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Review Article

Ionic Liquids: Synthesis and Applications in Catalysis

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Ionic liquids have emerged as an environmentally friendly alternative to the volatile organic solvents. Being designer solvents, they can be modulated to suit the reaction conditions, therefore earning the name "task specific ionic liquids." Though primarily used as solvents, they are now finding applications in various fields like catalysis, electrochemistry, spectroscopy, and material science to mention a few. The present review is aimed at exploring the applications of ionic liquids in catalysis as acid, base, and organocatalysts and as soluble supports for catalysts.

1. Introduction

One of the twelve principles of green chemistry is that the use of auxiliary substances such as solvents and separation agents should be made unnecessary and if used should be innocuous [1]. The toxic and hazardous properties of many solvents particularly chlorinated hydrocarbons pose crucial environmental concerns such as atmospheric emissions and contamination of water effluents. It is recognized that employing the use of nonconventional solvents as alternatives for environmentally unfriendly traditional solvents can reduce waste solvent production and hence reduce the negative impact on environment to a great extent [2]. The most prevalent of these new solvent systems includes, but not exclusively, water, supercritical fluids (like supercritical CO_2), ionic liquids, solventless processes, and fluorous techniques [3].

Of all the above mentioned nonconventional solvents of interest, ionic liquids have emerged as a promising alternative [4]. Ionic liquid is defined as a salt with melting point below the boiling point of water [5]. Ionic liquids are known by several different names like neoteric solvents, designer solvents, ionic fluids, and molten salts. Most of the ionic liquids are composed of organic cation and inorganic anions. In order to be liquid at room temperature, the cation should preferably be unsymmetrical; that is, the alkyl groups should be different. Polarity and hydrophilicity/hydrophobicity of ionic liquids can be tuned by suitable combination of cation and anion. It is this property of ionic liquids which has earned them the accolade "designer solvents."

As solvents, ionic liquids have found applications in a number of reactions [6–16]. Dupont et al. extensively reviewed the application of ionic liquids as catalytic phase in various organometallic reactions [17]. Catalytic applications of metal nanoparticles have been explored in ionic liquid media by Migowski and Dupont [18, 19].

Besides the use of ionic liquids as alternate solvents, lately further work has led to the progress in designing functional ionic liquids also referred to as "task specific ionic liquids" (TSIL) [20]. The term task specific ionic liquids or functionalized ionic liquids actually indicates an attempt to capitalize on the potential "design" capacity of ionic liquids and make them true working systems rather than just reaction media.

2. Synthesis of Ionic Liquids

The first room temperature ionic liquid $[EtNH_3][NO_3]$ (m.p. 12°C) was discovered in 1914 [21], but interest did not develop until the discovery of binary ionic liquids made from mixtures of aluminum(III) chloride and *N*-alkylpyridinium or 1,3-dialkylimidazolium chloride [22, 23].

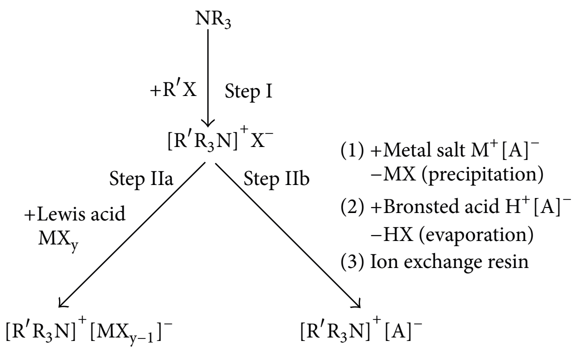


Figure 1: Synthesis path for the preparation of ionic liquids [24].

$$[\text{emim}]^+\text{Cl}^- + \text{AlCl}_3 \rightleftharpoons [\text{emim}]^+[\text{AlCl}_4]^- \tag{1}$$

$$[\text{emim}]^+[\text{AlCl}_4]^- + \text{AlCl}_3 \rightleftharpoons [\text{emim}]^+[\text{Al}_2\text{Cl}_7]^- \tag{2}$$

$$[\text{emim}]^+[\text{Al}_2\text{Cl}_7]^- + \text{AlCl}_3 \rightleftharpoons [\text{emim}]^+[\text{Al}_3\text{Cl}_{10}]^-. \tag{3}$$

Scheme 1: Series of equilibria in the reaction between [emim]Cl and $AlCl_3$.

Ionic liquids come in two main categories, namely, simple salts (made of a single anion and cation) and binary ionic liquids (salts where equilibrium is involved). For example, $[EtNH_3][NO_3]$ is a simple salt whereas mixtures of aluminum(III) chloride and 1,3-dialkylimidazolium chlorides (a binary ionic liquid system) contain several different ionic species, and their melting point and properties depend upon the mole fractions of aluminum(III) chloride and 1,3-dialkylimidazolium chloride present.

The synthesis of ionic liquids can be described in two steps (Figure 1).

(1) The Formation of the Desired Cation. The desired cation can be synthesized either by the protonation of the amine by an acid or through quaternization reactions of amine with a haloalkane and heating the mixture.

(2) Anion Exchange. Anion exchange reactions can be carried out by treatment of halide salts with Lewis acids to form Lewis acid-based ionic liquids or by anion metathesis.

The most extensively studied and used Lewis acid based ionic liquids are $AlCl_3$ based salts [25–27]. Such salts involve simple mixing of the Lewis acid and the halide salt which results in the formation of more than one anionic species depending upon the ratio of quaternary halide salt Q^+X^- and Lewis acid MX_n as illustrated by the reaction between [emim]Cl and $AlCl_3$ in Scheme 1.

When [emim]Cl is present in molar excess over $AlCl_3$ the ionic liquid formed is basic (1); however, the molar excess of $AlCl_3$ leads to the formation of an acidic ionic liquid (3). When both [emim]Cl and $AlCl_3$ are present in equimolar quantities, it results in the formation of neutral ionic liquids. Apart from $AlCl_3$, other Lewis acids used are $AlEtCl_2$ [28], BCl_3 [29], CuCl [30], and $InCl_3$ [31] to mention a few.

Anion metathesis is the methodology of choice for the preparation of water and air stable ionic liquids based upon 1,3-dialkylimidazolium cations. This method involves the treatment of the halide salt with the silver/sodium/potassium salts of NO_2^-, NO_3^-, BF_4^-, SO_4^{2-}, and $CO_2CH_3^-$ or with the free acid of the appropriate anion. Table 1 gives examples of the few ionic liquids prepared by anion metathesis.

Table 1: Examples of ionic liquids prepared by anion metathesis.

