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Short Review Article

Properties and Applications of Ionic Liquids

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Abstract:
Nowadays chemists seem more interested in using less toxic substances, which may result in reducing the environmental hazards. Ionic liquids (ILs) are less toxic than many common compounds. These compounds have emerged as environmentally-friendly alternative to the volatile organic solvents and catalysts. In this research study, the properties and applications of some ILs including, chiral ILs, high energetic ILs, task-specific ILs, supported ILs, polymeric ILs, acid ILs, basic ILs, and organometallic ILs were investigated. In addition, the advantages of the ILs in organic chemistry as solvents and catalysts were discussed.

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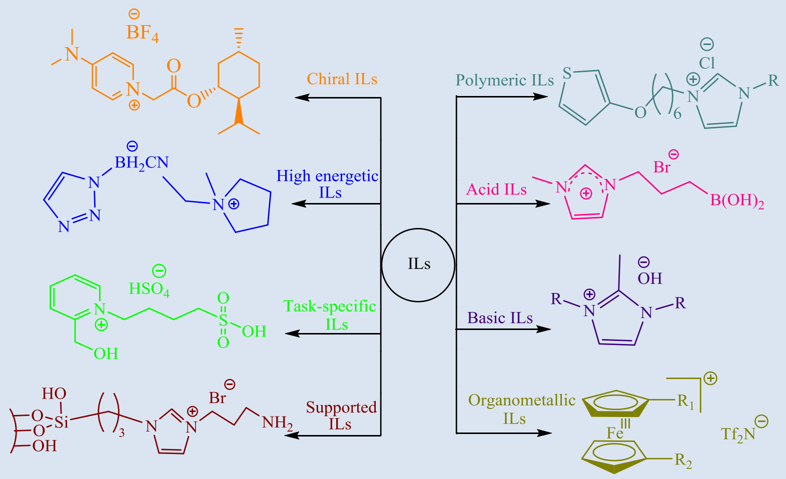
Keywords: Ionic liquids; Organic synthesis; Multicomponent reaction; Ethanol ammonium nitrate

Graphical Abstract:



Some ILs

Biography:

Omid Soleimani was born in 1991, in Iran. He obtained his BSc (**2014**) degree from Azad University of Ilam in pure chemistry. He completed his MSc (**2016**) degree from University of Hormozgan in organic chemistry. His favorite research fields are ionic liquids, organic synthesis and medicinal chemistry.

1. Introduction

Ionic liquids (ILs) are ionic compounds that possess a melting temperature below 100 ˚C. Their physical and chemical properties are attractive for various applications [1]. ILs is considered suitable substitutes for volatile organic solvents among the advantages of these compounds over other solvents can be mentioned: (1) ILs can dissolve a wide range of organic, inorganic and organometallic substances, (2) These compounds are highly polar, (3) Vapor pressure is low and non-volatile, (4) They are resistant to heat up to 300 ˚C, (5) ILs have high electrical conductivity, (6) ILs are insoluble in most organic solvents. ILs also have great potential as catalysts [2]. ILs has been widely utilized as green solvents [3]. These have

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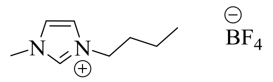
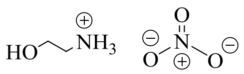
compounds some have applications in materials science [4], and electrochemistry [5]. ILs such as Scheme 1 are formed from a cation, which is usually an organic compound with an anion. The organic cation is usually asymmetric and has a larger volume than the anion. This difference in volume weakens the ionic bond between the cation and the anion, resulting in a lower melting point [6, 7]. The first ILs ethanol ammonium nitrate in 1888 reported by Gabriel *et al.* (Scheme 2) [8].



Scheme 1. Ionic liquids.

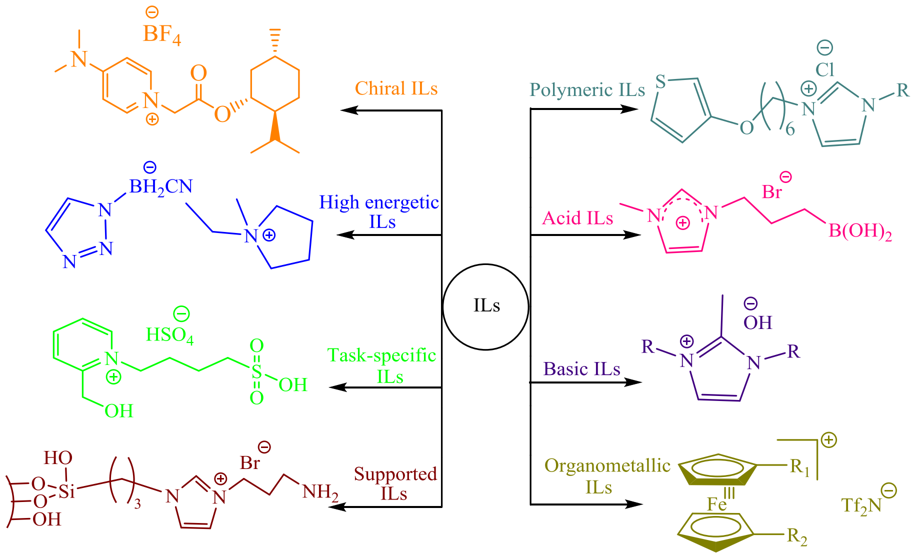


Scheme 2. Ethanol ammonium nitrate.

