Research Journal of Chemical Sciences ISSN 2231-606X
Vol. **5(3),** 77-89, March **(2015)** *Res. J. Chem. Sci.*

Review Paper

Use of Non-Conventional Reaction Media - A Green Approach

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Available online at: www.isca.in, www.isca.me
Received 11th February 2015, revised 10th March 2015, accepted 16th March 2015

Abstract

Use of volatile organic solvents, particularly the chlorinated hydrocarbons, lead to serious environmental issues like air and water pollution. It has been realized that the replacement of these environmentally harmful solvents with benign non-conventional media will be a great step towards achieving sustainable processes. The most prevalent of these new solvent systems include, but not exclusively, water, supercritical fluids (like supercritical CO_2), ionic liquids, solvent-less processes and fluorous solvents.

Keywords: Non-Conventional media, supercritical fluids, ionic liquids, fluorous media.

Introduction

Most chemical processes involve solvents in the reaction and separation step to dissolve solids, reduce viscosity, modulate temperature, and recover products by means of extraction or recrystallization as reaction media or for cleaning purposes. Solvents not only dissolve the reactants but they also affect the rates, chemo-, regio- and stereoselectivities of reaction. However, majority of the organic solvents used in industry, despite their inherent advantages, are associated with several ill effects on human health and environment. Moreover, these solvents are derived from non-renewable resources like petroleum. These parameters are in contradiction to the very basics of Green Chemistry[1]. Due to these reasons, the only alternative available is to substitute these environmentally harmful solvents with some benign solvents. Hungerbuhler et al discussed the following four directions towards the development of green solvents[2].

Substitution of hazardous solvents with one that show better EHS (Environment, Health, Safety) properties such as increased biodegradability or reduced ozone depletion potential[3]. Use of "bio-solvents" i.e solvents produced from renewable resources such as ethanol produced by fermentation of sugar-containing feeds, starchy feed materials or lignocellulosic materials[4]. Substitution of organic solvents with supercritical CO_2 in polymer processing avoids the use of chlorofluorocarbons, and reduces the ozone depletion[5]. With ionic liquids that show low or negligible vapour pressure, and thus fewer emissions to air[6].

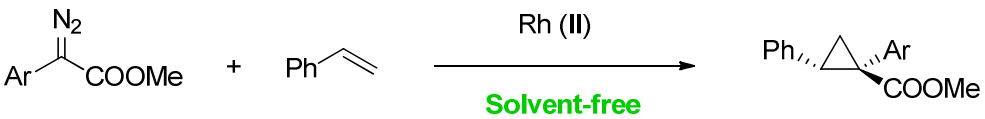
Sustainable processes can be developed using all the alternatives in different ways as it is unlikely that only one solvent will be the panacea for various chemical protocols[7,8].

Various Non-Conventional Approaches

Solvent-free Reactions: Solvent-free processes or reactions are the best solution for minimizing the solvent losses as they are clean, safer, efficient and economical[9-11]. They can be efficiently coupled to non-classical methods of activation like ultrasound and microwave[12-15]. The best solvent is no solvent (prevention is better than cure).

A reaction can be carried out without a solvent when the reagents are liquids or the reaction mixture can be melted to produce a liquid. Solvent-free separation step includes mechanical separation instead of extraction with an organic solvent. The work-up is considerably simplified, cost is reduced, energy consumption is lowered and an increased amount of reactants can be used in the same equipment with the added advantage of enhanced reactivity and selectivity in some cases as illustrated by the examples discussed below: Pelphrey and co-workers demonstrated efficient solvent-free reactions involving donor/acceptor substituted rhodium carbenoids[16] (Scheme-1).

Cruz et al carried out synthesis of a series of N-alkylpyrrolidino [60] fullerenes without solvent by phase transfer catalysis under microwave irradiation[17] (scheme-2).



Scheme-1

A one-pot synthesis of substituted coumarins via Pechmann condensation has been efficiently catalyzed by silica-gel supported sulfuric acid under solvent-free conditions[18] (scheme-3).