Salt	Anion source	References
$[\text{Cation}][PF_6]$	HPF_6	[32–34]
$[\text{Cation}][BF_4]$	HBF_4, NH_4BF_4, $NaBF_4$	[33–37]
$[\text{Cation}][(CF_3SO_2)_2N]$	$Li[(CF_3SO_2)_2N]$	[34, 38]
$[\text{Cation}][CF_3SO_3]$	$CF_3SO_3CH_3$, $NH_4[CF_3SO_3]$	[38]
$[\text{Cation}][CH_3CO_2]$	$Ag[CH_3CO_2]$	[35]
$[\text{Cation}][CF_3CO_2]$	$Ag[CF_3CO_2]$	[35]
$[\text{Cation}][CF_3(CF_3)_3CO_2]$	$K[CF_3(CF_3)_3CO_2]$	[38]
$[\text{Cation}][NO_3]$	$AgNO_3$, $NaNO_3$	[34, 38]
$[\text{Cation}][N(CN)_2]$	$Ag[N(CN)_2]$	[39]
$[\text{Cation}][CB_{11}H_{12}]$	$Ag[CB_{11}H_{12}]$	[40]
$[\text{Cation}][AuCl_4]$	$HAuCl_4$	[41]

It is clear from the above discussion that large number of ionic liquids can be envisioned by simple combination of different cations and anions. The estimated number of single ILs is 10^{18} which further increases if we include binary and ternary ionic liquids. Because of their “tailor-made” nature the ionic liquids find applications as storage media for toxic gases, catalysts/solvents in organic syntheses, performance additives in pigments, and matrices [42–44].

Several new and improved methodologies using nonconventional techniques, such as irradiation with microwaves (MW) and power ultrasound (US), whether used alone or in combination, have considerably improved the synthesis of ILs, cutting down reaction times and improving yields [45–47]. The recent introduction of efficient, solventless, one-pot synthetic protocols should make ILs cheaper and thus encourage a wider use of these neoteric solvents [48–50].

3. Task Specific Ionic Liquids (TSILs)

In 1999, Davis Jr. and Forrester demonstrated the concept of designing ionic liquid to interact with a solute in a specific manner by using a thiazolium based IL as a solvent-catalyst for the benzoin condensation and introduced the term “task specific ionic liquid” for such ILs in which functional group

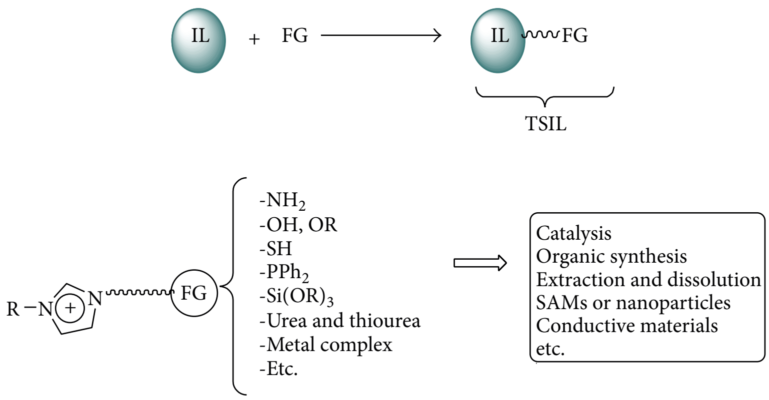


Figure 2

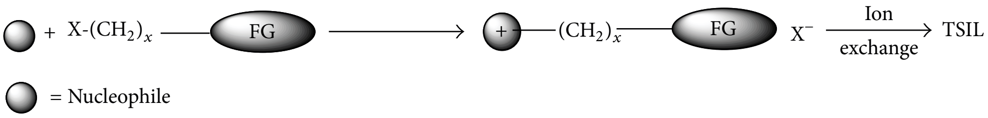


Figure 3

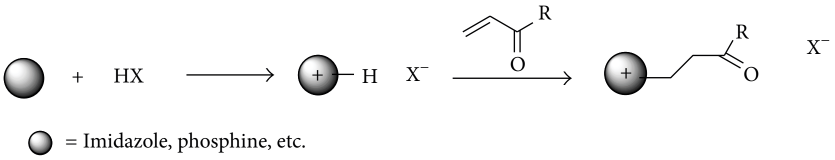


Figure 4

is incorporated as a part of the cation and/or anion structure [51, 52]. The covalent attachment of some functional group to cation/anion or both of an ordinary ionic liquid imparts it the capacity to behave not only as solvent but also as reagent and/or catalyst, catalyst in the chemical reactions [53, 54] (see Figures 2 and 3).

(i) For example, safe to handle Bronsted acidic ionic liquids containing sulphonic acid groups were used as solvent and/or catalyst for esterification and other acid catalyzed reactions [55].

(ii) Ionic liquids bearing appended amines can separate carbon dioxide from gas streams [56].

(iii) Ionic liquids with large aromatic head groups show enhanced activity for extraction of aromatics in aqueous biphasic systems [57].

(iv) Ionic liquids with a tethered hydroxyl group (–OH) have been used as phase transfer catalyst in the synthesis of ethoxybenzene [58].

(v) Ionic liquids containing metal ligating group find use in the extraction of metal ions from aqueous solution [59].

(vi) Ionic liquids with appended carboxylate groups have been used as supports for "IL-phase" synthesis which is a versatile extension of the solid phase synthesis concept [60].

A TSIL can be any of the following two types [61]:

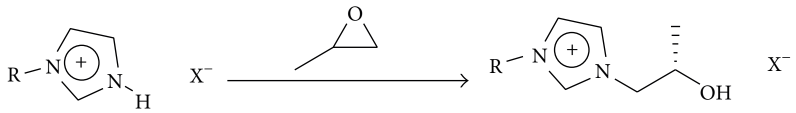
(i) A room temperature ionic liquid, having covalently attached functional group, behaves not just as reaction media but also as reagent/catalyst.

(ii) A binary system of some functionalized salt, which may be solid at room temperature, dissolved in conventional ionic liquid.

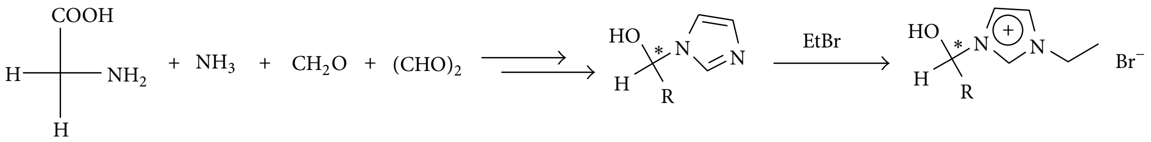
3.1. Synthesis of TSILs. Conventional method used for synthesizing a TSIL involves the displacement of halide from an organic by a parent imidazole, phosphine, and so forth whereby the organic halide already incorporates a desired functional group. The displacement reaction is followed by anion exchange (see Figure 3).

