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Ionic Liquids – A New Era in Green Chemistry

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ABSTRACT:-

Green chemistry aims to provide environmentally benign products from sustainable resources, using processes that do not harm people or the environment. Most chemical reactions have been correlated in molecular solvents. Recently , have even, a new clan of solvents has emerged

" Ionic Liquids ".". Ionic liquids (ILs) are new organic salts that exist as liquids at low temperature (<100°C). An important future of ILs is immeasurably low vapor pressure. For this reason they are called green solvents in contrast to traditional Volatile Organic Solvents (VOCs). ILs have many attractive properties such as chemical and thermal stability , inflammability , high ionic conductivity and a wide electrochemical potential window . Therefore they have been extensively investigated as solvents or co-catalyst in various reactions including organic catalysis and inorganic synthesis, Bio-catalysis and polymerization.

Ionic liquids find application in alkylations, allylations, hydroformylations, epoxidations, synthesis of ethers, Friedel craft reaction, Diel-Alder Reaction, Knoevengal condensation and Wittig reaction. ILs have been claimed as being ''green solvents'' and possible alternative to volatile organic solvents. This has been justified in some applications where ILs, because of their negligible vapour pressure and non-flammability, are used favourably instead of chlorinated solvents. An example is given by the development of an optimised process for degreasing and/or scouring metal, ceramic, glass, plastic composite material or semiconductor surface, by treatment of the surfaces in a solution comprising an IL .Some ILs have been the subject of toxicity and ecotoxicity studies and data are now available on a larger variety of organisms (bacteria, fungi, fish , algae.). Most studies have been carried out on imidazolium- and pyridinium-based ILs, with alkyl or alkoxy side chains. The variety of anions studied is limited mainly to bromide, chloride, hexafluorophosphate and tetrafluoroborate. Much less research has been devoted to the determination of the biodegrade-ability of ILs but the design of biodegradable ILs has been covered in recent papers. A high throughput screen based on the Agar Diffusion method was recently applied to test, in a first rapid approach, the toxicity of ILs towards microorganisms and to distinguish toxic and biocompatible ILs.

My case study is about to produce effective yield of product from the reactants by choosing selective Ionic Liquids through Green mechanism. Now in modern area of ILs stems from the work on "Alkyl pyridinium "and "Dialkyl imidazolium" salts are used as green solvents.

Key Words: ILs – Ionic liquids, (bmim)ClO_4- 1-butyl ,3-methyl imidazolium per chlorate VOCs - volatile organic solvents, (emim) BF4- 1-ethyl-3-methyl imidazolium tetraflouroborate

Introduction:-

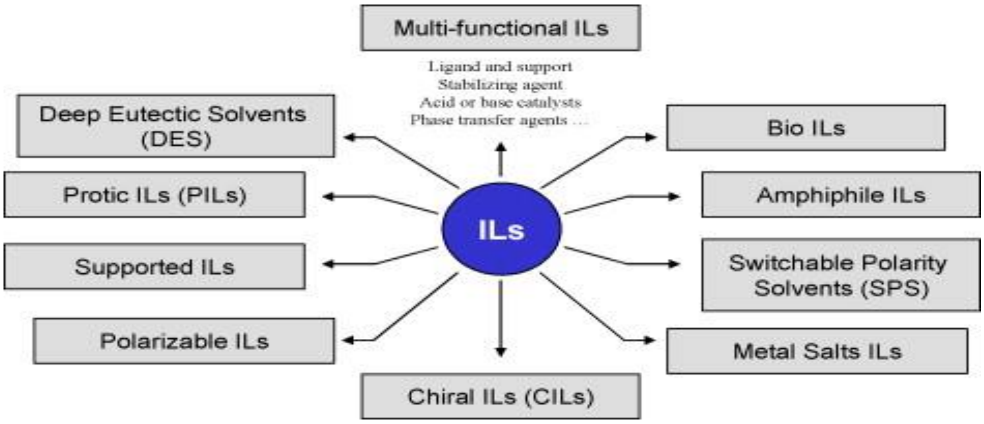
We know that 12 principles of Green Chemistry. The twelve principles essentially fall into four groups, although it should be appreciated that most examples of green chemistry in action could be placed under more than one heading:

- Efficient use of energy.
- Hazard reduction.
- Waste minimization.

