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Designing, Synthesis and Applications of Task Specific Ionic Liquids

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ABSTRACT

This review covers the brief details of synthesis and applications of task specific ionic liquids designed for organocatalysed reaction. Various scientists have anchored the different organocatalyst moieties to the structure of imidazolium-based ionic liquids and developed functionalized liquids capable of behaving as both solvent and organocatalyst. Basic idea behind task specific ionic liquids as their name suggest is to design the solvent-cum-organocatalyst for specific reactions as evident from this review. This review offers first ever compilation of the scientific work carried out in the field of task specific ionic liquids.

Key words: Task specific ionic liquids, Green chemistry, Organocatalysis, Catalyst recycling.

INTRODUCTION

Task specific ionic liquids are special kind of imidazole-based ionic liquids, which are synthesized by attaching the specific organo-functional group to the structure of imidazole-based ionic liquids. Since ionic liquids is no longer a new field to chemists of the world, different researcher tried to use them in different ways and forms.[1] There many organic reactions which are promoted by organocatalysts. Some of the organic chemists thought that the performance of the organocatalysed reaction can be further enhanced by making the organocatalyst the part of ionic liquid. By doing so, many of the draw backs of organocatalysed reaction can be overcome developing their ionic liquid versions, for instance, clean synthesis, reducing reaction time, improving product yield, recycling of catalyst system.[2] This excellent combination of advantages is made by developing the ionic liquid version of routine methods. The positive outcome of this methodology has triggered the ever increasing growth in the field of task specific ionic liquids. It is interesting to note that we can synthesize the specific ionic liquids for ant particular task i.e. chemical transformations. This fact justifies their name as task specific ionic liquids (TSILs) or designer solvents that contain specific functionalities and are capable of carrying out specific tasks. [3]

Ionic liquids are beneficial as environmentally benign reaction media for organic reactions.[4] This is due to some intriguing properties

of ionic liquids: high thermal and chemical stability, non-flammability, lack of measurable vapor pressure and high loading capacity. By modifying the structure of the cation or the anion, the solubilities of the ionic liquids can be tuned readily so that they can phase separate from organic as well as aqueous media. The use of ionic liquid-supported reagents allows recovery and recycle of the reagents.

The incorporation of functional groups into the ionic liquid represents one of the simplest and most effective strategies for the modification of the liquid's properties, and a large number of salts with functional groups attached to the cation have now been reported. These include, for example, amines,[5] amides,[6] nitriles,[7] ethers and alcohols,[8] acids,[9] urea and thiourea,[10] and fluorous chains.[11] In addition, functional anions have also received some attention, those giving rise to low melting salts include amino acids,[12] alkene substituted anions,[13] triazole anions,[14] selenium based anion,[15] functionalized borate anion,[16] carboranes[17] and transition metal-carbonyl anions. This line of thought gave birth to a revolutionary idea of a new class of reagents designed as TSIL an IL-Type part is combined in order to maintain the corresponding physical properties) with attached extra function designed for the specific property.

Inherited draw backs of the classical methods always keep chemists on track of hot pursuit of new and better methodologies. Task specific ionic liquid is very large field because different ionic liquids can be designed to perform various intended tasks[18] like homo and heterogeneous transition metal catalysed reactions, asymmetric synthesis,[19] solvent extractions. In this review we will only focus on task specific ionic liquids conceived and designed for organo-catalysed reactions. There is large number of task-specific ionic liquids that have been designed, synthesized and employed to generate various kinds of improvements. such as the Baylis–Hillman reaction,[20] the enantioselective photoisomerisation,[21] Michael additions,[22] and Heck oxyarylation.[23]

Brønsted acidic ionic liquids catalysed reaction

Keeping in view the importance of strong Brønsted acids in chemical catalysis various methodologies have been developed from time to time. Every technique is found to be associated certain draw backs. In continuation of trend of developing better catalytic systems A.C. Cole reported the first series of ionic liquids that are designed to be strong Brønsted acids.[24] In each of the new Brönsted acid task specific ionic liquids, an alkane sulfonic acid group is covalently tethered to the IL cation. .

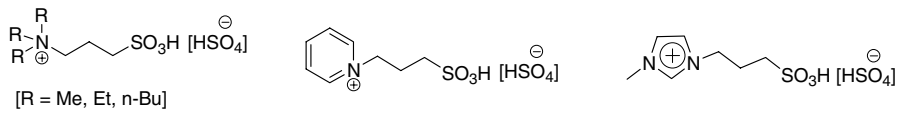


Fig. 1:

These inexpensive Brönsted acidic TSILs consist of alkane sulfonic acid group attached to suitable cation obtained from triphenyl phosphine, trialkylamine, 1-methyl imidazole and pyridine. These are SO_3H-functional halogen-free acidic ionic liquids which exhibit catalytic activity for acid-catalyzed reactions and have been screened as solvent/ catalysts for several classical acid-promoted organic reactions like Fischer esterification, alcohol dehydrodimerization, pinacol/benzopinacole rearrangement, Mannich reaction and synthesis of chalcones via the Claisen–Schmidt condensation. A.C Cole et al tested the potential of first imidazolium 1a and triphenyl phosphonium 1b based Brönsted task specific ionic liquids for Fischer esterification, alcohol dehydrodimerization, pinacol/benzopinacole rearrangement and got excellent results.

Fig. 2:

Suman Sahoo et al have investigated the potential of other SO_3H functional Brönsted acidic ionic liquids 2a and 2b for Mannich reaction.[25] The ionic liquids bearing triphenyl phosphonium sultone with p-toluene sulfonate anion (PS-PTSA) 2a or methyl immidazolium sultone with *p*-toluene sulfonate anion (MIS-PTSA) 2b were used as Brönsted acid task specific ionic liquid.

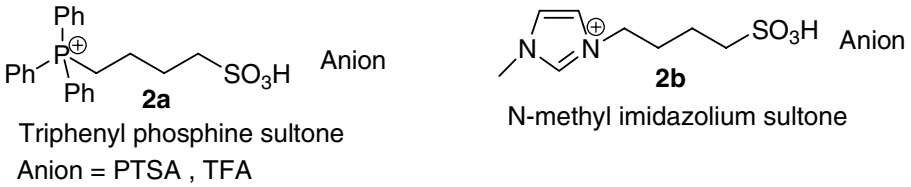
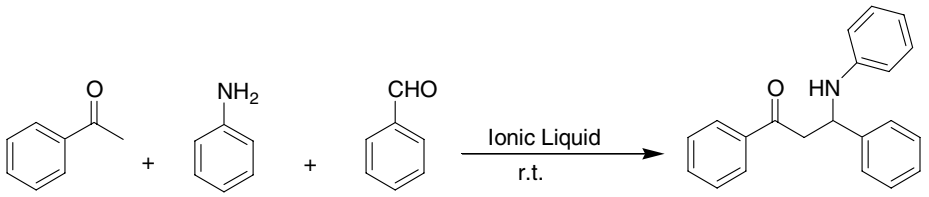


Fig. 3:

Using catalytic amount of these ionic liquids Mannich reaction of different aldehydes, ketones and amines afforded corresponding β-amino carbonyl compounds. The reactions proceeded very fast with high yield of the desired Mannich base using catalytic amount of ionic liquid



Scheme 1:

Fang Dong et al synthesized a series of acyclic SO_3H-functionalized halogen-free acids and tested the efficacy of Brønsted-acidic task-specific ionic liquids (TSILs) on the performance of Claisen–Schmidt condensation.[26] The best results were achieved with 3a.