This method is suitable for the synthesis of all ionic liquids which are stable towards bases; however, because of the strong basicity of imidazole, elimination of hydrogen halide or Hoffmann elimination occurs in some cases [62]. Generally the functional groups have been introduced directly to the imidazolium moiety using the direct quaternization route. For example, imidazolium cation with hydroxyl groups [58], carboxyl groups [60], thiol groups [63], alkyne groups [64], allyl groups [65], and fluorous chains [66] were successfully prepared.

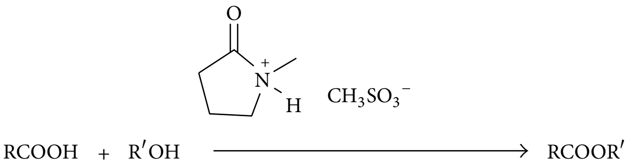
Wasserscheid and coworkers introduced a new methodology to synthesize TSILs by making use of Michael reaction.



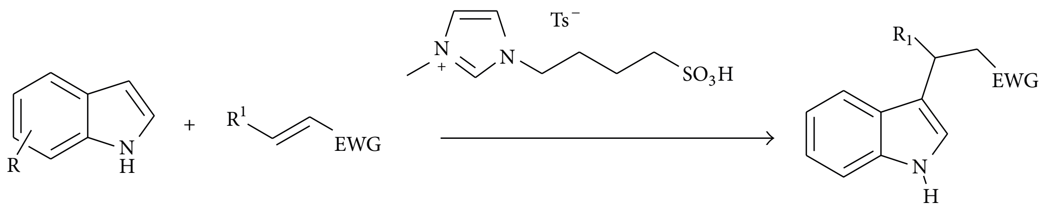
Scheme 2



Scheme 3



Scheme 4



Scheme 5

In this approach the nucleophile is protonated using the acid form of anion which will eventually be incorporated into the ionic liquid [67] (see Figure 4).

To synthesize –OH group containing TSILs two procedures have been reported as discussed below.

Holbrey et al. have described a simple, high yielding one pot method for the synthesis of alcohol-appended imidazolium TSIL, an ionic liquid type which was previously difficult to prepare cleanly. Preformed imidazolium-H salt of TSIL anion is allowed to react with an epoxide leading to ring opening without further alcohol-epoxide oligomerization [68] (see Scheme 2).

Bao et al. synthesized an imidazolium ring by the four components condensation of amino acids, ammonia, formaldehyde, and glyoxal. The procedure yields an optically active TSIL [69] (see Scheme 3).

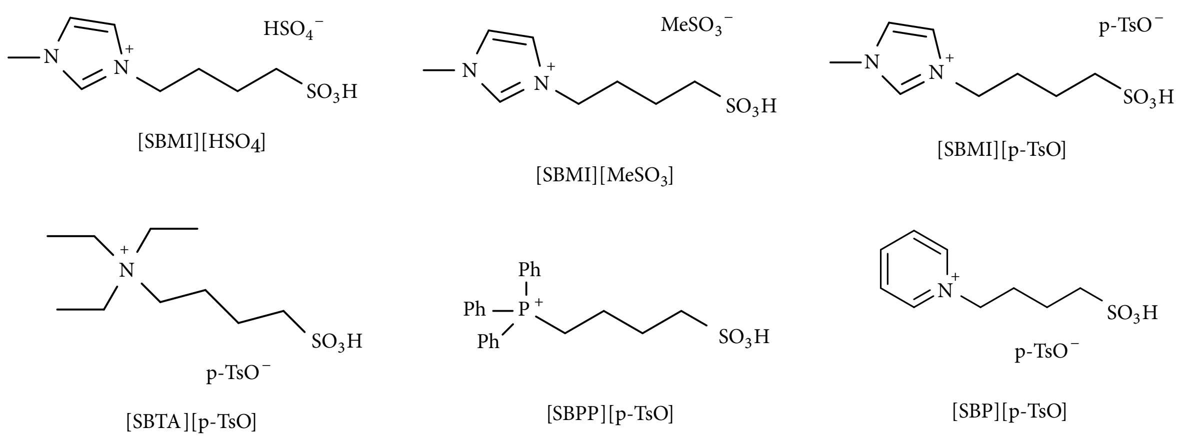
4. Ionic Liquids as Catalysts

Although ionic liquids were initially introduced as alternative green reaction media because of their unique physical and chemical properties, today they have marched far beyond this border, showing their significant role in controlling the reaction as catalysts [70–75]. Depending upon the functional group attached to the cation and/or anion, the ionic liquid may behave as an acidic, basic, or organocatalyst.

4.1. As Acid Catalysts. The application of acidic (Bronsted as well as Lewis) task specific ionic liquids (TSILs) as a catalytic material is growing rapidly in the field of catalysis [76, 77]. Combining the useful characteristics of solid acids and mineral acids, TSILs have been synthesized to replace the traditional mineral liquid acids, such as hydrochloric acid and sulphuric acid, in the chemical reactions. In view of green chemistry, the substitution of harmful liquid acids by reusable TSILs is one of the most promising catalytic systems in chemistry.

The acidic nature of Bronsted acidic ionic liquids as catalysts has been exploited for many organic transformations like Pechmann reaction, Koch carbonylation, asymmetric Aldol condensation, Aza-Michael reaction, Beckmann rearrangement, synthesis of chalcones, oxidation reactions and Prin's reaction, synthesis of furfural, biodiesel, Hantzsch reaction, and Mannich reaction to mention a few [78–89].

Esterification of alcohols by carboxylic acids has been carried out in a halogen-free Bronsted acidic ionic liquid, N-methyl-2-pyrrolidinium methyl sulphonate under mild conditions, and without additional solvent [90] (see Scheme 4).



[SBMI][HSO_4]

[SBMI][$MeSO_3$]

[SBMI][p-TsO]

[SBTA][p-TsO]

[SBPP][p-TsO]

[SBP][p-TsO]

Figure 5

$$PCl_3 + Ph\text{-}H \xrightarrow{[trEHAm]Cl\text{-}XAlCl_3} PhPCl_2$$

Scheme 6

In a very recent report of TSIL, Das and coworkers have reported a sulfonic acid functionalized IL for efficient synthesis of indole derivatives [91]. The advantage of this IL is that it could be reused up to 10 cycles without any substantial loss of catalytic activity. The catalyst is versatile as it is also applicable to both aliphatic and aromatic amines and in the synthesis of bis(indolyl) methane (see Scheme 5).