- Use of renewable resources.

Some solutions are "greener then others", and many necessitate significant financial investment. New technology will only be adopted if real benefit can be shown and sometimes adaptation of existing methods is the best option. The efficiency of processes must be assessed, not only in terms of the final yield, but also cost, environmental impact and waste toxicity.

Ionic Liquids (ILs) have attracted rising interest in the last decades with a diversified range of applications in following Figure.



The types of ionic liquid available have also been extended to include new families and generations of ionic liquids with more specific and targeted properties. This expanding interest has led to a number of reviews on their physico-chemical properties, the design of new families of ionic liquids, the chemical engineering and the wide range of arrangements in which ILs have been utilized (liquid phase, multiphase, immobilized on supports, ...) and pilot or industrial developments

In addition to the fact that they are now commercially available, there is a better understanding of the effect of ionic liquids (chemical and physical properties as well as engineering fluids). Consequently, ionic liquids have been used more widely and efficiently, with better control over the overall process. The introduction of structural functionalities on the cationic or anionic part has made it possible to design new ILs with targeted properties. More recently, ILs appear to be the subject of fundamental publications aimed at improving the understanding of these solvents, predicting their physico-chemical properties and publications describing their use in increasingly diverse applications such as sensors, fuel cells, batteries, capacitors, thermal fluids, plasticizers, lubricants, ionogels, extractants and solvents in analysis, synthesis, catalysis and separation, to name just a few. Some new applications, such as energetic compounds or pharmaceutical ILs, are still emerging. ILs can be used as more than just a alternative ‘‘green’’ solvents. They differ from molecular solvents by their unique ionic character and their ‘‘structure and organization’’ which can lead to specific effects. They are tunable, multipurpose materials.

Illustration 1 ;

A Green Protocol for Efficient Synthesis of 1, 8- Dioxo- Octahydroxanthenes Using Ionic Liquid (1-butyl ,3-methyl imidazolium per chlorate(bmim) ClO_4 and it was recovered and reused for three times.

1,8-dioxo-octahydroxanthenes are important class of Oxygen hetero cycles in which a phenyl substituted Pyran ring is fused on either side with two cyclohexanone rings. Presence of conjugated bis-dienone functionality makes these compounds sensitive to be attack by nucleophiles and light energy. In the past decade synthesis of xanthenes derivatives has been of considerable interest to organic chemists because they possess various biological and pharmaceutical activities such as Antiviral, Anti Bacterial, Anti-Inflammatory properties. These are utilized as Antagonists for paralyzing action of zoxazolamine and in photodynamic therapy.

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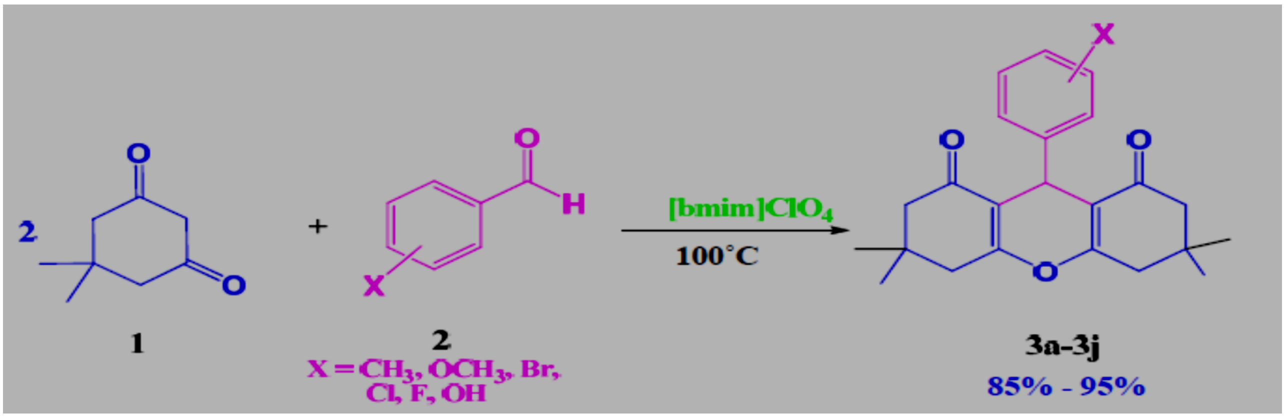


Scheme 1. Synthesis of 1,8-dioxo-octahydroxanthene using [bmim]ClO_4 ionic liquid.