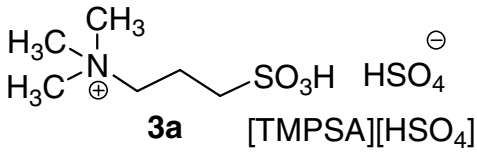
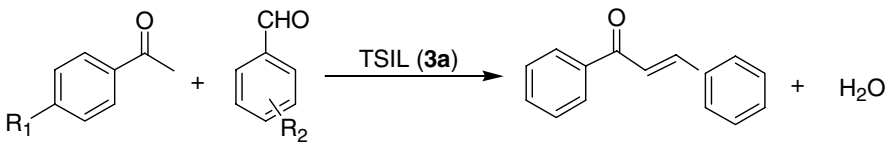


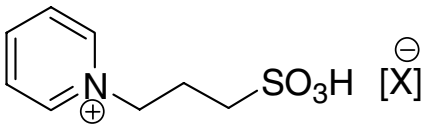
Fig. 4:

The Claisen–Schmidt condensation reactions of other substituted benzaldehydes and acetophenones in the presence of [TMPSA][HSO_4] were accomplished under the optimized reaction conditions.



Scheme 2:

Tao Wang et al reported several water-stable, SO_3H-functional Brønsted-acidic TSILs that bear an alkane sulfonic acid group in a pyridinium cation. These TSILs show good catalytic activities in the esterification reactions of benzoic acid with methanol, ethanol, and butanol. [27]



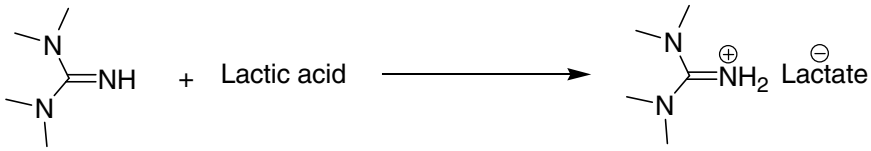
[PSPY][X]

[X] = [BF_4], [H_2PO_4], [HSO_4], [pTSA]

Fig. 5:

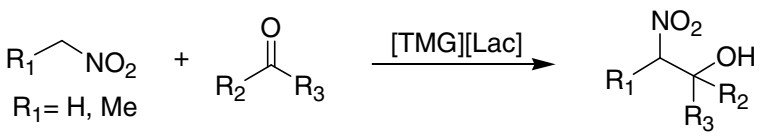
These TSILs show good catalytic activity to esterification reactions of benzoic acid with methanol, ethanol, and butanol. [PSPy][HSO_4] exhibited the best catalytic activity in the esterification reaction. Furthermore, the high degree of partial immiscibility of TSILs with the produced esters facilitates the esterification reaction equilibrium, shifting it to the product side. The produced esters could be separated by decantation, and the TSILs could be reused after the removal of water.

Tao Jiang et al have shown 1,1,3,3-tetramethylguanidinium (TMG)-based Brönsted acidic task specific ionic liquid (BATSIL) to catalyze the Henry reactions of nitroalkanes and carbonyl compounds to form 2-nitroalcohols.[28] Different kinds of carbonyl compounds like aliphatic and aromatic aldehydes and cycloalkanones proceeded to form products with good yields at room temperatures moreover the catalyst can be reused repeatedly. The guanidine-based ILs, 1,1,3,3-tetramethyl-guanidinium (TMG) trifluoroacetate ([TMG][F3Ac]) and TMG lactate ([TMG][Lac]) were prepared by neutralizing TMG with trifluoroacetic acid or lactic acid. Both of the ionic liquids are liquids at ambient temperature.



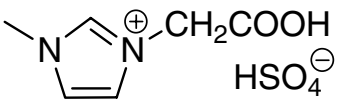
Scheme 3:

The successful results were obtained with [TMG][Lac], it catalyzed Henry reactions of aromatic and aliphatic aldehydes giving higher yields than ([TMG][F3Ac])

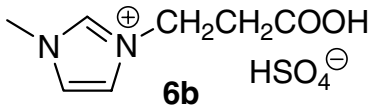


Scheme 4:

Dan Liu et al developed task specific ionic liquids possessing two Brönsted acid sites with -COOH, HSO^-_4, or $H_2PO^-_4$ as a series of nonchloroaluminiate, air and moisture stable acidic ionic liquids.[29] These new task specific ionic liquids have been used for the esterification of isopropanol by chloroacetic acid under mild conditions and without any additional organic solvent with good yields. There was no need of tedious work-up because the ester produced, formed a separate phase that was simply decanted. The ionic liquid could be reused and recycled after removal of water under vacuum. Being acidic ionic liquids, they have other great potential applications as catalysts or both as a media-cum-catalyst in many other acid catalyzed reactions, such as polymerization, etherification, Friedel-Crafts reaction, oxidation reaction, and so on.



6a



6b

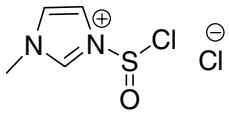
Fig. 6:

The esterification of isopropanol and chloroacetic acid was tested for using all different TSILs as the solvent/catalyst in a batch-type process. The yields of isopropyl chloroacetate esters were considerably higher (94.5% and 87.8%) in 6a and 6b ionic liquid versions.

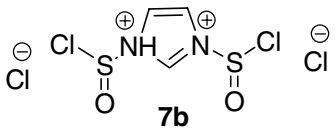
Scheme 5:

Ionic liquids possessing two adjacent acid sites for acetalization of carbonyl compounds

Dongmei Li et al reported imidazole-based mono and disulfonyl chloride task specific ionic liquid 7a and 7b for the acetalization of aldehydes and ketones with good catalytic performance under mild reaction conditions.[30]



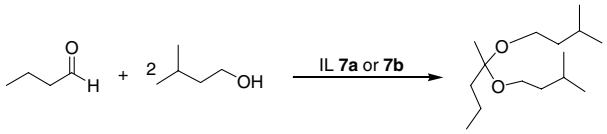
7a



7b

Fig. 7:

Acetalization of Butyl aldehyde with isoamyl alcohol was tested in 7a and 7b gave excellent results.

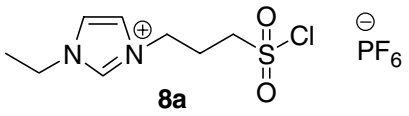


Scheme 6:

The catalytic activity was found to be excellent with7a, by achieving 94.0% conversion and 98.9% selectivity. However 7b demonstrated lower activity (81.8%), which may be attributed to the steric hindrance of this ionic liquid.