Z.-W. Wang and L.-S. Wang reported the Friedel-Crafts reaction of PCl_3 and benzene in [trEHAm]Cl-X$AlCl_3$ ionic liquid for the clean synthesis of dichlorophenylphosphine (DCPP) [93] (see Scheme 6).

Compared with the classical methods this protocol allows the simple product isolation and lesser reusable catalyst consumption, which contributes to the greenness of the procedure.

Wang et al. screened various ionic liquids for Saucy-Marbet reaction between unsaturated alcohols and unsaturated ethers leading to corresponding unsaturated ketones [94]. It was observed that, with five ionic liquids bearing [HSO_4^-] anion, the conversion decreases as the chain length of ionic liquid increases due to its lipophilic character. Among the various acidic ionic liquids [Et_3NH] HSO_4 gave the best results in terms of conversion (88%) and selectivity (97%) for the model reaction involving dehydrolinalool and 2-ethoxypropene.

With neutral ionic liquids like [bmim]BF_4, the conversion was less than 10%. No reaction was observed when [bmim]Cl or [bmim]PF_6 was used as catalyst. This cost effective, solvent-free protocol has the advantages of easy work-up, recyclability with only slight decrease in activity, low toxicity of ammonium based ionic liquids, high activity, and selectivity (see Scheme 7).

Brandt et al. extensively reviewed the use of ionic liquids as deconstruction solvents for lignocellulosic biomass [95]. Ionic liquid disrupts the lignin and hemicellulosic network while decrystallizing the cellulose portion which further enhances the speed of saccharification.

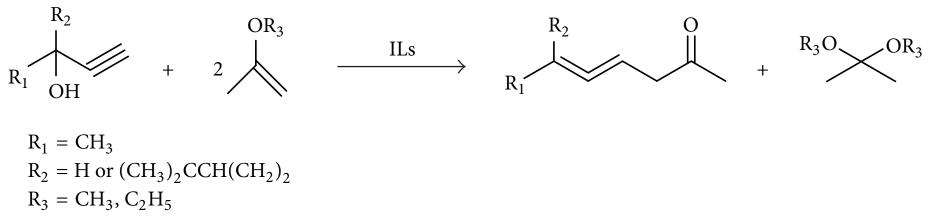
The use of ionic liquids [C_4C_1im][HSO_4] and [C_4C_1im][$MeSO_3$] for lignocellulosic biomass treatment was successfully investigated even in the presence of significant quantities of water, thus eliminating the need for anhydrous conditions during pretreatment [96].

The use of acidic ionic liquids for the saccharification of cellulose and its subsequent conversion into important platform molecules like hydroxymethylfurfural, furfural, and levulinic acid has been well explored [97–103].

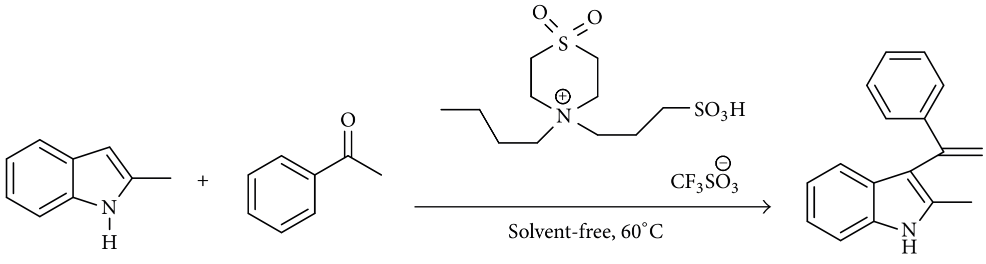
A green solvent-free, metal-free, mild, and efficient protocol for the synthesis of 3-vinyl indoles starting from indoles and ketones has been developed using a sulfonyl containing ionic liquid as a recyclable catalyst [104]. The simultaneous presence of sulfonyl and sulphonic acid groups in the same ionic liquid leads to an augmented catalytic activity. Even the challenging substrates like bulky ketones or ortho-substituted ketones gave satisfactory yields (see Scheme 8).

Six different Bronsted acidic ionic liquids (BAILs) have been synthesized and used as recyclable reaction media as well as acid promoters for Pd-phosphine catalyzed methoxy carbonylation of ethylene to produce methyl propionate in excellent yields [105] (see Figure 5). The use of BAILs not only hampered the formation of undesirable palladium black but also leads to the formation of a biphasic reaction media with the product thereby facilitating the product as well as catalyst recovery. The catalytic system has been found to be recyclable up to fifteen cycles without any appreciable loss in activity (see Scheme 9).

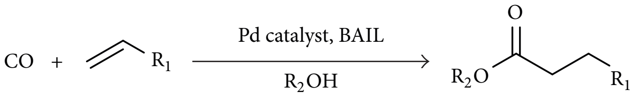
Titze-Frech and coworkers developed an efficient and selective methodology for the alkylation of phenol and anisole using Bronsted acidic triflate ionic liquid [MIMBS] [OTf] as catalyst in a biphasic reaction medium [106]. This protocol is advantageous over the existing ones as it negates the need for the neutralization of excess acid formed as a by-product. Also, ionic liquid catalyst being less oxophilic as compared to mineral acids leads to greater selectivities (see Scheme 10).



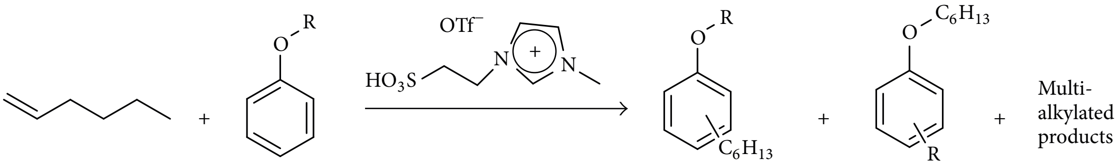
Scheme 7



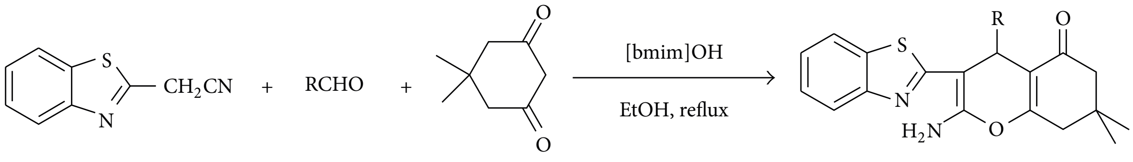
Scheme 8



Scheme 9



Scheme 10



Scheme 11

4.2. As Base Catalysts. Basic functionalized ionic liquids have aroused unprecedented interest because they showed more advantages, such as convenient recycling and higher catalytic efficiency than the mixture of inorganic base and ionic liquid for some base-catalyzed processes [107].