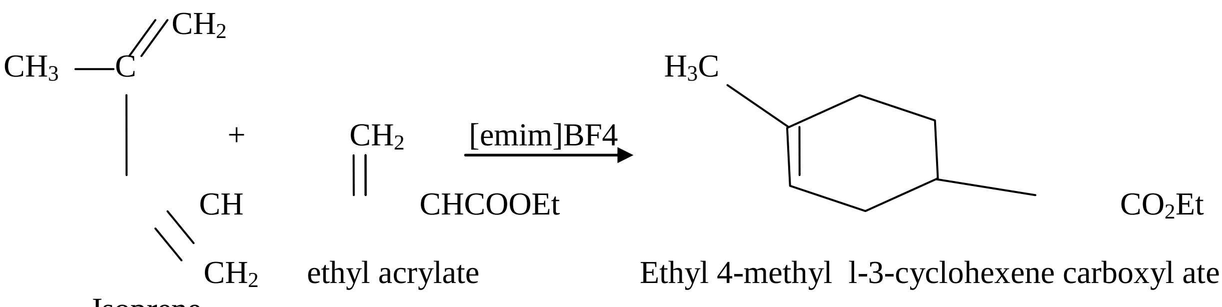
Table 1. Comparison table with various reported catalysts.

Entry	Catalyst used	Time	Solvent	Temperature	Yield (%)
1	Tetrachloro silane	3 hrs	CH_2Cl_2	60 - 70°C	92
2	$SmCl_3$	8 hrs	No solvent	120°C	98
3	Cellulose sulfonic acid	6 hrs	No solvent	110°C	95
4	Heteropoly acid supported MCM-41	5 hrs	Ethanol	90°C	90
5	[Bmim]HSO_4	3.5 hrs	No solvent	80°C	76 - 94
6	[Hbim]BF_4	45 min.	Methanol	Ultrasonic 25 - 30°C	85
7	Trimethyl silyl chloride	8 - 10 hrs	Acetonitrile	Reflux	72 - 84
8	[Bmim]ClO_4	40 - 90 min.	----	100°C	85 - 95

Illustration2:

Ethyl 4-methyl-3-cyclohexene carboxylate synthesis

It is prepared by Diels-Alder reaction of isoprene (dienophile)with ethyl acrylite(diene)in natural ionic liquids ,viz 1-ethyl-3-methyl imidazolium tetraflouroborate [emim]BF_4.



ethyl acrylate

Ethyl 4-methyl l-3-cyclohexene carboxyl ate

Isoprene

ENTRY	Reactants	Catalist used	Time	Solvent	Temperature	Yield
1	isoprene , ethyl acrylate	[emim]BF4	24 hrs	No Solvent	70^oc	97%
2	Isoprene, but-2-en-3-one	[bmim]BF4	2hrs	No solvent	20^0c	90%

Illustration3:

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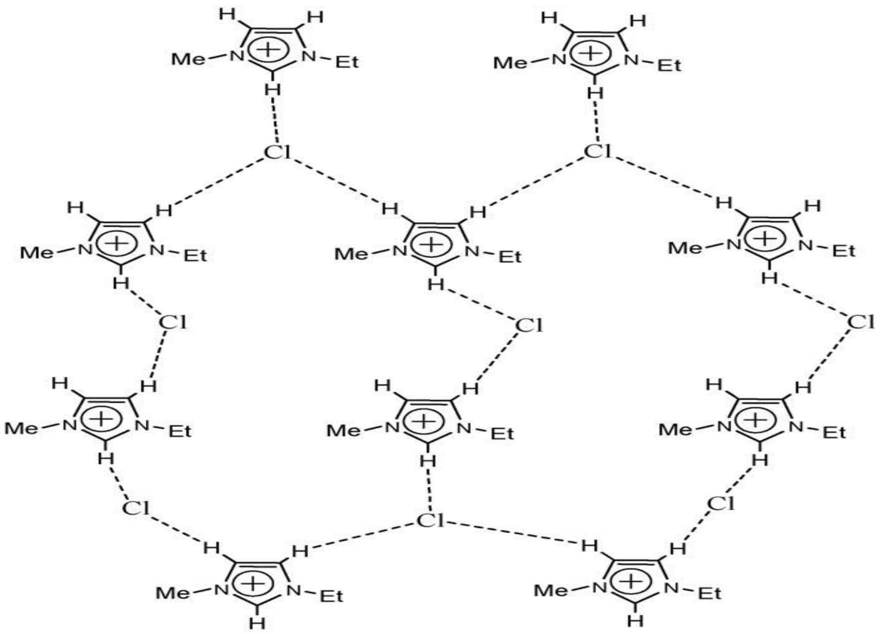
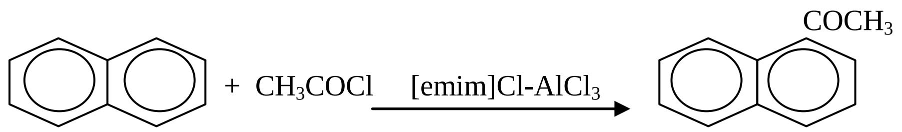
<u>Preparation of 1-Acetylnapthalene by using ionic liquid</u>



Representative scheme of extended three-dimensional network of H-bonds in [EMIM][Cl] ionic liquid.

<u>1-Acetylnapthalene</u> is obtained by Friedal-Crafts reaction of naphthalene with acetyl chloride in presence of ILs **such as the[emim]Cl-AlCl$_3$.[emim=1-methyl 3-ethyl imidazolium cat ion]**

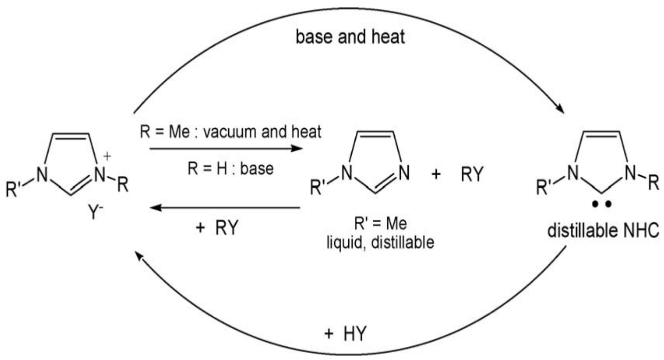


Naphthalene acetyl chloride 1-acetyl naphthalene

Entry	Reactants	Catalist used	Time	Solvent	Temperature	Yield
1	**Napthalene,acetyl chloride**	[emim]Cl -AlCl$_3$	**1 hr**	**No Solvent**	**0^{o}c**	**89%**
2	**Toluene,chlorobenzene and anisole**	[emim]Cl -AlCl$_3$	**1 hr**	**No Solvent**	**0^{o}c**	**97-99%**

Recover of ILs.

The ionic liquid used can be recovered and reused three times without significant decreasing in the yield of the product



Different possible routes to recover ILs.

Conclusion

The aim of this review was not to give an exhaustive, full description of all the catalytic reactions that can be performed in ILs. Our objective was rather to stand back from the huge quantity of publications and patents and to try to give a general overview of what can be done. In this context, many topics have not been broached while being the object of much interest.

Ionic liquids present the potential to have a huge impact on organo-catalysis. This potential has been demonstrated in Diels-Alder reactions in which ILs can display interesting H-bonding with the reactants and then can direct the reaction selectivity. Imidazolium-derived organo-catalysts which can be recycled because of their insolubility have also been reported**.**

In summary we discussed high yielding simple convenient straight for word and practical one pot procedure for the synthesis of different types of economically and medicinally used organic compounds using Alkyl imidazolium and Alkyl Pyridinium ionic liquids. The ionic liquid used can be recovered and reused three times without significant decreasing in the yield of the product. Green Chemistry is not a solution to all environmental problems But the most fundamental approach to preventing pollution.

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