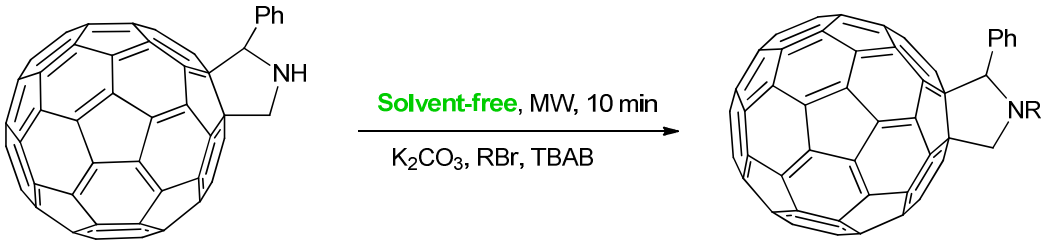
Jiang et al carried out solvent-free synthesis of substituted ureas from CO_2 and amines using [bmim]OH as catalyst[19] (scheme-4).

A chemoselective solvent-free protocol was developed by Hua and co-workers for the reaction between ortho-aminocinnamate and isothiocyanates[20]. It has been found that when $Yb(OTf)_3$ was used as a catalyst 2-Amino-3,1-benzothiazines were obtained in high yields whereas $[(Me_3Si)_2N]_3La(\mu\text{-}Cl)Li(THF)_3$ leads to 3,4- dihydroquinazoline-2-thiones (scheme-5).

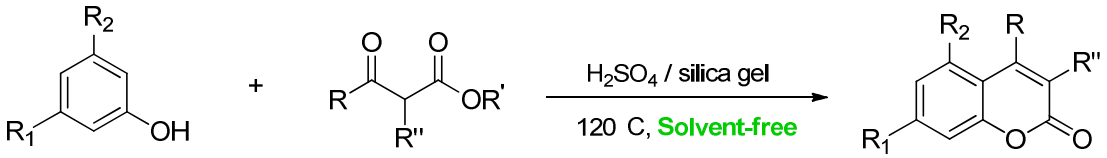
Pooladian and co-workers developed a solvent-free and catalyst-free, one-pot protocol for the synthesis of novel symmetrical bisthioglycolic acid derivatives starting from thioglycolic acid and aldehydes/ketones[21]. The green attributes of the reaction are absence of organic solvents at any stage of reaction, shorter reaction times, easy work-up, no requirement of purification of products by column chromatography (scheme-6).

Aurones and hydroxyaurones have been efficiently prepared by grinding aldehydes with substituted 2-hydroxyphenacyl chlorides under solvent-free conditions using activated barium hydroxide as solid base[22] (scheme-7).

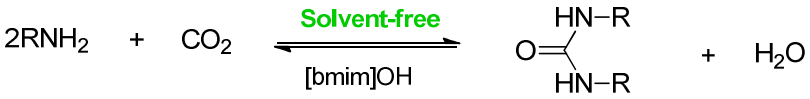
Supercritical Fluids: Supercritical fluids have emerged as useful solvents for extractions, chromatography and some specific chemical reactions[23-25]. They differ from ordinary liquids and gases in their properties which can be tuned as per the requirement of a process simply by changing the temperature and pressure.