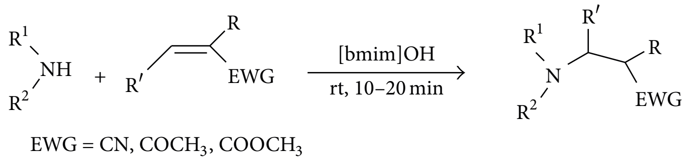
Basic ionic liquids have been used to catalyze a number of reactions like aza-Michael addition reaction, Michael addition of active methylene compounds, condensation reaction of aldehydes and ketones with hydroxylamine, synthesis of quinolines, pyrroles, and AGET ATRP of methyl methacrylate to mention a few [108–113].

A facile, mild, and quantitative procedure for the preparation of tetrahydrobenzo[b] pyran derivatives in the presence of an easily accessible basic ionic liquid [bmim]OH as catalyst has been developed by Wen et al. [114]. The ionic liquid was used for at least nine times with consistent activity (see Scheme 11).

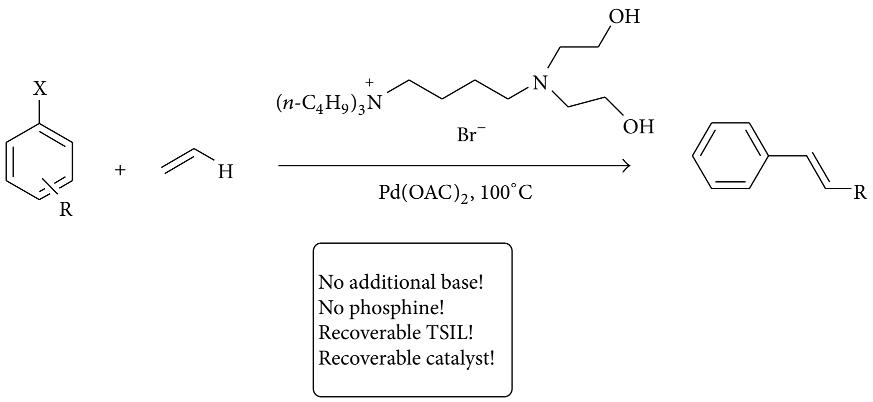
Xu et al. developed a green protocol for the Michael addition of N-heterocycles to α,β-unsaturated compounds at room temperature using a basic ionic liquid [bmim]OH as a catalyst and reaction medium [115] (see Scheme 12).

Wang and coworkers described synthesis and application of ethanolamine functionalized TSIL for the palladium-catalyzed Heck reaction [116] (see Scheme 13).

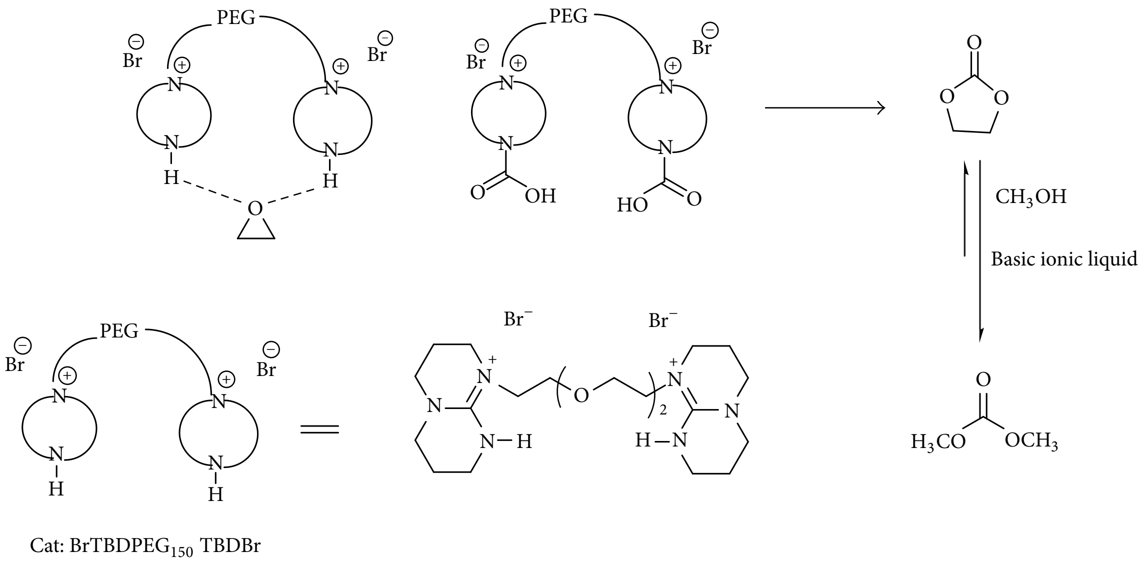
Here this IL performs a multifunctional role of base, ligand, and reaction media with added advantage of recyclability of the system. The catalyst system is very effective for a wide spectrum of substrates giving excellent yields.



Scheme 12



Scheme 13

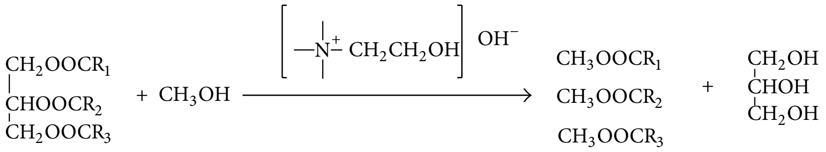


Scheme 14

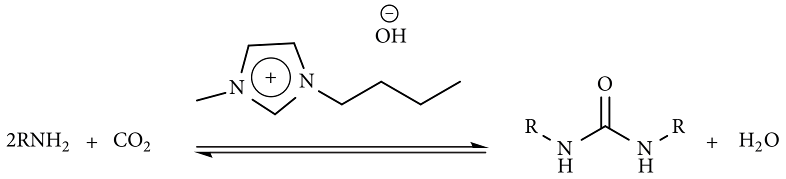
Yang et al. designed a series of PEG functionalized basic ionic liquids based on 1,2-dimethyl imidazole (DMIm); 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU); 1,5-diazabicyclo [4.3.0] non-5-ene (DBN); 1-methyl imidazole (MIm) and 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD); and tested them as catalysts, under identical conditions, for the conversion of carbon dioxide into useful organic carbonates [117]. Of all these catalysts $BrTBDPEG_{150}$ TBDBr has been found to be excellent recyclable catalyst under solvent-free conditions at low pressure (see Scheme 14).

The presence of both secondary and tertiary nitrogens in the cation of $BrTBDPEG_{150}$ TBDBr endows it with the ability to activate methanol leading to high activity for transesterification of ethylene carbonate with methanol. Therefore the use of basic ionic liquid $BrTBDPEG_{150}$ TBDBr as catalyst allows the integration of cycloaddition as well as transesterification as a single process.