A novel task-specific ionic liquid for Beckmann rearrangement

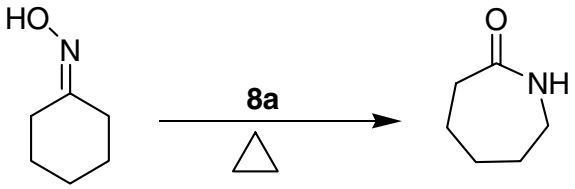
The rearrangement of a ketoxime to the corresponding amide, known as Beckmann rearrangement, is a powerful method both in organic synthesis and chemical manufacturing, particular for the preparation of ε-caprolactam from Cyclohexanone oxime in industry. Zhaolin Sun et al. has reported a novel task-specific ionic liquid consisting of sulfonyl chloride specifically designed to promote Beckmann rearrangement.[31]



8a

Fig. 8:

The proposed TSIL demonstrated high activity for Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam and cyclohexanone oxime was smoothly transformed to ε-caprolactam in high yield at ca. 80 °C. Other variety of ketoximes exhibited similar results



Scheme 7:

Geminal dicationic ionic liquids as solvents for high-temperature reactions

D. W. Armstrong et al has reported synthesis and application of a series of geminal dicationic ionic liquids with high thermal stabilities.[32] The degradation/volatization onset temperatures of these geminal dicationic ionic liquids ranged from 330 to > 400°C. These high-stability ionic liquids are promising solvents for high-temperature organic reactions including the isomerization reaction, the Claisen rearrangement, and the thermo-induced Diels-Alder reaction.

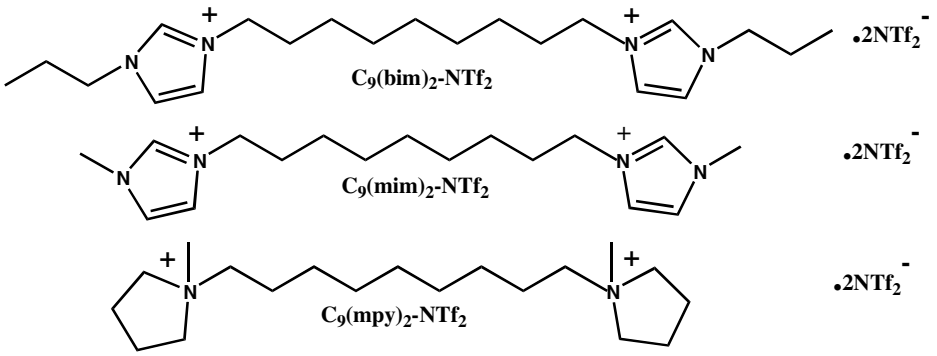
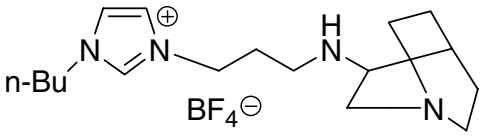


Fig. 9:

The yield of isomerization of carvone to carvacrol at 300°C was higher in $C_9(mpy)_2$-NTf_2. The Claisen rearrangement of allyl phenyl ether at 250°C produced much better yields in the $C_9(mim)_2$-NTf_2 and $C_9(bim)_2$-NTf_2 ionic liquids. The thermally induced Diels-Alder reaction of anthracene with diethyl fumarate was finished in 10 min at 220°C. Reasonable yields were obtained in the $C_9(mim)_2$-NTf_2 (51%) and $C_9(mpy)_2$-NTf_2 (47%) ionic liquids.

Ionic Liquid-Immobilized Quinuclidine for Morita-Baylis-Hillman Reactions

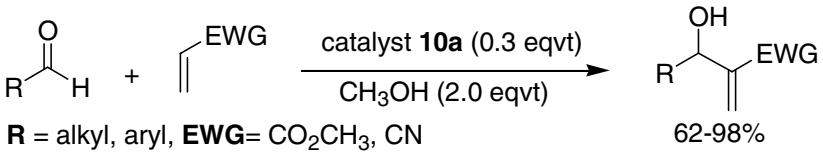
The Morita-Baylis-Hillman reaction is one of the most versatile carbon-carbon bond-forming reactions in modern organic synthesis and has great synthetic utility as it converts simple starting material into densely functionalized products. Xueling Mi et al have designed and synthesized quinuclidine-based TSIL to catalyze Baylis-Hillman reactions under the biphasic conditions, i.e., homogeneous reaction and heterogeneous separation.[33] The efficiency of ionic liquid-supported quinuclidine as a Baylis-Hillman catalyst found equally good as its non immobilized counterpart. The corresponding Baylis-Hillman adducts were obtained in moderate to high yields in all the cases tested. The IL-supported quinuclidine can be readily recovered and reused six times without significant loss of catalytic activity.



10a

Fig. 10:

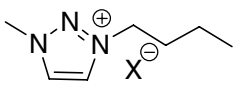
Under the optimum conditions, the 11a-catalyzed Baylis"Hillman reactions of acrylates with a variety of aldehydes were examined at room temperature. Both aliphatic and aromatic aldehydes underwent very efficient Baylis-Hillman reactions with acrylates in the presence of 0.3 equiv of 11a, giving the corresponding Baylis-Hillman adducts in good to excellent yields (62-98%).



R = alkyl, aryl, **EWG**= CO_2CH_3, CN

Scheme 8:

1,3-dilakylimdazolium cation has acidic hydrogen at C-2 which undergoes deprotonation under strongly basic conditions as in case of Baylis"Hillman reaction which forms carbene which undergoes addition reaction with aldehydes. Yunkyung Jeong et al solved this problem by reporting novel 1,3-dialkyl-1,2,3-triazolium ionic liquids which are chemically inert under basic conditions and more suitable media for the reactions involving bases like Baylis"Hillman reaction than the common 1,3-dialkylimidazolium ionic liquids.[34]



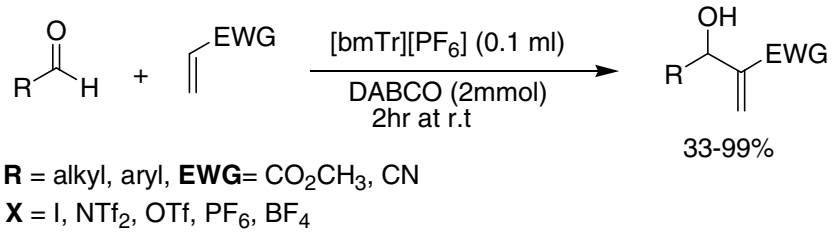
11a [bmTr][X]

X = I, NTf_2, OTf, PF_6, BF_4

Fig. 11:

The stereotype of novel 1,2,3-triazolium ionic liquid is shown in Figure 11 in which the problematic acidic C-2 proton of 1,3-dialkylimidazolium cation has been replaced by the nitrogen of the 1,3-dialkyl-1,2,3-triazolium cation to obtain the stability under basic conditions. The reported novel ionic liquids could be used as an efficient reagent for the Baylis-Hilmann reaction.