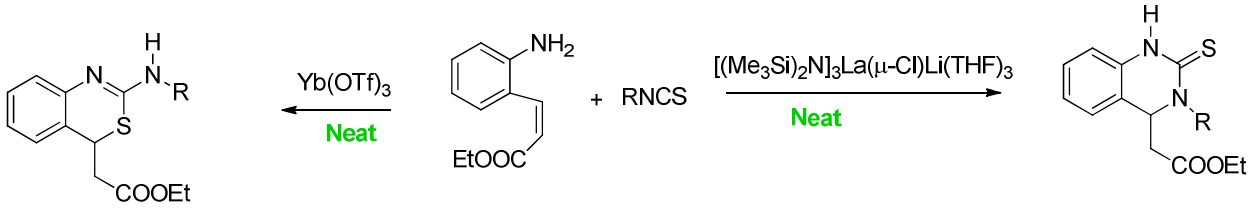
Scheme 2



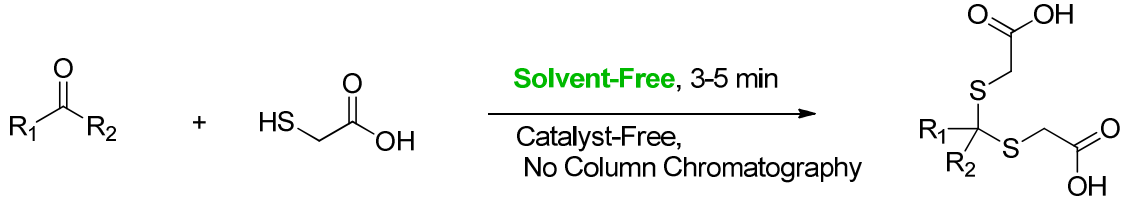
Scheme 3



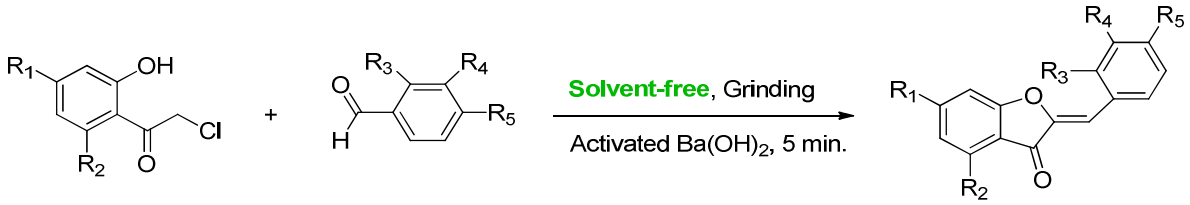
Scheme 4



Scheme-5



Scheme-6

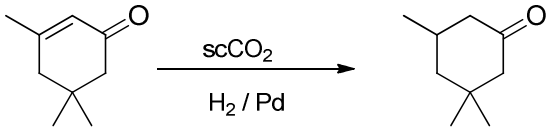


Scheme 7

The most popular supercritical fluid is supercritical carbon-dioxide ($scCO_2$)[26]. Supercritical carbon-dioxide is readily available, with a critical temperature (T_c) of 31.1°C and critical pressure (P_c) of 72.9 atm. There are various advantages associated with the use of $scCO_2$ and are discussed in a number of recent articles[27-31].

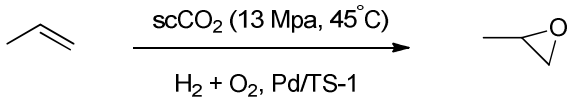
CO_2 is available in abundance, non-toxic, non-flammable, and relatively inert towards reactive compounds. The most remarkable property of scCO2 is that by changing the pressure and temperature it can be made to behave like a gas or a liquid, giving it the ability to diffuse or solvate respectively. Moreover the critical temperature being very low, allows the heat sensitive reactions to be carried out at ease. The use of $scCO_2$ permits selective extraction as all chemical reactants do not solubilize in it easily. Moreover, it's removal from the reaction mixture is quite easy by depressurization. The use of CO_2 do not lead to global warming as its usage involve no net addition to the atmosphere, it is taken from atmosphere and returned there. Supercritical carbon-dioxide find application in a number of industrial processes.

Poliakoff pioneered the use of $scCO_2$ as a solvent for catalytic hydrogenation and Thomas Swan and Co. commercialized it for the manufacture of trimethyl cyclohexanone by palladium catalyzed hydrogenation of isophorone[32] (scheme-8).



Scheme 8

Recently, much interest has also been inclined towards catalytic oxidations with hydrogen peroxide, generated in situ by Pd-catalyzed reaction of hydrogen with oxygen, in $scCO_2$-water mixtures. This system was effectively used by Danciu et al for the direct epoxidation of propylene to propylene oxide over a Pd/TS-1 catalyst (scheme-9)[33].