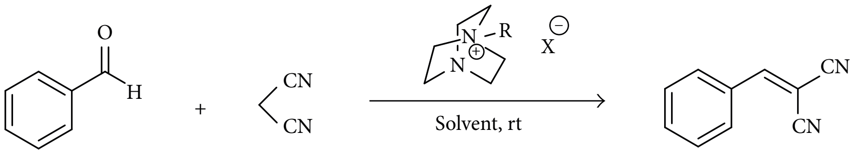
Basic ionic liquids choline hydroxide [ChOH], choline methoxide (ChOMe), and choline imidazolium (ChIm) have been synthesized and checked for their catalytic activity for the production of biodiesel from soybean oil [118]. Of all the three ionic liquids, choline hydroxide was found to give the best results in terms of yield, efficiency, and recyclability. After studying various reaction parameters, 4 wt% catalyst



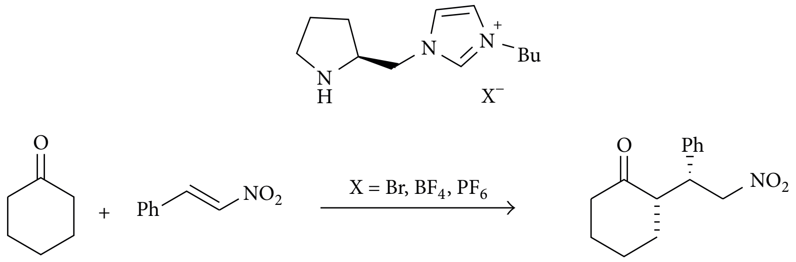
Scheme 15



Scheme 16



Scheme 17



Scheme 18

dosage at a temperature of 60°C was optimized to give the best results when the ratio of methanol to soybean oil was 9 : 1 (see Scheme 15).

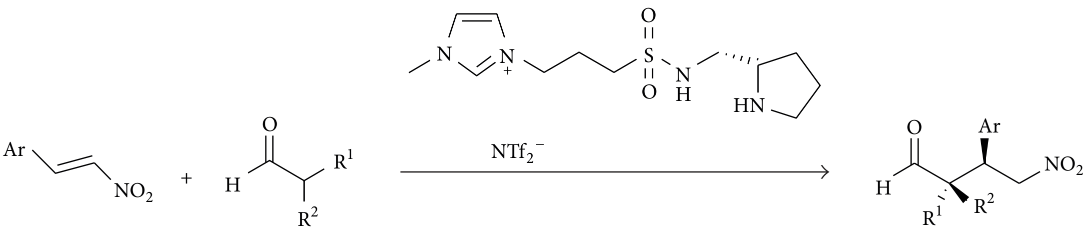
Basic ionic liquid [bmim]OH has been successfully used as an efficient catalyst for the synthesis of substituted ureas starting from carbon dioxide and amines [119]. The main advantages of this methodology are solvent-free reaction conditions, no need of dehydrating agents to remove the water formed as a by-product, recyclability of catalyst, and operational simplicity. The developed protocol is quite general as aliphatic amines, cyclohexylamine, and benzylamine were converted to corresponding ureas efficiently and selectively (see Scheme 16).

Various [DABCO] based ionic liquids have been screened for executing Knoevengeal condensation reaction [120]. Of all these ionic liquids [C_4dabco] [BF_4] was found to give the best results. Using [C_4dabco] [BF_4] as catalyst in aqueous media various aromatic/aliphatic/heterocyclic/α,β unsaturated aldehydes and cyclic/acyclic ketones have been found to undergo efficient Knoevengeal condensation with active methylene compounds. No product purification was required and the catalyst was found to be recyclable up to seven cycles without any decrease in activity. The reaction is highly stereoselective giving alkenes with E-geometry only (see Scheme 17).

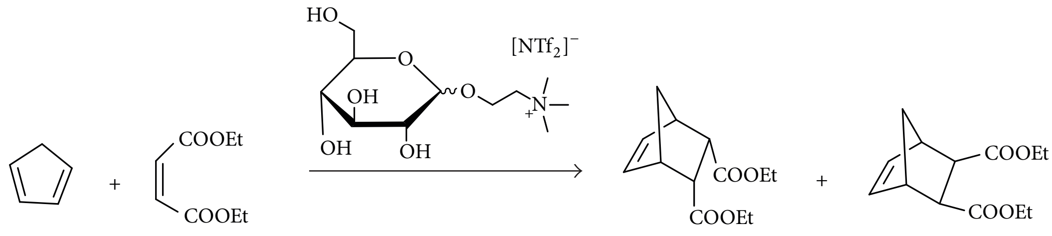
4.3. As Organocatalysts. In the last few years a renewed interest in the use of organic compounds as catalysts has begun to emerge. Ionic liquids have the potential to have a huge impact in this area [121–124]. One of the promising approaches to organocatalysis is through hydrogen bonding interactions, and the reactions to which this has been most often applied are Diels-Alder cycloadditions and their derivatives.

Luo and coworkers used a functionalized chiral ionic liquid as an efficient reusable organocatalyst for asymmetric Michael addition of ketones/aldehydes with nitroalkenes [125] (see Scheme 18).

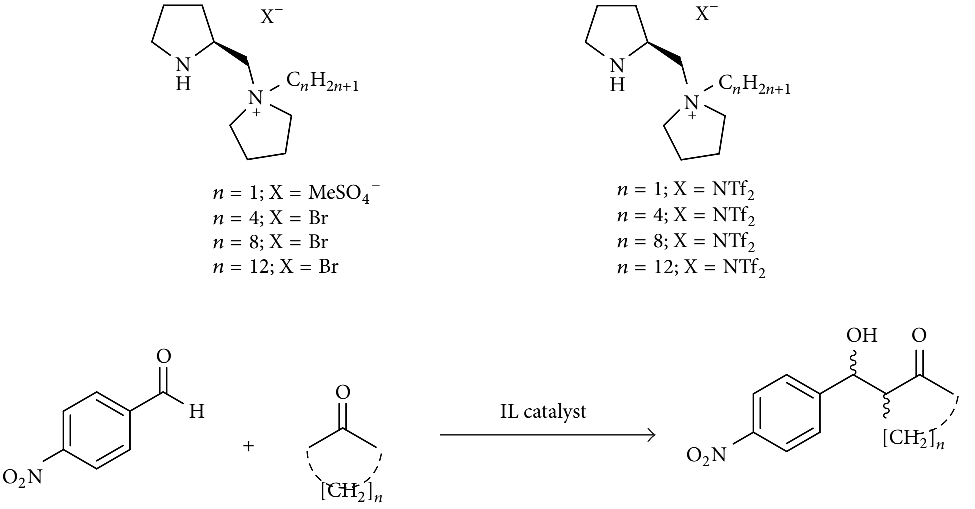
Pyrrolidine-based chiral ionic liquid has been developed by Ni and coworkers [126]. This chiral ionic liquid was found to catalyze the Michael addition reaction of aldehydes