The reaction rates of Baylis-Hillman reaction in these novel ionic liquids, were compared using different aldehydes (1 mmol), acrylates (2 mmol), and DABCO (2 mmol) in the presence of 1,2,3-triazolium ionic liquids (0.1 mL). The results clearly demonstrated that the Baylis-Hillman reaction can be greatly accelerated in [bmTr][NTf_2], [bmTr][PF_6], and [dbTr][NTf_2].



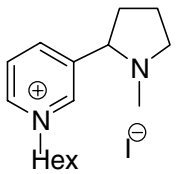
R = alkyl, aryl, **EWG**= CO_2CH_3, CN

X = I, NTf_2, OTf, PF_6, BF_4

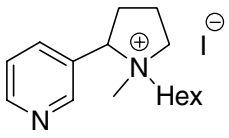
Scheme 9:

Nicotine- based task specific ionic liquids

Nucleophilic conventional solvents (pyridine, HMPA) are of particular importance in synthesis as catalytic solvents for acylation reactions, but are also highly toxic and hazardous compounds. As a result, a non-volatile and recyclable alternative would be of great potential practical benefit. Handy et al have investigated the use of nucleophilic solvents RTILs based on nicotine[35].



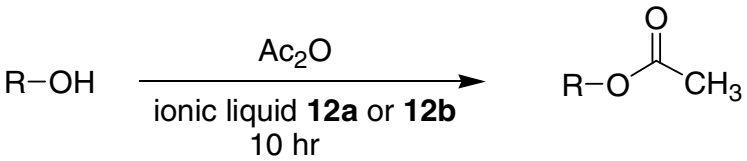
12a



12b

Fig. 12:

Both of RTILs 13a and 13b were used in standard acylation reactions. In contrast to RTIL 13b, 12a lacks nucleophilic pyridine thus not expected to catalyse acetylation. However it did effectively mediate the acylation of 2-phenylethanol as well as a more hindered secondary alcohol,1-phenylethanol with acetic anhydride and no reaction was observed with a tertiary alcohol at room temperature.



Scheme 10:

The RTIL 12b displayed similar reactivity to pyridine itself. Thus, a primary alcohol was cleanly acylated at room temperature in either solvent, while a secondary alcohol was only slowly acylated, the reaction still not being complete after 20 hours in either solvent. The more hindered substrates could be acylated by simply heating the RTIL 9 solution to 70 °C, thereby affording excellent yields of the ester of 1phenylethanol and more modest yields of the ester of 2-phenyl-2-propanol. RTIL 12b is also compatible with acid chlorides, and these more active acylating agents afforded good yields of the esters of both secondary and tertiary alcohols. Catalysts were recycled after removal of products.

Handy et al also reported synthesis and applications of fructose-based RTIL.[36] Although fructose is not capable of being transformed into cations due to lack of quaternizable elements but converted into hydroxymethylene imidazole 13a RTIL using a slight modification of the method of Trotter and Darby.[37] After two sequential alkylations and an anion metathesis step, RTIL 13b is obtained.

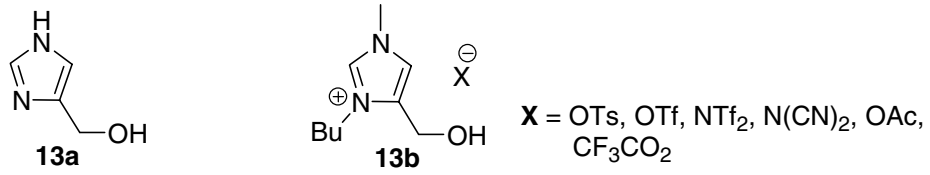
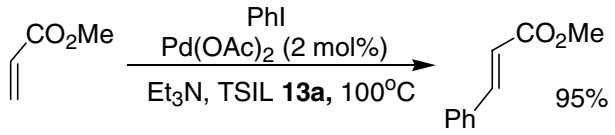


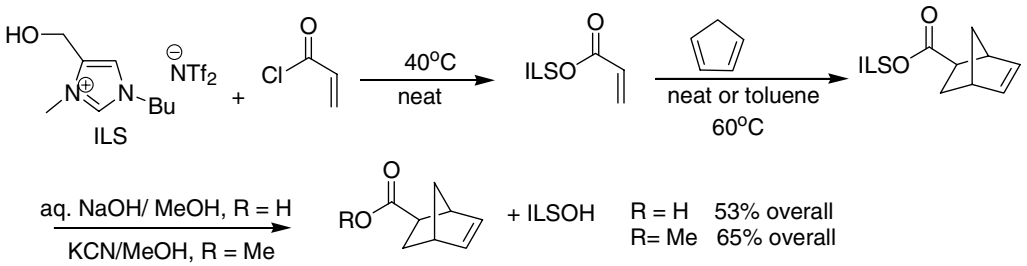
Fig. 13:

This protic RTIL was utilized in two different applications. The first is for transition metal catalyzed reactions (Scheme 11). Thus, the Heck reaction was performed using RTIL 13b in combination with a simple homogeneous catalyst, palladium acetate. The yields were uniformly >95 %, with no side reactions being observed.



Scheme 11

As a second application, RTIL 13b was used as a support for homogeneous supported-phase synthesis.



Scheme 12

Pyrrolidines -based chiral task specific ionic liquids

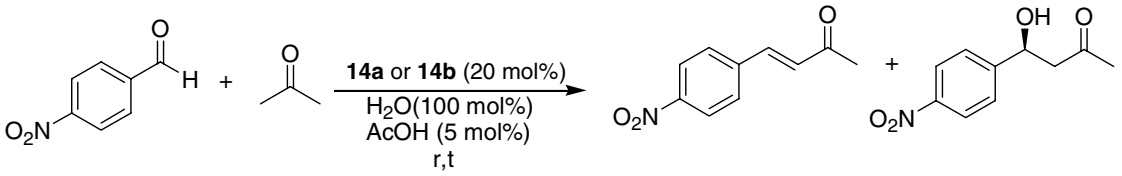
Chiral molecules are often used as chiral organocatalyst to achieve asymmetric versions of different reactions. Pyrrolidine is one of such powerful chiral organocatalysts, it is cyclic five-membered secondary amine which is now regarded as one of the "privileged" backbones for asymmetric catalysis.[38] Its high potential for achieving enantioselective synthesis has inspired many chemists to explore its potential. Some of the chemists have developed the Chiral task specific ionic liquids(CTSILs) based on chiral pyrrolidine unit which is covalently tethered to an ionic liquid moiety like imidazole, so that the former can serve as a catalytic site and the latter as both the phase tag and a chiral-induction group. Some of the important contributions from different chemists are as under.