So far, various types of these compounds have been prepared including (Scheme 3): chiral ILs [9], high energetic ILs [10], task-specific ILs [11], supported ILs [12], polymeric ILs [13], acid ILs [14], basic ILs [15] and organometallic ILs [16].

2. Synthesis of ILs

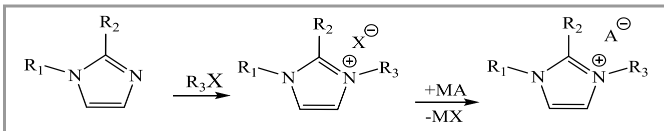
ILs can be synthesized directly through the acid-base neutralization reaction, or in other words**,** the reaction of the fourth type of amines and phosphines. For example, ethylamine aqueous solution is reacted with nitric acid and the IL is synthesized by ethyl ammonium nitrate. To obtain the pure ethyl ammonium nitrate IL, it is only necessary to vacuum the excess water from the IL. The purity of ILs is of particular importance because of their many applications in industry. Due to the low vapor pressure of the ILs, volatile impurities can be removed by distillation. In cases where ILs are insoluble with water, impurities are separated from the ionic liquids by washing water. Where IL is soluble with water, impurities are removed by extraction with various solvents [17-19].



Scheme 3. Some types of ILs.

2.1. *Synthesis of ILs by Reaction with Haloalkanes*

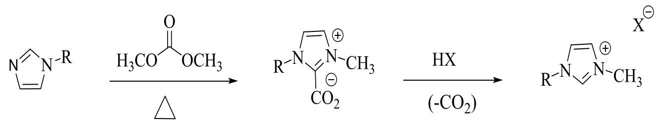
This method is one of the most widely used methods for the synthesis of ILs, and using the Tertiary amines and haloalkanes methods can provide the ILs (Scheme 4) [20].



Scheme 4. Synthesis of ILs by reaction with haloalkanes.

2.2. *Synthesis of ILs Using Carbonate*

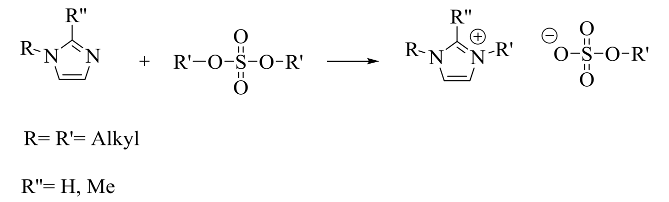
In this method, dimethyl carbonate is used as a methylating agent (Scheme 5). Dimethyl carbonate as a methylating agent is a good alternative to the compounds such as methyl halides, dimethyl sulfate, and phosgene [20, 21].



Scheme 5. Synthesis of ILs using carbonate.

2.3. *Synthesis of ILs by Reaction with Dialkyl Sulfate*

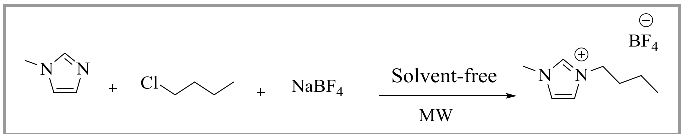
Another method for synthesis of ILs is the use of methyl and ethyl-sulfate anions and imidazole derivatives, from of the advantages of this method is its lower cost due to non-use of alkyl halides, ease of preparation, wide electrochemical window, and air stability (Scheme 6) [20, 22].



Scheme 6. Synthesis of ILs by reaction with dialkyl sulfate.

2.4. Synthesis of ILs Using Microwave Radiation

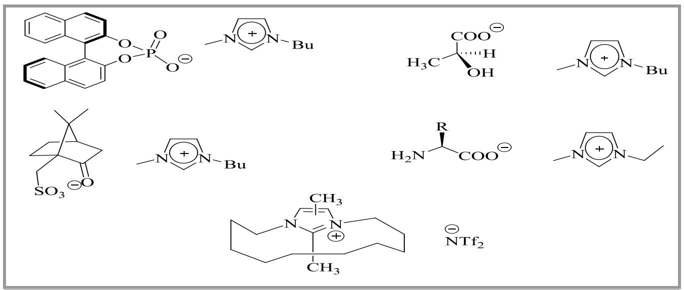
Time-consuming synthesis of the ILs is one of the leading problems in the synthesis process of these compounds. Therefore, it sometimes takes a day or a few days to get the right returns. In 2008, synthesis of these compounds by microwave radiation has been reported (Scheme7). Its advantages include lower reaction time, better efficiency and a solvent-free environment cited. $NaBF_4$ makes it easier to purify ILs. In 2019, there was a report on the use of microwave radiation for the synthesis of the ionic liquids [23].