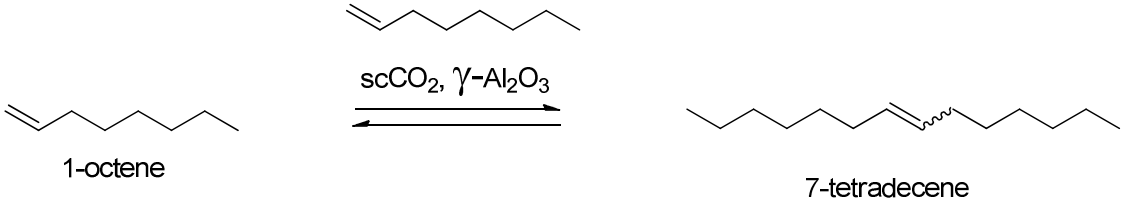
Scheme 9

Supercritical carbon-dioxide is an ideal solvent for metathesis reactions because of high solubility of alkenes in it. Selva et al used $scCO_2$ as a reaction media to execute the selective self metathesis of α-olefins (1-hexene, 1-heptene and 1-octene) in the presence of heterogeneous Re catalyst[34] (scheme-10). Effect of carbon-dioxide pressure, amount of catalyst and nature of catalytic support were studied extensively. It was observed that Re-oxide showed good activity when supported on γ-Al_2O_3 while silica supported systems were found to be inactive. The self metathesis of 1-octene at 35°C in $scCO_2$ gave conversion over 35% higher than the conventional solvents. Under the optimized conditions, the recyclability was successfully studied upto two cycles.

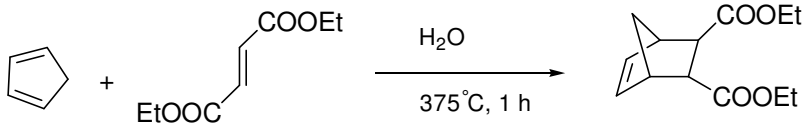
Supercritical water (374°C, 218 atm) has been recognized as an attractive and green reaction medium due to its unique properties and environmentally favorable nature[35,36]. Dielectric constant of supercritical water roughly corresponds to that of common organic solvents so organic reactions get facilitated in this medium. Lower viscosity (2.98 x 10^{-5} PaS) at critical point provides high diffusion coefficient.

Hayashi and Hakuta carried out the synthesis of metal oxide particles in supercritical water which allows control of the crystal phase, morphology, and particle size. They emphasize the use of supercritical water in the formation of fine particles[37].

Korzenski and Kolis performed Diel's Alder reaction of cyclopentadiene and various electron poor dienophiles in supercritical water and obtained medium to high yields of clean products in the absence of catalysts[38] (scheme-11).



Scheme10



Scheme 11

Dreher and co-workers carried out the conversion of biomass into methane in supercritical water using carbon-supported ruthenium catalyst in a realistic continuous flow process[39]. In-situ XAS studies revealed that sulphur poisoning of Ru/C is an irreversible process and possible regeneration procedure may involve chemical treatment of sulphur poisoned catalyst.

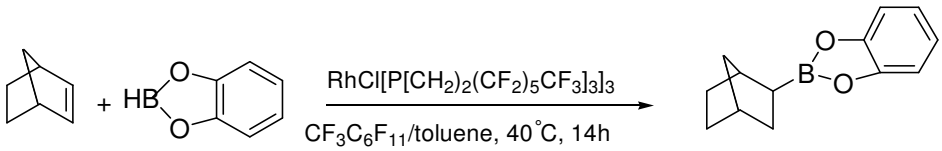
Fluorous Media: "Fluorous" is the term coined for highly fluorinated (or perflourinated) solvents by Horvath[40,41]. Now a days, fluorine chemistry constitutes an important part of clean technology, both in catalysis and as an alternative reaction media[42]. Fluorous solvents possess unique physico-chemical properties, such as low dielectric constant, high chemical and thermal stability, and low toxicity. Due to temperature-dependent miscibility with organic solvents, fluorous solvents find numerous applications in biphasic catalysis[43,44].

Juliette et al have reported hydroboration in perfluoromethyl cyclohexane and toluene using a rhodium complex catalyst with fluorous ligands (scheme-12). After the reaction was complete, the product was separated and the fluorous phase containing the catalyst was reused[45,46].