Sanzhong Luo et al achieved successful direct asymmetric aldol reaction through Pyrrolidine-based chiral TSILs 2a and 2b. The reacton occurred via an enamine intermediate (Figure 14), and the procedure maintained the biphasic properties of ionic liquid, thereby ensuring good recyclability and reusability.[39]

14a **14b**

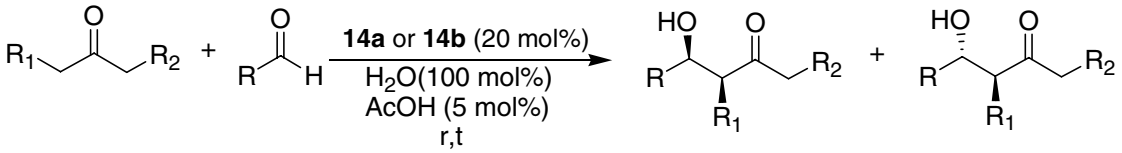
Fig. 14:

Chiral TSILs 14a and 14b catalyzed the model reaction of *p*-nitrobenzaldehyde and acetone the reaction with best yields in presence of water and acetic acid, providing the required direct aldol products along with some dehydration by-products. Other aldehydes and ketones also provided good results.



Scheme 13:

Similarly other carbonyls were treated with different aldehydes. The two diastereomeric products of aldol products were obtained in reasonable yield.



Scheme 14:

These experimental observations can be rationalized by assuming the reactions to occur via *syn*-enamine intermediate and the ionic-liquid moiety in the FIL provides some space shielding for the participating aldehyde acceptors that accounts for the modest enantioselectivities observed in the reactions.

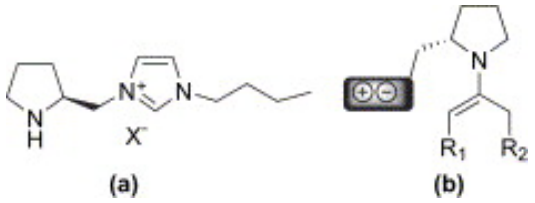
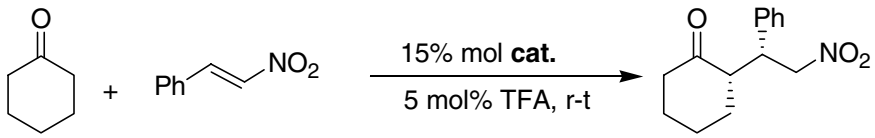


Fig. 15:

Sanzhong Luo et al also investigated the potential of same pyrrolidine-type Chiral TSILs 14a and 14b for the Michael addition of cyclohexanone to trans-β-nitrostyrene..[40] The proposed Chiral TSILs demonstrated the best performances with nearly quantitative yields and high diastereoselectivity (syn/anti=99:1) and enantioselectivity (98 % ee).

The asymmetric Michael addition of cyclohexanone to nitrostyrene furnished 75 % yield after 60 h (d.r.= 95:5 and 75 % ee for the syn diastereomer). The best performances was quantitative yields with high diastereoselectivity (syn/anti=99:1) and enantioselectivity (98 % ee).



Scheme 15:

Both electron-rich and electron-deficient nitrostyrenes were excellent Michael acceptors for cyclohexanone and cyclopentanone showing moderate diastereoselectivity and enantioselectivity for both diastereomers. Acetone also served as an efficient Michael donor to produce the desired adduct with good yield and moderate enantioselectivity. In the presence of 14a, the reaction of acetone with cyclic nitroolefins afforded the desired Michael adducts with high yields and good enantioselectivities (syn: 76% ee, anti: 80 % ee).

The Chiral TSILs 14 a and 14 b also catalyzed the Michael addition of aldehydes. Under the optimized conditions, the addition of isobutyraldehyde to trans-β-nitrostyrene gave the desired adduct in good yields and up to 89 % ee. The high diastereoselectivities and excellent enantioselectivities of Chiral TSILs catalysis in the Michael additions can be explained by the concept of an acyclic synclinal transition state. In this model, the ionic-liquid moiety would effectively shield the Si face of the enamine double bond in the ketone donor and the reaction would occur through a Re–Re approach (Figure16). The ionic and highly polar nature of the imidazolium group may also contribute in the transition state and this feature is currently under investigation.

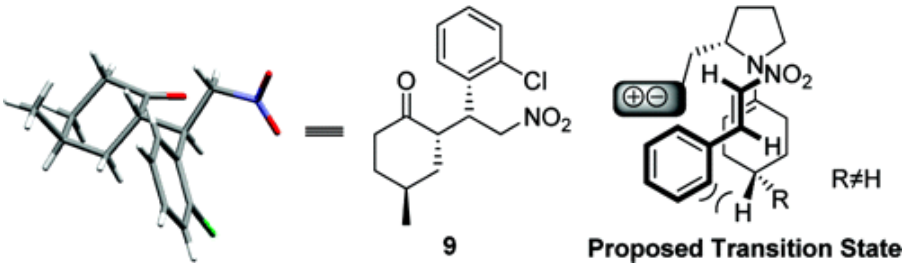


Fig. 16:

Bukuo Ni et al have the designed and synthesized new type of pyrrolidine-based chiral ionic liquid by attaching the pyrrolidine moiety on imidazolium cation.[41] This chiral task specific ionic liquids serve as chiral organocatalyst and chirality is controlled by pyrrolidine which contains N-H bond to control the stereoselectivities by hydrogen bonding. This chiral ionic liquid was found to catalyze the Michael addition reaction of aldehydes and nitrostyrenes to give moderate yields, good enantioselectivies, high diastereoselectivities.

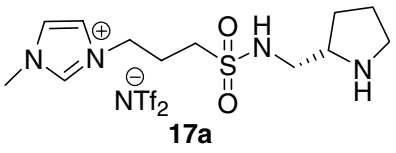
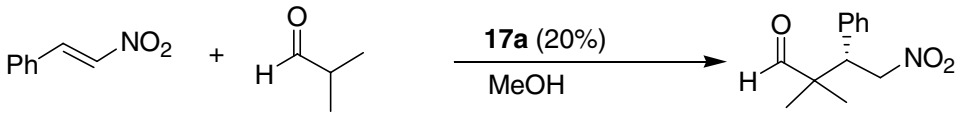


Fig. 17:

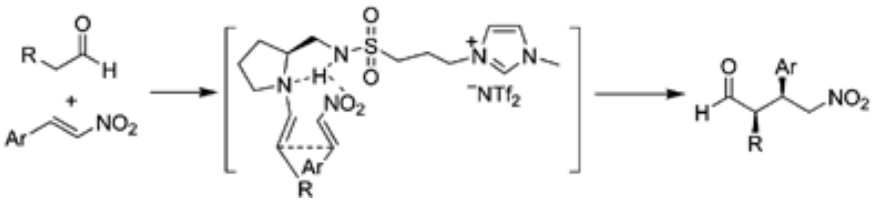
The chiral TSIL catalyst 17a catalysed a series of asymmetric Michael addition reaction of different aldehydes with nitroolefins. the Michael reaction of isobutyraldehyde and nitrostyrene in at room temperature using chiral TSIL catalyst 17a as organocatalyst in MeOH and *i*-PrOH, the reaction proceeds smoothly and gave the desired Michael adduct in good yields (62–80%) and enantioselectivities (66–67% ee).