Scheme 7. Synthesis of ILs using microwave radiation.

3. Chiral ILs

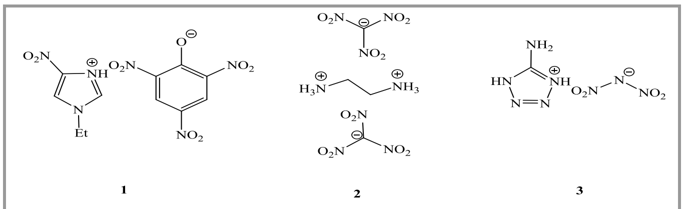
Many advances in the synthesis and application of chiral ILs have been made today. The chirality characteristic rests on the cationic or anionic part or both the cationic and anionic parts. A range of these compounds has been presented based on the chiral amino acid anions and ammonium, imidazolium and phosphonium cations. These ILs have been utilized as solvents and catalysts for the asymmetric increase of carbon dioxide to epoxides. Concerning the structure of the ILs with chiral cations, mainly imidazole rings are attached to a chiral component. For example, an ILs with proline amide units is an ILs with a chiral cation. This ILs has been used as an organocatalyst in the asymmetric aldol reactions between ketones and aldehydes. The problem with chiral ILs is their high cost. Scheme 8 shows some cationic and anionic species of chiral ILs [20, 24-29].



Scheme 8. Chiral ILs.

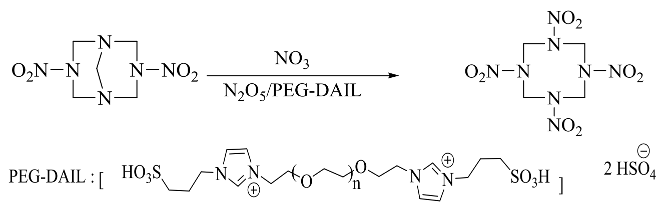
4. High Energetic ILs

It is often thought that ILs are safe; however, it is not always the case. Some of these compounds have significant flammable and explosive properties. These capabilities have led to the emergence of a new field of research called high-energy ILs. High-energy ILs are compounds that release a lot of energy due to combustion.Benefits of using high-energy ILs as a new generation of high-energy materials: (1) These compounds have unique properties of ILs such: Low melting point, low viscosity, and high thermal stability, these properties are an advantage over common high-energy materials (2) These compounds are usually less volatile, so they are less toxic and cause fewer problems for users (3) They are less sensitive to other high-energy compounds, so they are easier to transport and store. As the TNT production process produces toxic effluents and causes problems, the earliest studies on detonation applications of the EILs started with the purpose of searching for alternative 2, 4, 6-trinitrotoluene (TNT) replacement in melt-pour explosives [30-32].

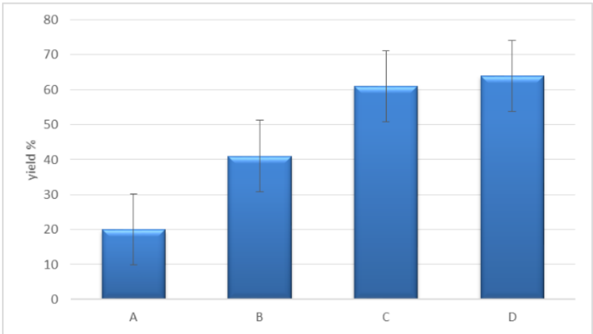


Scheme 9. High energetic ILs.

Compound 3 in Scheme 9 at the melting points below 100 $^{\circ}$C is stable up to about 160 $^{\circ}$C and has a density of 1.856 g cm^{-3}. It also has a good explosive performance, as its speed and pressure were 9429 ms^{-1} which is higher than the analogous values of the Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (HMX) [30]. ILs are in addition to being used as high-energy materials, some explosives are used as solvents or catalysts in the synthesis. At the presence of these liquids, nitration of aromatic compounds has been performed with proper efficiency and orientation [33-37]. Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) is a high-energy substance commonly used as an explosive in the military industry. The typical process for synthesis RDX is direct nitrolysis of hexamethylenetetramine with concentrated nitric acid or with a mixture of concentrated nitric acid and ammonium nitrate in an acetic anhydride medium. These methods are associated with the problems such as the production of waste caused by nitric acid and oxidation [38-40]. Presence of the $[(CH_2)_4SO_3HPyr]NO_3$ ILs, in addition to reducing these problems, yields of 72.7% were obtained [41]. HMX is one of the most powerful military explosives. Typical methods Scheme 10, for 1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (HMX) synthesis, are associated with problems such as low speed, low yields, environmental pollution. In an alternative way to use dinitrogen pentoxide (N_2O_5), the dicationic ILs are used in this work, this compound is soluble in water as well as in HNO_3 and has high thermal stability. As seen in Scheme 11, the use of ILs has increased the reaction yields [42].