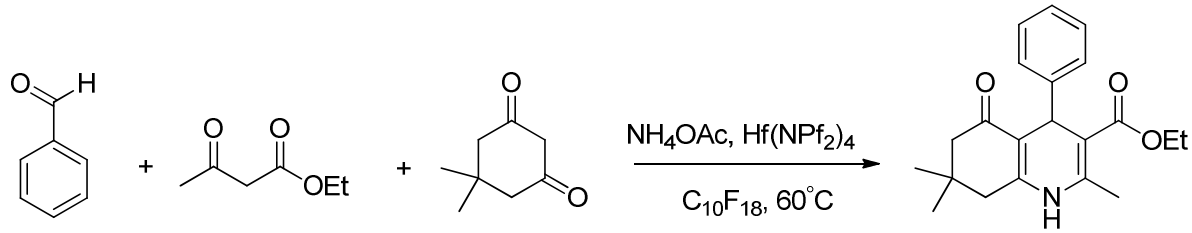
Using fluorous solvent as reaction media and Hafnium (IV) bis (perfluorooctanesulfonyl) imide complex as catalyst, Hantzsch synthesis of polyhydroquinoline derivatives was executed in an efficient way [47] (scheme-13). Shorter reaction time, easy work-up, reusability of catalyst and excellent yields are the highlighting advantages of this methodology.

Yu et al synthesized a novel Pd-NHC complex bearing fluorous tags. Using a reaction medium consisting of ethanol and perfluorobenzene (1:1 v/v), the Pd-NHC complex was used as an efficient catalyst to execute Suzuki coupling of aryl halides with aryl boronic acids[48] (scheme-14). The catalytic system could be recycled thrice without any appreciable loss of activity.

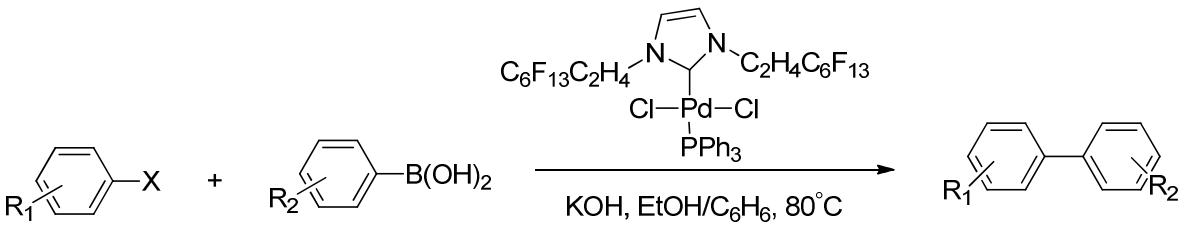
Due to their disadvantages like high cost, low biodegradability and global warming issues, perflourinated solvents are now days replaced by hydrofluoroethers (HFEs). Commercial HFEs, such as HFE-7100, HFE-7500 and F- 626 possess a higher polarity than perflourinated solvents due to the presence of an oxygen atom between a fluoroalkyl group and alkyl group (figure-1).



Scheme 12



Scheme 13



Scheme 14

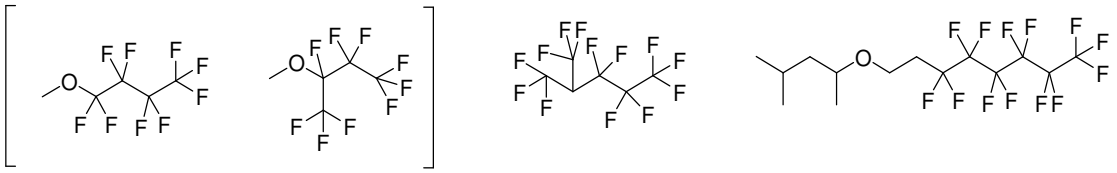


Figure 1

The fluorous ether F-626 was used by Ryu et al as the reaction medium in the Heck β- arylation of α, β-unsaturated acids and esters with aryl iodides, in the presence of a fluorous palladium carbene complex[49] (scheme-15). After work-up the recovered F-626 phase containing the palladium catalyst was reused for further five runs without any appreciable loss in catalytic activity.