Scheme 16:

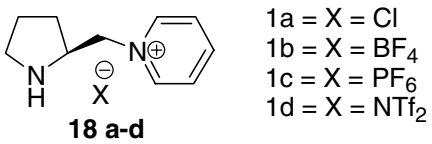
Then various aldehydes underwent successful Michael reactions with different aryl-substituted nitrostyrenes in the presence of 20 mol% of 17a in Et_2O at 4 °C, giving the corresponding Michael adducts in moderate yields (29–64%), with good enantioselectivities (64–82% ee), and high diastereoselectivities (*syn*/*anti* ratio up to 97 : 3).

The N–H acidic hydrogen plays an important role in the reaction by forming hydrogen bonds to the nitrostryene substrate in a manner that C–C bond formation would take place by the preferential enamine addition to the less hindered *Si* face of the nitrostyrene. In addition, pyrrolidine-sulfonamide-based chiral TSIL catalyst 17a, being a bifunctional catalyst, is expected to stabilize the transition state and make the selectivity possible.



Scheme 17:

Pyrrolidine-type chiral imidazolium TSILs, catalyses the assymetric synthesis with high diastereo- and enantioselectivity, but there are major problems associated is the formation of side products often result due to the relatively acidic nature of the C2 hydrogen of the imidazolium ring. Pyridinium derived ionic liquids offer a better alternative since most of the problems encountered in the use of imidazolium ionic liquids can be avoided or minimized in these ionic liquids. Bukuo Ni et al reported the design and synthesis of a novel class of pyrrolidine-based chiral pyridinium ILs, which are very effective organocatalysts for highly enantioselective Michael addition of cyclic ketones to nitroalkenes, in addition, they are easily recoverable for reuse.[42]



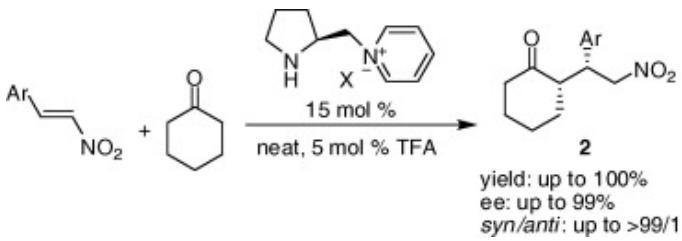
18 a-d

1a = X = Cl
1b = X = BF_4
1c = X = PF_6
1d = X = NTf_2

Fig. 18:

All the chiral TSILs synthesized were soluble in polar solvent, such as MeOH, CH_3CN, DMF, and DMSO, but were immiscible in Et_2O, EtOAc, and hexane. Chiral TSILs 18a–c were soluble in H_2O, while the anion NTf_2 18d was immiscible in H_2O. The different solubility allows them to be easily extracted for reuse.

All chiral pyridinium TSILs 18a–d catalyzed the asymmetric Michael reaction of cyclohexanone with nitrostyrene. The catalytic and enantioselective activities varied significantly with different anion moieties of chiral ILs and the additive acid. Compound 18a with Cl^- as anion was used as a catalyst to show the high diastereo- and enantioselectivity with moderate yield at room temperature .



Scheme 18:

The high diastereo- and enantioselectivities may be explained by an acyclic synclinal transition state A, in which the pyridinium ring plays an important role in shielding the *si*-face

of enamine double bond. The possible ionic attraction between pyridinium cation and nitro group of the substrate (transition state B in (Figure 19) should also contribute to the enantioselectivity observed.

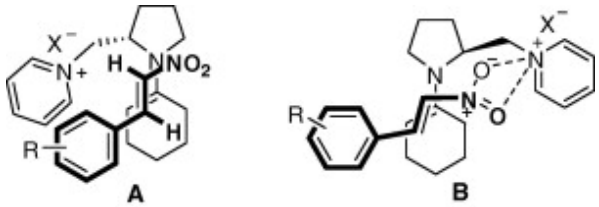
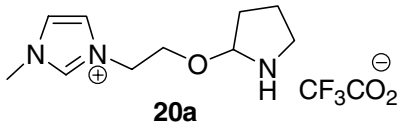


Fig. 19:

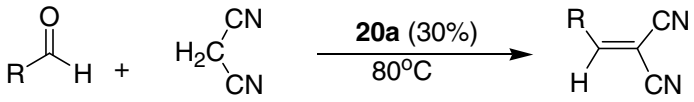
Chen Zhuo et al have already used same ionic liquid-supported proline to catalyze direct asymmetric aldol reaction[43]. This time they used it for Knoevenagel condensation reactions. The Knoevenagel condensation reaction of aldehydes with malononitrile was found to be catalyzed by ionic liquid-supported proline efficiently.[44] The method represented a better alternative to the classical synthesis strategies and exhibited the advantage of performing.



20a

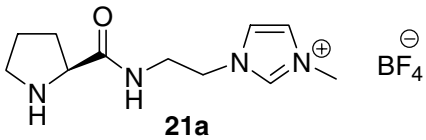
Fig. 20:

The [Promim][CF_3CO_2] (22a) was used to catalyze the Knoevenagel condensation of malononitrile with varying aldehydes and carbonyl derivatives (Scheme 19).The reactions were performed with 30 mol % of the catalyst for 24 h at 80^{o}C, resulting in expected Knoevenagel condensation products in good yield..



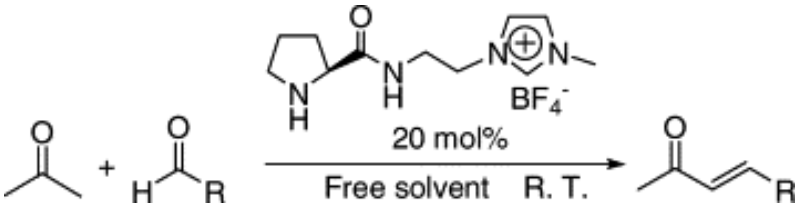
Scheme 19:

Yang Shang-Dong used pyrrolidine amide-based task specific ionic liquid for Claisen–Schmidt condensation reaction to be carried out under standard homogeneous conditions.[45] The Claisen–Schmidt reaction with acetone or cyclic ketone and various aromatic aldehydes gave (*E*)-α,β-unsaturated ketone products in good yields at room temperature under free-solvent condition.



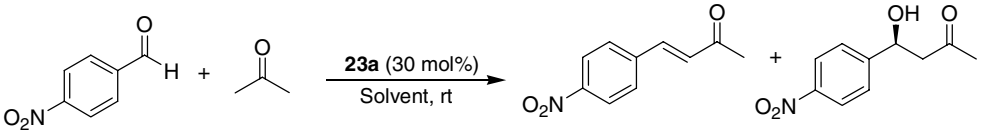
21a

Fig. 21:



Scheme 20:

The application of 23a to the direct catalysis of the Claisen–Schmidt condensative reaction between unmodified ketones and aldehydes gave desirable results under mild reaction conditions. Initially 23a was applied to the aldol condensation reaction of 4-nitro benzaldehyde with acetone in the presence of 23a (30 mol%) at room temperature in DMSO. Instead of β-hydroxy ketone, it gave dehydration product, α,β-unsaturated ketone with (*E*)-configuration in excellent yield. This indicates that 23a was an effective catalyst for direct preparation of the synthetically useful α,β-unsaturated carbonyl compounds from simple aldehydes and ketones.