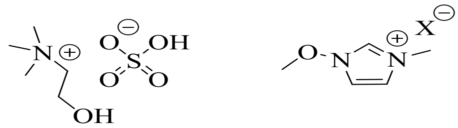
Scheme 10. Synthesis of HMX.



Scheme 11. Nitrolysis of different nitration system. Reaction conditions: 300 mmol HNO_3, 5 g DPT, 4.6 g NH_4NO_3, 60–65 °C, 2.4 g (3 mmol) PEG200-DAIL, 100 mmol N_2O_5. (A: HNO_3 B: PEG-DAIL/HNO_3, C: N_2O_5/HNO_3, D: PEG-DAIL/N_2O_5/ HNO_3).

5. Task-specific ILs

These ILs have special properties due to the positioning of a functional group on the cation or anion significant changes in their behavior are observed. Task-specific ILs are often designed to perform a specific task. For example, an ILs whose cation contains an amine functional group can separate CO_2 from the gas stream [43]. Whereas it is a sulfonic acid functional group instead of an amine group, it acts as a solvent and catalyst in the esterification reaction [44]. Over the last few years, various types of specific ILs have been used for specific tasks such as catalytic processes, organic synthesis, synthesis and stability of nanoparticles, electrochemical applications. The general classification of the task-specific ILs is as follows: Acidic ILs, Basic ILs, Organometallic ILs, chiral ILs, task-specific ILs. It is necessary to note that the uses of acid and basic words are relative ILs. For example, the N-methylmorpholinium methyl sulfonate is a task-specific IL that has been used as a catalyst for the synthesis of 5-hydroxymethylfurfural by the reaction of d-fructose and sucrose. Due to the mechanism provided by the Li atom of oxygen in the structure of the IL act as a base and its ammonium group act as an acid. However, according to the measurements taken, the acidic strength of this IL overcomes its basic strength, and its acidic property is the driving force behind the reaction. ILs are composed of cations and anions, each of which can exhibit an acidic or base property [45-46].

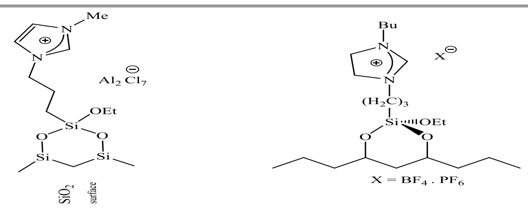


Scheme 12. Task-specific ILs.

Task-specific ILs Scheme 12 is highly potent due to the presence of the groups such as acid, base, alcohol, and ether [47-50].

6. Supported ILs

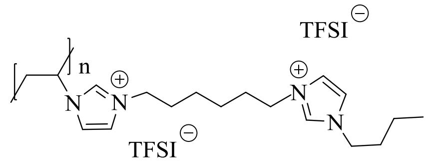
These batches of ILs that are fixed on a solid substrate are suitable solutions problems caused by environmental damage are common materials [51].The use of ILs has some problems, including: (1) Due to the high viscosity of ILs, most of them are Honey mode, so working with them is difficult. (2) The amount of ionic liquid consumed in organic reactions is high and not economically viable. To solve these problems, chemists fix ILs on solid substrates [52-54]. This method, in addition to increasing the activity and selectivity of the ILs in organic reactions, it also reduced their use [55]. Supported ILs by grafting chemicals attach to the substrate. This improved the stability of the ILs allowing it to be recycled several times [56]. These compounds also have the advantages of simple separation from the reaction medium, selectivity, and high activity [57]. In addition, they have a combination of the benefits of the ILs and stabilized heterogeneous materials [58]. One of the substrates commonly used for the stabilization of ILs is silica gel. The silica gel surface has two types of siloxane (Si-O-Si) and silanol (Si-OH) functional groups. Therefore, modification of silica gel and installation of different groups on it can be accomplished by reacting with the siloxane or silanol groups. Reaction with the silanol group is generally accepted as the main route of stabilization of different functional groups on silica gel (Scheme 13) [59-63].



Scheme 13. Supported ILs.

7. Polymeric ILs

Polymeric ILs Scheme 14 have been actively used in polymer chemistry and materials science**. T**hese compounds not only have unique properties of ionic liquids, they also benefit from properties of polymeric materials including, high mechanical stability, process improvement, durability, and adjustable architecture. Applications of these compounds include solar cells, lithium batteries, and electrochemical cells [64-66].

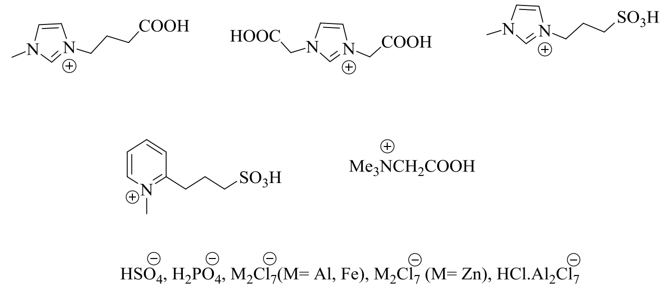


Scheme 14. Polymeric ILs.