Scheme 19



Scheme 20



Scheme 21

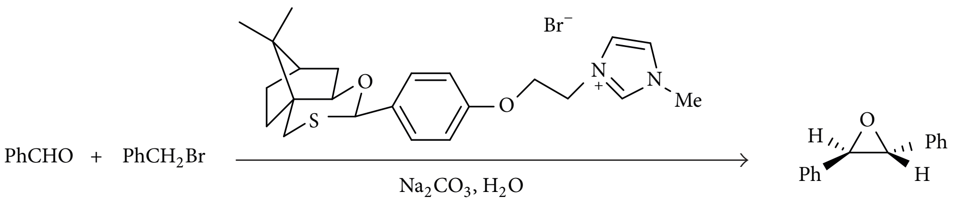
and nitrostyrenes to give moderate yields, good enantioselectivies, high diastereoselectivities, and recyclability (see Scheme 19).

Though ionic liquids are green solvents, they are synthesized from the materials which use fossil fuels as their resource. Synthesizing ionic liquids from renewable raw materials will add to the green attributes of ionic liquids. Sugars are suitable, abundantly available raw material for the synthesis of ionic liquids. Also the presence of hydroxyl groups in the ionic liquids derived from sugars makes them highly coordinating solvents thus enabling them to be used in stereoselective and metal catalyzed reactions.

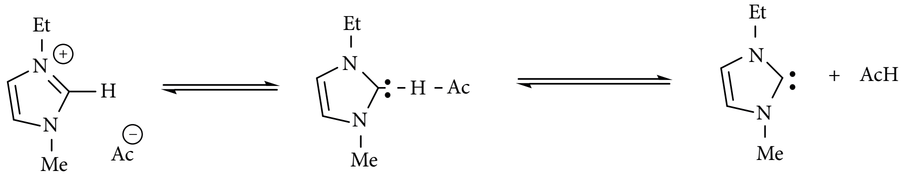
Erfut et al. synthesized novel hydrogen bond rich ionic liquids based on D-glucosopyranoside derivatives as cation precursor and low coordinating bistriflimide as anion [127]. Chloroalcohols have been utilized as source of hydroxyl groups for the construction of ionic liquid cation. The synthesized ionic liquids were successfully used as organocatalysts (4 mol% with respect to dienophile) for Diels-Alder reaction of various dienes and dienophiles. Influence of number of hydroxyl groups on the reaction course has been thoroughly investigated. With all the ionic liquids the endo selectivity was found to be prevalent (see Scheme 20).

Starting from (S)-proline, several chiral ionic liquids have been synthesized by Vasiloiu and coworkers [128]. These ionic liquids were successfully used as organocatalysts to execute asymmetric aldol condensation giving good yields and selectivity up to 80% ee.

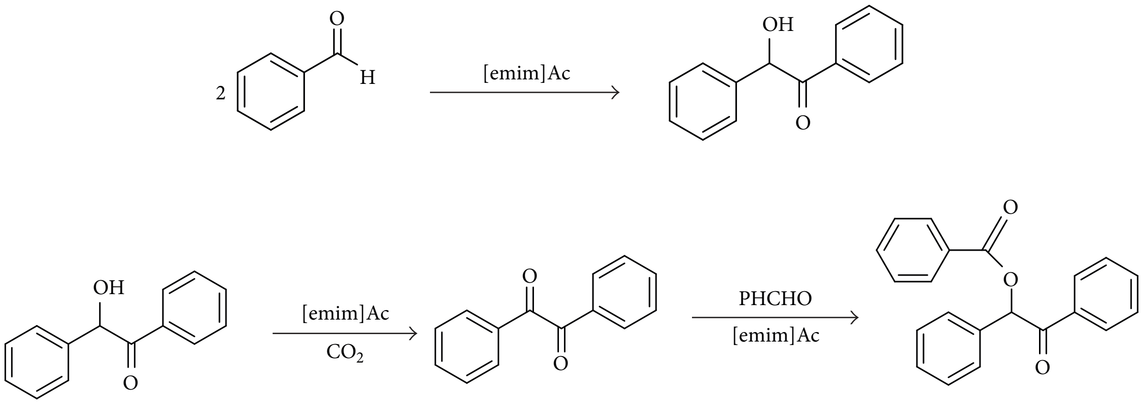
It has been observed that hydrophilic triflimide based chiral ionic liquids lead to greater yields and higher selectivities as compared to ionic liquids bearing methyl sulphate or bromide anions. This methodology not only negates



Scheme 22



Scheme 23



Scheme 24

the requirement of corrosive trifluoroacetic acid but also widens the substrate scope for organocatalysis towards acid sensitive compounds (see Scheme 21).

Li et al. synthesized a sulphur functionalized chiral ionic liquid which has been used as an organocatalyst for epoxidation reaction of various aromatic aldehydes with benzyl bromide in water giving trans-epoxides with high diastereoselectivity and enantioselectivity up to 72% ee [129]. Sodium carbonate has been found to be the best base for this process. Work-up of this reaction is quite simple as the organocatalyst is insoluble in ether and soluble in water. The catalytic system is recyclable up to five cycles without any appreciable reduction in yields and enatioselectivities (see Scheme 22).

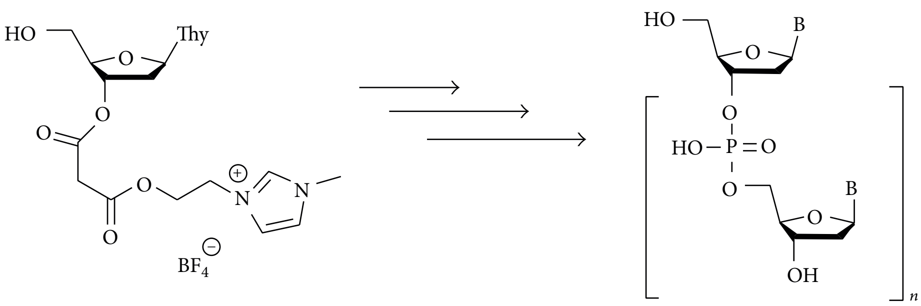
Imidazolium based ionic liquids can be used as pre-catalysts for N-heterocyclic carbene catalyzed reactions whereby the catalyst can be obtained by deprotonation (see Scheme 23).

Kelemen and coworkers successfully used imidazolium acetate as organocatalysts for benzoin condensation, hydroacylation and oxidation of alcohols using carbon-dioxide and air [130] (see Scheme 24).