Scheme 21:

New task specific ionic liquid for Swern oxidation

Swern oxidation is most powerful method of converting almost every type of alcohol into corresponding carbonyl compounds quantitatively under milder conditions. However Swern oxidation involves use sulphur compounds which are difficult to handle due to their toxicity and pungent smell. Tak Hang Chan et al developed a sulfide based task ionic liquid clean and odorless method for Swern oxidation.[46]

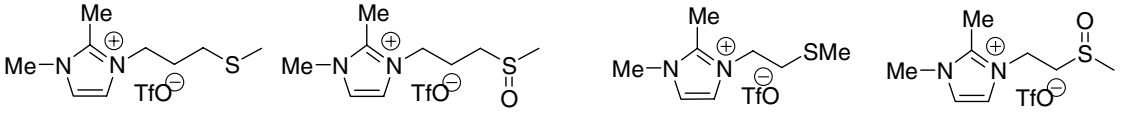
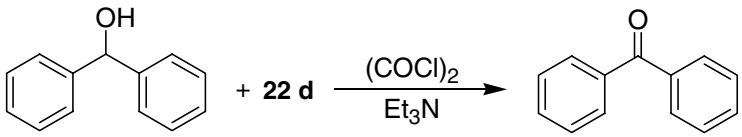


Fig. 22:

The Swern oxidations were conducted under standard conditions, using oxalyl chloride as activator and triethylamine as base in acetonitrile/dichloromethane at low temperature. The ionic liquid-attached sulfoxides 22d or 22b were quite reactive.



Scheme 22:

A number of primary and secondary alcohols with structural diversity were converted to the corresponding aldehydes or ketones in high yields. The use of ionic liquid-supported reagents allows for the opportunity of recovery and recycles. The sulfide 22c or 22a, insoluble in ether, was recovered after aqueous treatment with K_2CO_3 and extraction with acetonitrile/dichloromethane. The recovered sulfide 10b or 10c can be re-oxidized with periodic acid and used for the Swern oxidation again.

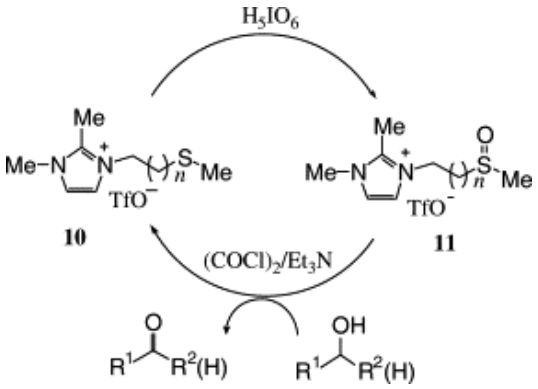
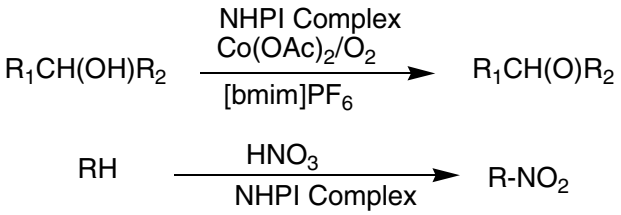


Fig. 23:

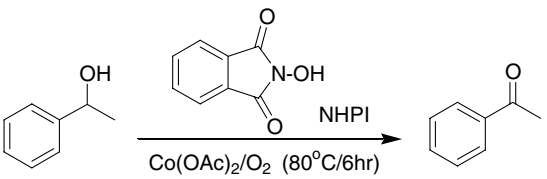
Synthetic utilities of ionic liquid-supported NHPI complex

Catalytic oxidation of carbohydrates using the stable phthalimide N-oxy (PINO) radical is one of the most promising procedures to convert carbinols into the corresponding carbonyl compounds.[47,50] It is also known that N-hydroxyphthalimide (NHPI) acts as a catalyst for the transformation of alkanes to alcohols, ketones, carboxylic acids, and/or nitroalkanes under mild oxidation conditions.



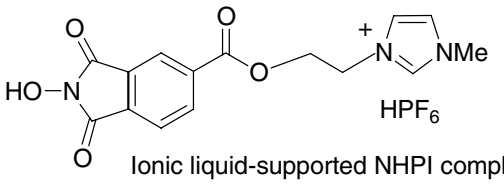
Scheme 23:

The oxidation reaction from 1-phenyl ethanol to acetophenone in the NHPI–$Co(OAc)_2$–O_2 system shows that ionic liquids like [bmim][PF_6] [bmim][CF_3SO_3] and [bmim][BF_4] are efficient medium for the oxidation reaction using NHPI as a catalyst. However, yields are drastically decreased from the first cycle (93%) to the second (80%) and the third cycles (26%).



Scheme 24:

These results show that NHPI is separated smoothly from ionic liquid with organic solvents, and that it is impossible to construct the reusable reaction system because of the disappearance of NHPI as a catalyst. Tomoya Kitazume et al have reported the utilities of ionic liquid (IL)-supported NHPI complexes as recoverable and recyclable system for the oxidation and nitration with HNO_3.[51]



Ionic liquid-supported NHPI complex

Fig. 24:

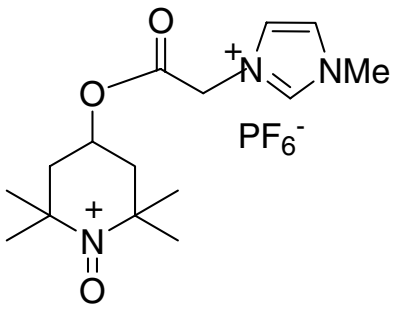
The oxidation reaction of 1-phenyl ethanol to acetophenone shows that the system using by the IL-NHPI (10 mol %)–$Co(OAc)_2$–O_2 in ionic liquid ([bmim][PF_6]), is reusable. In the same system, various types of carbinols are transformed into the corresponding aldehydes and/or ketones in good yield and secondary hydroxy group is selectively oxidized in this system. Products of oxidation in IL-supported NHPI complex-ionic liquid [bmim][PF_6] were extracted with supercritical carbon dioxide.

Direct nitration of carbon–hydride bond was also examined in this novel catalytic system. Nitration is an important process in the organic synthesis. However, the temperature (250–400 °C) for the nitration of alkanes using nitric acid and/or NO_2 is not convenient for the greener chemistry. Therefore, the nitration of alkanes was examined in IL-supported NHPI complex (25 mol %)–HNO_3–ionic liquid [bmim][PF_6] system. From the results shown in this reaction system is reusable, and then the nitrations proceed at 80 °C smoothly.

Tempo-derived task specific ionic liquids for oxidation of alcohol

The use of metal free catalyst for selective oxidation of alcohols with stable nitroxyl radicals of the 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) derivatives. These reagents present low toxicity and an interesting reversible redox behavior. Such oxidations are carried out in presence of 1 mol% of catalyst and a stoichiometric amount of a terminal oxidant such as bleach, sodium chlorite, N-chloro succinimide, MCPBA according to the protocol introduced by Aneli et al.[52] However, the separation of products from TEMPO could require lengthy workup procedures in these systems, especially when reactions are run on large scale.