These materials exhibit interesting properties as tunable solubility, good ionic conductivity and chemical compatibility towards ILs [67]. In a study, some polymer ionic liquids were made based on cation imidazole and pyridine and used in polyoxymethylene dimethyl ethers synthesis. These compounds have good catalytic activity, are easily separated from the reaction medium and recycle [68].

8. Acidic ILs

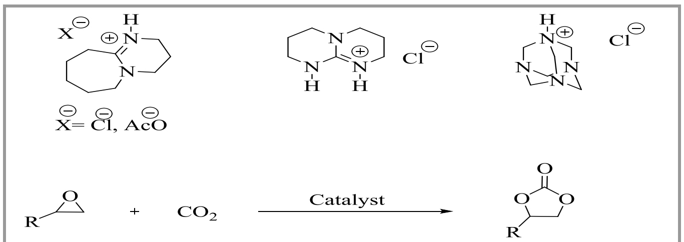
These compounds are of particular importance due to their good acidity and the properties of ILs (Scheme 15) [20]. These compounds exist in two types of Brønsted–Lewis acidic ILs. Lewis acid ILs are synthesized by the reaction of type IV ammonium salts with metal chlorides. The presence of different cation or anion species changes the acidic properties of these compounds. The good performance of these compounds makes them widely used as solvents and catalysts in the organic chemistry reactions [69, 70]. Isolation of reaction of these compounds due to their high polarity easily done. Synthesis of ILs of Brønsted acid is accomplished by the proton transfer from a Brønsted acid to a Brønsted basic. These compounds have good thermal stability and are widely used in organic chemistry. For example, using IL N-methyl-2-pyrrolidonium methyl sulfonate has been used as a catalyst in the esterification reaction. This IL has high catalytic activity so that the reaction is easily carried out at room temperature. The preparation of IL is also simple and low-cost [71, 72]. In another work the biginelli reaction under solvent-free conditions in the presence 1-methyl-3-(3-trimethoxysilylpropyl) imidazolium hydrogen sulfate with High efficiency (90–98%) was performed [73]. Hantzsch reaction in the presence of IL1-(4-Sulfonicacid)butyl-3-methylimidazolium hydrogen sulfate as a catalyst with aromatic, aliphatic, and heterocyclic aldehydes with dimedone, ethyl acetoacetate, and ammonium acetate with good efficiency [74].



Scheme 15. Acidic ILs.

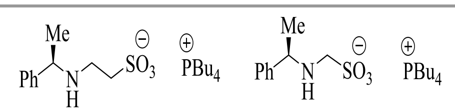
9. Basic ILs

Basic ILs have a great potential be replaced with the conventional catalysts. These compounds non-volatile, flexible, and insoluble in many organic solvents [20]. These compounds are favored by organic chemists because of their easy separation, good stability, and good performance in the reaction medium. These compounds can be divided into two classes of Brønsted–Lewis basic ILs. Basic ILs are capable of replacing old basic such as Et_3N, KOH, NaOH, K_2CO_3, NaOAc and $NaHCO_3$ act in organic reactions such as Michael addition reaction [75], esterification [76], and Markovnikov addition [77]. Some ILs have been used as catalysts in the reaction of carbon dioxide conversion to cyclic carbonates (Scheme 16) [78]. The hydroxyl group in the structure of some of these ILs makes them more efficient. For example, 1-butyl-3-methylimidazolium hydroxide has been used in the knoevenagel condensation of aliphatic and aromatic carbonyl compounds with a variety of active methylene compounds, including its advantages (1) easy to use, (2) mild reaction conditions, (3) less reaction time, (4) high yield, (5) Reusable catalyst [79]. In 2012, efficient protocol for the synthesis of compounds 1H-pyrazolo[1,2-b]phthalazine-5,10-diones using basic ILs 1,8-diazabicyclo[5.4.0]-undec-7-en-8-ium acetate, pyrrolidinium formate, and pyrrolidinium acetate are provided [80].



Scheme 16. Basic ILs.

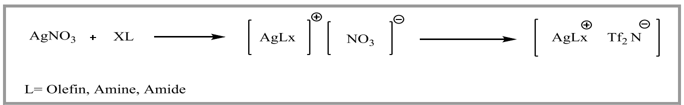
Scheme 17 shows some Brønsted basic ILs. These compounds are also liquid at ambient temperature [81].



Scheme 17. Brønsted basic ILs.

9. Organometallic ILs

A novel method for the synthesis of ILs is the use of inorganic cations of silver or zinc complexes with organic ligands such as olefins, amides, and amine-containing compounds, characteristics of these compounds are low viscosity, high conductivity, and the low melting temperature (Scheme 18) [82].



Scheme 18. Synthesis of Organometallic ILs.

