2-selective separation media for capture/sequestration of sour gases like CO_2, H_2S and SO_2 was one of the most exciting and of increasing interest.

The development of improved, highly efficient and economically viable separation and storage processes was gaining a special interest both by academia and industry. Nonetheless, and despite of the promising properties of ionic liquids, further research was required in order to make this neoteric solvents feasible candidates for these applications.

Being a key parameter in the design of equilibrium stage-and rate-based separations, reliable gas solubility data was of great interest and a fundamental step towards the development of industrial applications, either by the data itself or by developing predictive and simulation tools to aid in such applications development. The absorption of sour gases was one of the processes that were enhanced by the basic character of the ionic liquid [46].

Gas Storage

Many processes in the semiconductor industry require a reliable source of process gases for a wide variety of applications. Often these gases are stored in cylinders or vessels and then delivered to the process under controlled conditions from the cylinder. The semiconductor manufacturing industry, for example, used a number of hazardous specialty gases such as phosphine (PH_3), arsine (AsH_3), and boron trifluoride (BH_3) for doping, etching, and thin-film deposition. These gases pose significant safety and environmental challenges due to their high toxicity and pyrophoricity (spontaneous flammability in air). In addition to the toxicity factor, many of these gases are compressed and liquefied for storage in cylinders under high pressured. Storage of toxic gases under high pressure in metal cylinders is often unacceptable because of the possibility of developing a leak or catastrophic rupture of the cylinder.

In order to mitigate some of these safety issues associated with high pressure cylinders, on-site electrochemical generation of such gases has been used. Because of difficulties in the on-site synthesis of the gases, a more recent technique of low pressure storage and delivery systems has been to adsorb these gases onto a solid support. These storage and delivery systems suffer from poor capacity and delivery limitations, poor thermal conductivity, and so forth.

Gases having Lewis basicity to be stored and delivered from Lewis acidic reactive liquids, *e.g.* ionic liquids, may comprise one or more of phosphine, arsine, stibine, ammonia, hydrogen sulfide, hydrogen selenide, hydrogen telluride, basic organic or organometallic compounds, *etc*.

With reference to Lewis basic ionic liquids, which are useful for chemically complexing Lewis acidic gases, the anion or cation component or both of such ionic liquids can be Lewis base and in some cases, both the anion and cation are Lewis basic, such as carboxylates, fluorinated carboxylates, sulfonates, fluorinated sulfonates, imides, borates, chloride [147].

Ionic liquids comprising cations that contain Lewis basic groups were also used in reference to storing gases having Lewis acidity. Examples of Lewis basic cations included N,N-dialkylimidazolium and other ring with multiple heteroatom. A Lewis basic group was also part of a substituent on either the anion or cation. Potentially useful Lewis basic substituent groups included amine, phosphine, ether, carbonyl, nitrile, thioether, alcohol, thiol, *etc*. [47].

Electrochemical Applications

Oxidation of Sn(II)/Sn(V). Room temperature ionic liquids are expected to be the alternative media for various practical electrochemical processes, because they possess wide electrochemical potential windows, acceptable ionic conductivity, high thermal stability and negligible vapor pressure. In EmiCl-$AlCl_3$ ionic liquids, the oxidation of Sn(II) to Sn(IV) was possible in a basic ionic liquid but not in an acidic one, probably because tetravalent species was stabilized by the complex formation with chloride ions in the basic ionic liquid [148].

Lithium electrochemistry. One key area of research was the development of IL-based electrolyte materials for lithium ion rechargeable batteries, fuel cells, capacitors, solar cells, actuators, and so on. Since ionic liquids were composed only of ions, they were realized high ionic conductivity, often over 10^{-2} S cm^{-1} at room temperature. In most cases, however, such electrolyte applications needed target ion transport, for instance, lithium ions in the case of lithium batteries, since the IL component ions were inert to typical electrode processes. Therefore, it was necessary to add these ionic species to the ILs. Unfortunately, the addition of target ions, especially the lithium ion, generally brings about a decrease of ionic conductivity and an increase in viscosity induced by the strong electrostatic interactions of the lithium ion.

In ILs based on aliphatic and alicyclic ammonium cations, which were very stable electrochemically, dissolved lithium salts was reversibly deposit and strip lithium metal. Furthermore, when a zwitterion was added to the IL/lithium salt mixture as a salt dissociator, the coulombic efficiency of the electrolyte system was significantly improved. An IL containing a cyano substituted cation used as a lithium battery electrolyte. Interestingly, the cyano IL showed slightly higher ionic conductivity after the addition of LiTFSA. Thus according to these results, the incorporation of a functional group that promoted dissociation of the lithium salt seems an attractive way forward in the design of new ILs for lithium batteries.

Lewis-base ionic liquid (IL) based on mono-charged 1,4-diazabicyclo[2.2.2]octane (dabco) with bis(trifluoromethanesulfonyl)amide (TFSA) anion showed a surprisingly wide electrochemical window of over 4 V and was able to deposit and strip lithium from a nickel substrate. Further exploration of Lewis-base ILs will open up new pathways for IL electrolytes to improve both the target ion transport and electrochemical stability [74].

Electrochemical study of transition-metal ions chemistry in BILs. Transition-metal ions form very stable anionic chloro complexes in basic ionic liquids BPC (1-n-butylpyridinium chloride)-$AlCl_3$ or basic EmiCl (l-methyl-3-ethylimidazolium chloride)-$AlCl_3$.