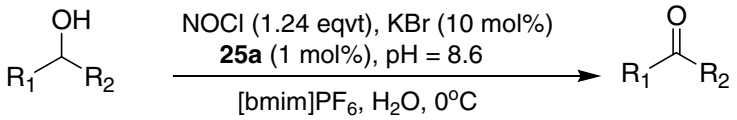
Weixing Qian has reported the synthesis of a TEMPO derived TSIL, and its use as catalyst for the metal-free, chemoselective oxidation of primary and secondary alcohols to aldehydes and ketones in aqueous-[bmim]PF_6 biphasic conditions, respectively[53].



25a

Fig. 25:

The IL-supported TEMPO radical was applied as catalyst in the oxidation of various alcohols according to the Anelli protocol. aldehydes and ketones were formed in high yield from corresponding primary and secondary alcohols respectively. Scheme 25



Scheme 25:

Ion liquid-supported hypervalent iodine(III) reagent For highly selective oxidation of alcohols

The use of organo hypervalent iodine reagents for oxidation of alcohols to carbonyl compounds is quite common. The extensively studied pentavalent iodine reagents, for example, Dess–Martin periodane (DMP) and its direct precursor *o*-iodoxybenzoic acid (IBX), oxidize alcohols efficiently to carbonyl compounds in organic solvents such as DMSO, CH_2Cl_2, and acetone. These iodine(V) oxidants are potentially explosive. Many reaction protocols have been reported. Weixing Qian et al incorporated the hypervalent iodine reagent to ionic liquid and have reported some additional advantages over the routine procedure.[54]

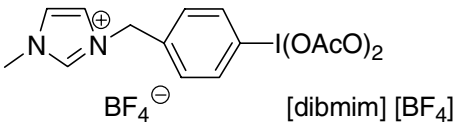
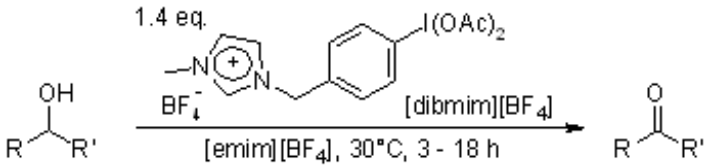


Fig. 26:

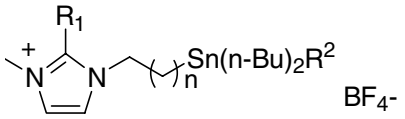
The oxidation of alcohols was conducted in the ionic liquid [emim][BF_4] using [dibmim][BF_4] as an oxidant in the presence of a low concentration of bromide ions under mild conditions (30 °C, a 1:1.4 ratio of substrate 2:oxidant 1. A variety of primary and secondary alcohols were oxidized to carbonyl compounds in moderate to excellent yields at room temperature Under these conditions primary alcohols were oxidized in less than four hours to the corresponding aldehydes in 57–95 % yields without any noticeable over oxidation to the carboxylic acids. Secondary alcohols were oxidized to the corresponding ketones over longer reaction times.



Scheme 26:

Ionic liquid supported tin reagents for Stille cross coupling reactions

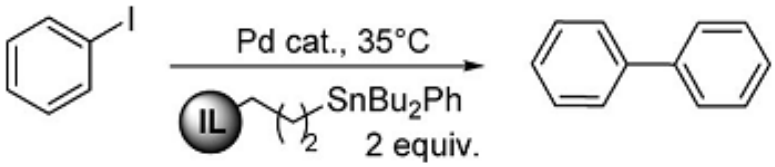
Stille cross-coupling reaction is one the powerful methods for formation of C–C bond leading to biarylation. Jürgen Vitz et al developed a new ionic liquid-supported tin reagent was synthesized for use as a catalyst in Stille cross coupling reactions.[55] This method was found to have many edges over the classical method i.e., lowered reaction temperature and recycling ionic liquid version of the Stille reagent.



R1 = H (**27a** n=2) (**27b** n=5)

Fig. 27:

With this tin reagents supported on ionic liquids, the catalysts $Pd_2dba_3{\cdot}CHCl_3$ and $Pd(dba)_2$ provided good yields of the desired biaryl products from aryl iodides and other cross-coupling reactions were successful even at low reaction temperatures without addition of copper salts or ligands. In all cases of Stille reactions of aryl iodides, very high levels of conversion could be achieved with 2 equiv. of 27a (n =2, Iodide) within 6 h in the presence of $Pd_2dba_3{\cdot}CHCl_3$, at the temperature of 35 °C to afford a product in 94% yield.



Scheme 27:

In case of substituted aryl iodides, alkyl- and methoxyiodobenzenes needed longer reaction times than unsubstituted iodobenzenes. 3-iodo-substituted pyridine and underwent successful stille coupling.

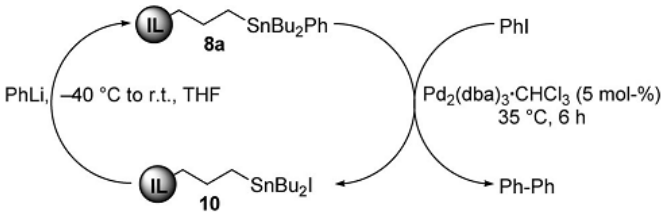


Fig. 28: Recycling of the tin compounds

It is possible to recycle the tin compound/ palladium catalyst system at the end of the reaction. Products and remaining starting materials and/or side products are extracted by organic solvents such as pentane, which is immiscible with the ionic liquid, whereas the ionic liquid phase still contains the halogenotin-supported ionic liquid 10. Simple addition of PhLi to a solution of compound 10 in THF regenerates the Stille starting material 27a. The tin reagent could be recycled five times without appreciable loss of effectiveness. The 2-positions in imidazolium ionic liquids are known to be relatively acidic, leading to substitution and exchange. In this case, however, no substitution at the 2-position of imidazolium 10 was observed with phenyllithium.

CONCLUSION

This review consists of compilation and description of different attempts and strategies to convert the conventional organocatalysed reactions involving organic solvents and expensive sometimes toxic organocatalysts into green and recyclable task specific ionic liquids. A thorough study of this article will inculcate a strategic line of thought underlying the conversion of tedious classical reactions into their modern ionic liquid version. This in turn will stir and spur further interest in converting more organocatalysed reactions into more environmentally friendly and economically feasible and little investment of time and energy. Almost cases discussed here involve betterment of the process in terms of all factors involving the reactions. A fascinating aspect of this chemistry is the emergence of a new paradigm in organic synthesis the concept of 'tailor-made' solvent, which could be in the future specifically designed for a given reaction and could be used at industrial scale. Worthy of interest is the possibility to immobilize organocatalytic systems, thus allowing to recycle both the solvent and the catalyst for further reactions. ILs open up new perspectives in organocatalysis. In particular, highly polar anhydrous ionic liquids should serve for of polar substrates such as amino acids, nucleotides and carbohydrates with enhanced activity, enantioselectivity and stability. Future of this approach seems to be enviable as these reactions can be scaled up for industrial applications.

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