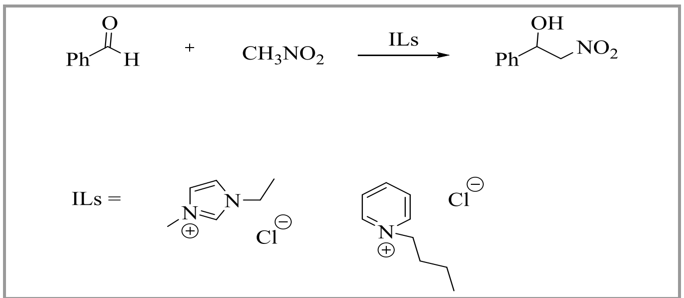
Many ILs have been developed based on the metal anions, as the first time of using anion of chloroaluminate and imidazolium and pyridinium cations. Recently some other metal species have been used instead of chlorine in the structure of these anions; one advantage of these salts is their insensitivity to water. Including metal anions can be used $[AlCl_4]^-$, $[Al_2Cl_7]^-$, $[Al_3Cl_{10}]^-$, $[CuX_3]^-$, $[InCl_4]^-$, $[AuCl_4]^-$, $[CoCl_4]^{2-}$, $[PdCl_4]^{2-}$ such as cited [83].

10. Application of ILs in organic synthesis

ILs have been widely used as solvents and catalysts in organic chemistry. These compounds often perform better compared with that of the conventional solvents and catalysts.

10. 1. Henry Reaction

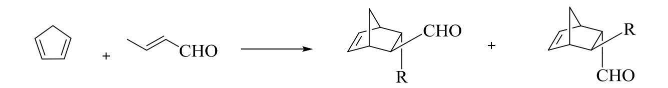
This reaction is of particular importance as a carbon-carbon bond formation reaction, in which the coupling reaction between a carbonyl compound and a nitroalkyl is carried out with the help of organic or inorganic catalysts in different solvents and under different conditions. In one sample, the reaction was carried out at the absence of ILs with a yield of 20% in 46 h and at the presence of some ILs Scheme 19, the reaction yield reached 82% in 16 h. Also, ILs have been recycled several times [84].



Scheme 19. Henry reactions.

10. 2. Diels–Alder Reaction

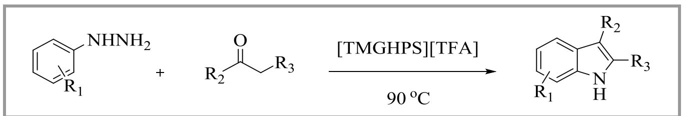
The Diles-Alder reaction Scheme 20 is a very useful method for the synthesis of compounds with a ring structure. The reaction was performed in the presence of pyrrolidinium ILs as a solvent, resulting in better conversion and less reaction time than conventional organic solvents [85].



Scheme 20. Henry reactions.

10. 3. Fischer Indole Synthesis

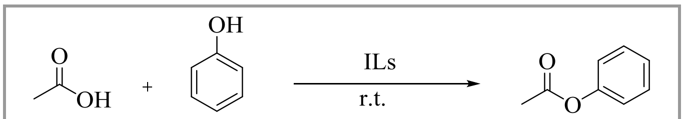
This reaction is carried out using different ketones. The reaction is important due to the synthesis of some biologically active substances and pharmaceutical compounds such as indomethacin, reserpine, yohimbine, and some amino acids as well as some antioxidants. The usual catalyst for this reaction is triphosphoric acid. It is harmful to the environment and should be used in large volumes [86]. In one reaction sample Scheme 21 performed in the presence of tetramethylguanidinium propanesulfonic acid trifluoromethylacetate ([TMGHPS][TFA]) ILs with 66-99% yield plus the ILs reused ten times [87].



Scheme 21. Fischer indole synthesis.

10. 4. Fischer Esterification

Esterification of carboxylic acids using inorganic acid catalysts is a common method. In this reaction, inorganic acid catalyst recovery is difficult. Some of these inorganic acids can corrode containers and test equipment. ILs are compounds with beneficial properties of solid and inorganic acids, which can be suitable substitutes for traditional liquid acids such as sulfuric acid and hydrochloric acid. For example, the reaction between acetic acid and benzyl alcohol was carried out in the presence of various ionic liquids. The ionic liquid has the dual role of solvent and catalyst (Scheme 22). As seen in Table 1, different percentages are obtained in different ILs. It is observed that with the anion change the percentage of product yield also changes. Also, ILs are highly soluble in water but are insoluble in the resulting ester. The performance of the compound *N*, *N*, *N*-trimethyl-*N*-propane sulfocic acid ammonium hydrogen sulfate [TMPSA] $[HSO_4]$ in the reaction of benzyl alcohol with acetic acid is discussed in the following Table 2. The reaction with this compound was performed with higher yield due to the high acidity of $[HSO_4]$. The data suggest that the above compound has been used six times without losing a significant percentage of its activity [88].



Scheme 22. Fischer esterification.