Basic ionic liquids BPC-$AlCl_3$ or basic EmiCl-$AlCl_3$ were excellent solvents in which to study the solution chemistry of transition-metal chloride complexes at room temperature since the solvation and solvolysis reactions commonly associated with these complexes in aqueous solution were absent in the melts.

Some of the factors that were believed to contribute to the unusual stability of these species in these ionic liquids relative to other solvents include the absence of both the solvation and solvolysis reactions encountered in molecular solvents and the thermally promoted dissociation and disproportionation reactions associated with high-temperature molten salts.

A number of first-row transition-metal chloride complexes had been investigated in room-temperature chloroaluminate melts, including cobalt(II), copper(I) and copper(II), iron(II) and iron(III), nickel(II), and titanium(III) and titanium(IV), while studies with second- and third-row transition-metal ions have been limited to silver(I)**,** molybdenum(III) and molybdenum(IV), ruthenium(III) and ruthenium(IV), and tungsten(III) through tungsten(V) [69,149-150].

TOXICITY OF IONIC LIQUIDS

Although the information about physical, thermodynamic, kinetic or engineering data had been extended continuously, only little data with regard to the toxicity and ecotoxicity of ionic liquids have been available until now. The green character of ionic liquids has usually been justified with their negligible vapor pressure, but even if ionic liquids will not evaporate and will not contribute to air pollution most of them are water soluble and might enter the environment by this path (*e.g.* accidental spills, effluents).

Experimental studies have been helpful in establishing general guidelines for the selection of ILs with low potential for toxicity. However, relatively little is still known about the toxicity of these materials as a class, especially when compared to conventional organic solvents. Several recent toxicity studies have documented IL effects on organisms and following results obtained.

Polymeric materials with pyridinium functionality can exhibit significant toxicity to bacteria. Antimicrobial activity increased as the alkyl chain length increased on pyridinium, imidazolium, and quaternary ammonium salts [151].

Many ILs are similar to cationic surfactants, which are known to induce polar narcosis due to their ability to be incorporated into biological membranes. Therefore, longer alkyl chains may be incorporated into the polar head groups of the phospholipids bilayer, which are the major structural components of membranes. Narcosis then results because membrane-bound proteins are disrupted by the toxicant.

Many of the imidazolium and pyridinium compounds were more toxic than common high-volume solvents such as acetonitrile, acetone and methanol. Some exceptions include low alkyl chain length quaternary ammonium ILs and those ILs containing choline as the cation, which were relatively nontoxic. The data suggest that choline or quaternary ammonium solvents may be more environmentally friendly alternatives than both aromatic ILs and some traditional industrial solvents.

Varying the anion has a minimal effect on the toxicity of pyridinium and imidazolium salts, which suggests that toxicity is largely driven by the cation, although recent studies indicate that the anion can play a role in toxicity.

Toxicity was predicted to increase slightly with the number of nitrogen atoms having two aromatic bonds and one single bond. Thus ammonium cations are less toxic than pyridinium cations, which are slightly less toxic than imidazolium cations.

If true, this would mean that triazolium-based ILs would be even more toxic than imidazolium-based compounds. The IL toxicity should decrease as the number of negatively charges atoms on the cation increases.

Although anions play a secondary role in determining toxicity, the results indicate that the presence of positively charged atoms in the anion leads to higher toxicity than those systems with a single negative anion atom. The correlations also indicate that methylating the aromatic ring of the cation should reduce toxicity [152-154].

COST AND LIFE CYCLE OF BASIC IONIC LIQUIDS

The development of a catalytic system that may be green, cost-effective, mild, easily separable, and reusable has long been awaited. Basic ionic liquids have been successfully used in organic reactions due to their unique properties such as vaporless and reusability.

The demonstrated ability of the ionic liquid to be reused indefinitely will enable production of large quantities of product per unit ionic liquid catalyst. This will provide a substantial increase in ratio of product value to cost of production. Additionally, since catalyst is not lost or consumed during the process, addition of fresh catalyst is not necessary. The ability to indefinitely reuse catalyst will also substantially reduce the amount of waste generated and will substantially lower the cost of disposal and environmental impact of the process.

However, for practical utilization, imidazolium-based ionic liquids still suffer from the relatively expensive cost. Non-imidazolium-based ILs should be of particular interest due to their availability in technical quantities and lower cost compared to their imidazolium-based counterparts [155].

CONCLUDING REMARKS

In this review we have paid attention to types, properties, synthesis and applications of basic ionic liquids. Basic ionic liquids used in some base-catalyzed processes such as Michael addition, Heck reaction and Markovnikov addition, Knoevenagel condensation, Henry reaction, Mannich reaction, synthesis of heterocyclic compounds, Feist-Benary reaction and *etc*.

Using bases such as NaOH, KOH, K_2CO_3 and *etc.* in base-catalyzed reactions have numerous disadvantages such as waste production, corrosion and no catalyst recovery. However ionic liquids offering a new possibility for developing environmental friendly basic catalysts regard to the combination of the advantages of inorganic bases and ionic liquids. Therefore basic ionic liquids exhibited great potential for the replacement of conventional basic catalysts because they are flexible, nonvolatile, noncorrosive, and immiscible with many organic solvents.

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