5. Ionic Liquids as Soluble Supports

Due to their tunable solubility and practically nonvolatile nature, ionic liquids have been used as soluble supports for catalyst/reagent immobilization [92] (see Figure 6). Ionic liquid supported synthesis (ILSS) has been successfully applied for a number of organic reactions like 1,3-cycloadditions [131], Knoevengeal reaction [60], Suzuki coupling [132], synthesis of thiazolidinones [133], oligosaccharide synthesis [134], and Grieco's multicomponnet synthesis of tetrahydroquinolines [135].

Donga and coworkers described the synthesis of oligonucleotides in solution using a soluble ionic liquid support.



Scheme 25

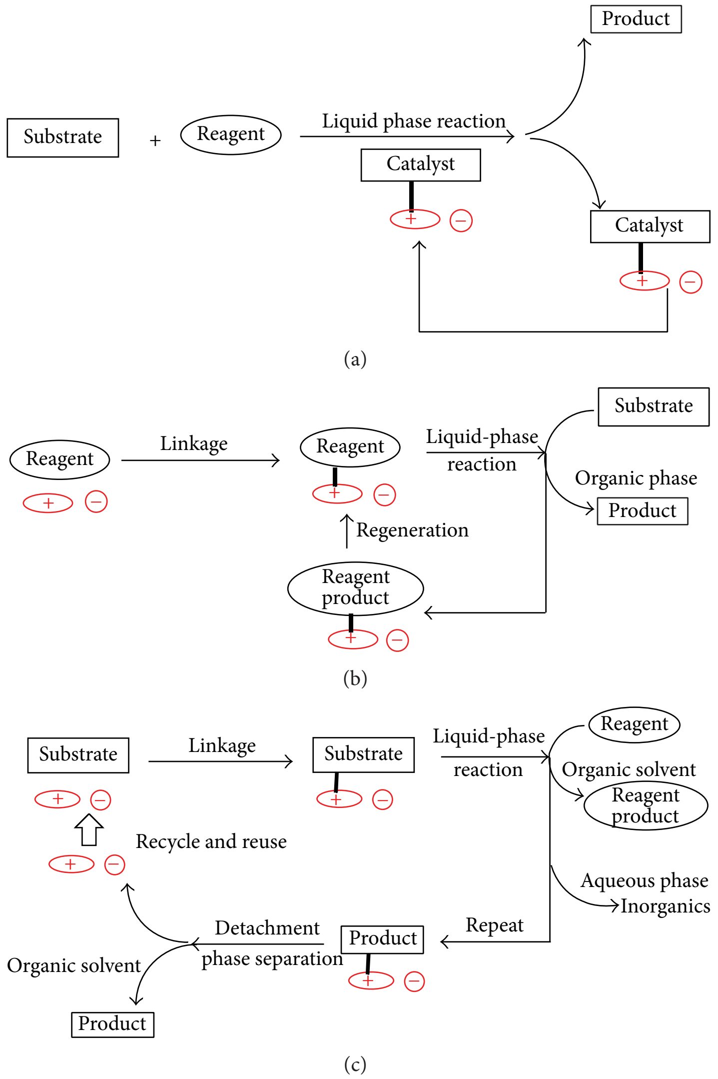
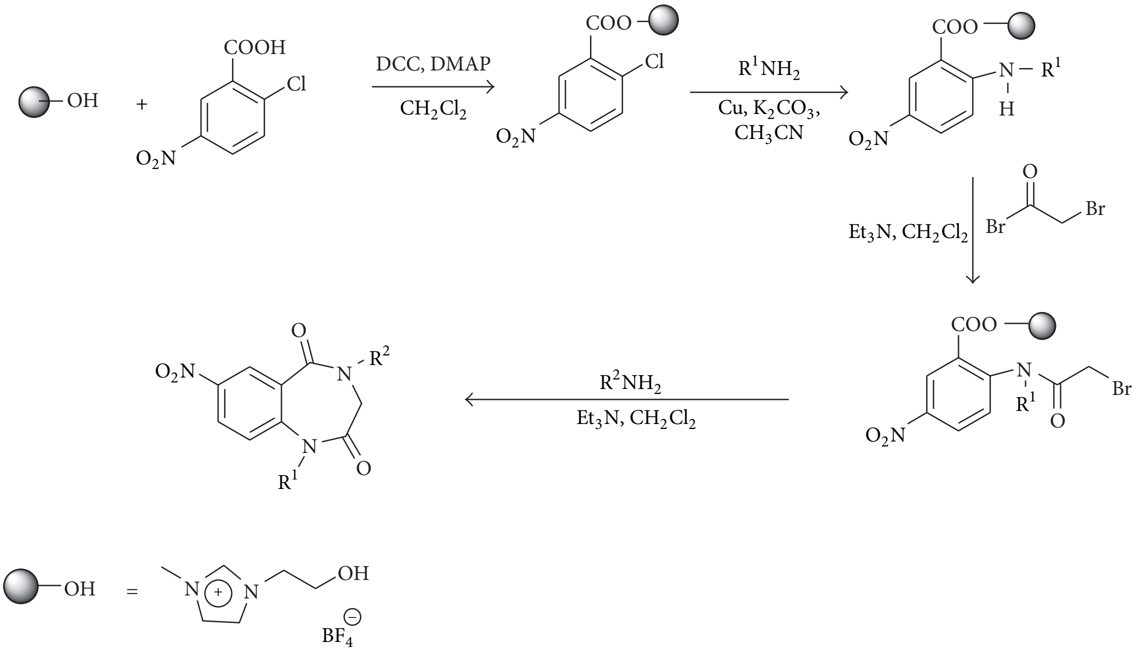


Figure 6: Ionic liquid supported synthesis (ILSS) (a) catalyst, (b) reagent, and (c) substrate [92].

Oligonucleotides up to tetrameric species have been synthesized and shown to be comparable to the products generated using standard automated DNA synthesis techniques [136] (see Scheme 25).

A novel and efficient route using ionic liquids as soluble supports has been reported for the synthesis of 1,4-benzodiazepine-2,5-dione by Xie et al. [137] (see Scheme 26).



Scheme 26

6. Conclusion

This review is focused on the synthesis, importance, and applications of ionic liquids. Not particularily as solvents, they are nowadays finding use as catalysts and catalytic supports in organic chemistry. Their scope has marched beyond academic research laboratories to industries where their practical applications have been leading to various sustainable technologies. Flexibility to modulate properties by changing design endows freedom to a chemist to design an ionic liquid according to one's own requirement. To conclude it can be said that the field of ionic liquid catalysis holds enormous possibilities to be explored.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

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