Table 1. Result for Benzyl Acetate with Different TSILs[a].

Entry	TSILs	Water content in TSILs[b] (wt %)	Conversion[c] (%)	Yield of ester[d] (%)	
				light phase	Heavy phase
1	[TMPSA][HSO_4]	5.5	96.8	92.5	2.0
2	[TMPSA][H_2PO_4]	5.3	88.9	85.0	2.1
3	[TEPSA][HSO_4]	5.2	95.7	91.2	2.6
4	[TEPSA][H_2PO_4]	5.1	85.2	82.4	2.5
5	[TBPSA][HSO_4]	4.6	92.6	90.1	2.4
6	[TBPSA][H_2PO_4]	4.5	85.9	92.0	3.5

[a]Reaction conditions: 10 mmol of benzyl alcohol/acetic acid ratio (1:1.3), TSILs 2 mL, r.t., 2.5 h. [b]Water content in the TSILs was determined by Karl Fischer titration. [c]Conversion of benzyl alcohol. [d]Yield of ester is based on isolated crude product.

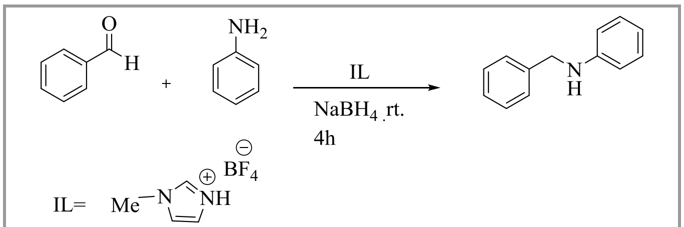
Table 2. Reuse of [TMPSA][HSO4] of the Esterfication of Benzyl Alcohol with Acetic Acid[a].

Entry	Conversion[b]	Selectivity of ester (%)	Yield of ester (%)[c]
1	96.8	98.8	92.5
2	97.5	99.8	93.9
3	97.2	99.8	92.0
4	96.5	99.8	92.2
5	96.2	99.7	91.7
6	94.6	99.6	89.7

[a]Reaction conditions: 10 mmol of benzyl alcohol/acetic acid ratio (1:1.3), TSILs 2 mL, r.t., 2.5 h. [b]Conversion of benzyl alcohol.
[c]Yields of esters are based on isolated crude product.

10. 5. Reductive amination of carbonyl compounds

There are various reagents and catalysts for converting the carbonyl group to amines. But issues such as being expensive, flammable and having to use a lot of raw materials in some cases are always problematic. Alternative methods using ILs to reduce these compounds have been proposed. For example, the ILs 1-methylimidazolium tetrafluoroborate Scheme 23 is used as a recyclable and reducing sodium borohydride catalyst for the synthesis of functional amines. In this reaction, the reduction of aniline and benzaldehyde initially results in the formation of imines due to the simultaneous addition of sodium borohydride reducing agent and ILs and finally N-benzylaniline with 70% yield. In another method, the ILs is first added, after 30 minutes of sodium borohydride is added to the medium, which increases the yield to 94% [89].



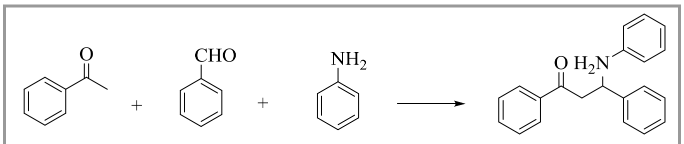
Scheme 23. Reductive amination of carbonyl compounds.

11. Multicomponent reactions

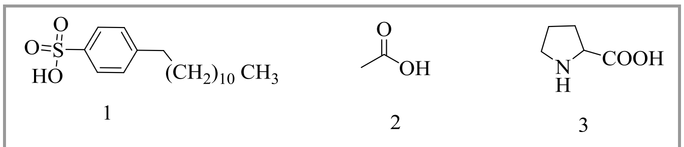
A multicomponent reaction can be described as a reaction in which three or more raw materials are mixed in a container to produce a product. Strecker first used this method in 1850 to synthesize amino acids [90]. With 170 years of experience in the field of multicomponent reactions, there has recently been resurgence in this sector, and this is related to the development of multicomponent reactions in the presence of ILs. In addition to less environmental damage, it also increases the yield of the reaction [91].

11. 1. Mannich Reaction

The Mannich reaction Scheme 24 is a classical method for the synthesis of beta-amino carbonyl compounds. These compounds are widely used in pharmaceuticals and other biological fields. This reaction is carried out with one amine group and two carbonyl groups **at** the presence of **the** acidic or base catalysts (Scheme 25).



Scheme 24. Mannich reaction.

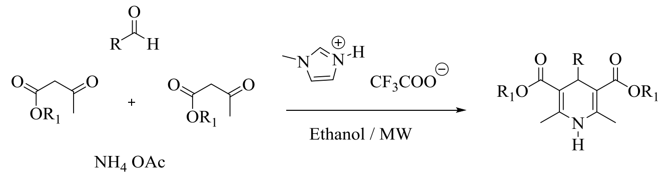


Scheme 25. Para-dodecyl benzene sulfonic acid (1). Acetic acid (2). Proline (3).

These compounds, despite their high catalytic activity, are often toxic and corrosive and difficult to separate from the reaction medium. In such reactions, acidic ILs can be a suitable substitute for common acidic catalysts. Advantages of using ILs in the reaction of Mannich: (1) Reacting in the presence of these compounds improves time and yield (2) Preparation of ILs is easier and less costly than some conventional catalysts (3) These compounds are easily separated from the reaction medium and can be reused. The ILs used in this reaction: 1-butyl-3-methylimidazolium hydrogen sulfate, 1-butyl-3-methylimidazolium hydrogen phosphate, 1-methylimidazolium para-toluene sulfonic acid, and 1-methyl imidazolium trifluoroacetic acid [92].

11. 2. Hantzsch Reaction

A multicomponent organic reaction is between an aldehyde such as formaldehyde, a β-ketoester such as an ethyl acetoacetate, and a nitrogen donor such as ammonium or ammonia acetate. This reaction was first introduced by Hanisch in 1881 **[93].** In 2012, an example of this reaction was reported **at** the presence of the ILs 1-methylimidazolium trifluoroacetate (Scheme 26). This ILs has been recycled and reused after the reaction, and the reaction at the presence of this IL revealed a good yield [94].

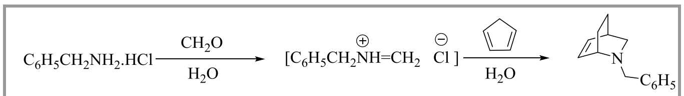


Scheme 26. Hantzsch reaction in the presence of IL.

In 2019, there was a report on the use of the supported ILs in the hantzsch reaction. The reported method provided a simple, efficient, and environmentally benign alternative for the hantzsch reaction. Also, this heterogeneous catalytic route demonstrated excellent reusability and could be reused for five runs with negligible loss of activity [95].

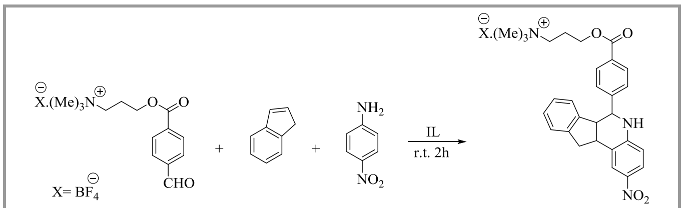
11. 3. Grieco Triple Component Density

This reaction was first introduced by Grieco in 1985. The reaction is between the aldehyde, aniline, and an electron-rich alkene. The reaction process initially involves the creation of an iminium ion followed by the Diles-Alder reaction (Scheme 27) [96, 97].



Scheme 27. Grieco triple component density.

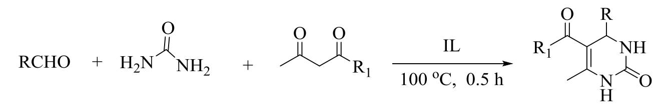
In 2007, there was a report on the use of some task-specific ILs in this reaction (Scheme 28). Among the ILs used are 1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium hexafluorophosphate [98].



Scheme 28. Grieco triple component density in the presence of IL.

11. 4. Biginelli reaction

The reaction between the aldehyde, urea, and ethyl acetoacetate, which leads to the formation of 3,4-dihydropyrimidin compounds, is known as the biginelli reaction. This reaction was first reported in 1891 by biginelli [99]. In 2001, a report on the use of 1-n-butyl-3-methylimidazolium tetrafluoroborate and hexafluorophosphate in the biginelli reaction is presented (Scheme 29). The most important advantages of this method are: (1) relatively simple catalyst system, (2) shorter reaction times, (3) higher yields, (4) free of organic solvent, and (5) easy synthetic procedure [100].



Scheme 29. Biginelli reaction in the presence of IL.

In 2018, there was a report of the use of some supported ILs in the biginelli reaction. The catalyst system used has several attractive features such as simple operation, high to excellent yields with good purity, short reaction times at moderate temperature, high catalytic activity, low loading of catalyst, environmentally benign and safe. Also, for some ionic liquids used, are thermally stable up to 260 °C [101].

12. Conclusion

This work discussed the applications and properties of the ILs. These compounds were found to be less harmful to environment, and their effectiveness has been proven in many research studies. These compounds are very diverse and have been used in various fields of chemistry. Many organic chemistry reactions, such as Henry reaction, Diels–alder reaction, Fischer indole synthesis, Fischer esterification, Mannich reaction, Hantzsch reaction, Biginelli reaction, Grieco triple component density at the presence of these compounds have been performed with higher efficiency and less time. These compounds demonstrated great potential in various fields of chemistry. The unique properties of the ILs are promising for further use of these compounds.

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Disclosure statement

No potential conflict of interest was reported by the author.

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