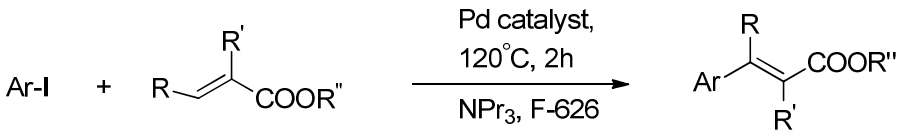
Aqueous Media: Water has emerged as a versatile green solvent for organic reactions in recent years[50]. It is not only cheap, eco-friendly, innocuous but also exhibits an entirely new reactivity owing to its unique physico-chemical properties. Research, using water as a solvent, is focused on the development of environmentally friendly and recyclable techniques, which can be commercialized for large scale applications[51]. Water also finds application in biphasic processes in combination with other solvents. The use of water as a solvent generally eliminates the requirement of protection-deprotection of sensitive functional groups, thereby enhancing the overall synthetic efficiency.

Due to its high dielectric constant, water is an appropriate solvent for microwave mediated synthesis[52]. The type of organic reactions studied in aqueous media are wide including pericyclic reactions, reactions of carbocation equivalent, reactions of radicals, reactions of carbanion equivalent,and carbenes, transition metal catalyzed reactions and various redox reactions[53,54].

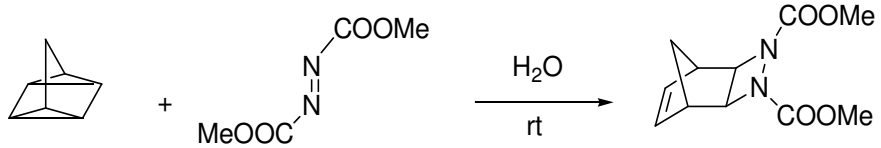
Narayan et al reported 2σ + 2σ + 2π cycloaddition of quadricyclane with azidocarboxylates at room temperature which occurs at a faster rate in water than in other organic solvents[55] (scheme-16).

Suzuki-Miyaura coupling reaction has been reported in water at room temperature using a palladacycle catalyst by Marziale and co-workers. Under the optimized reaction conditions, a broad range of products has been obtained in good to excellent yields and high purity by simple filtration[56] (scheme-17).

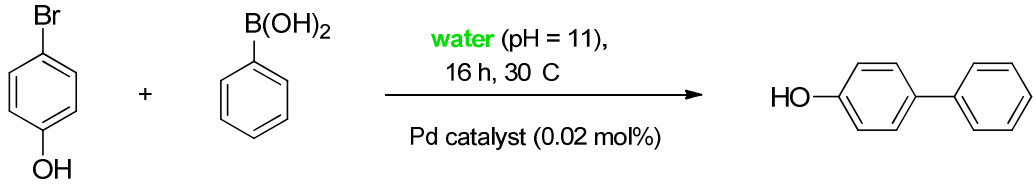
Buxaderas and collegues developed a protocol for Sonogashira coupling of deactivated and hindered aryl bromides and chlorides using a chloro-bridged oxime derived palladacycles, 2-dicyclohexylphosphanyl-2′,4′,6′-triisopropylbiphenyl (XPhos) as ancillary ligand, pyrrolidine as base, and SBDS as surfactant in aqueous media[57]. The main green attributes of the reaction are air and moisture insensitive catalyst, execution of reaction in aqueous media under microwave irradiation, requirement of catalyst in low concentration (0.1- 1 mol%) and short reaction time (scheme-18).



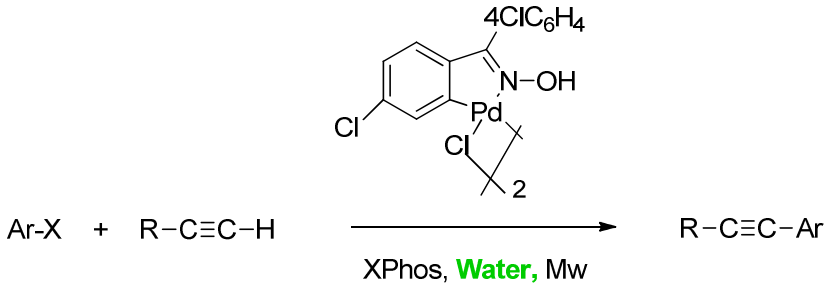
Scheme 15



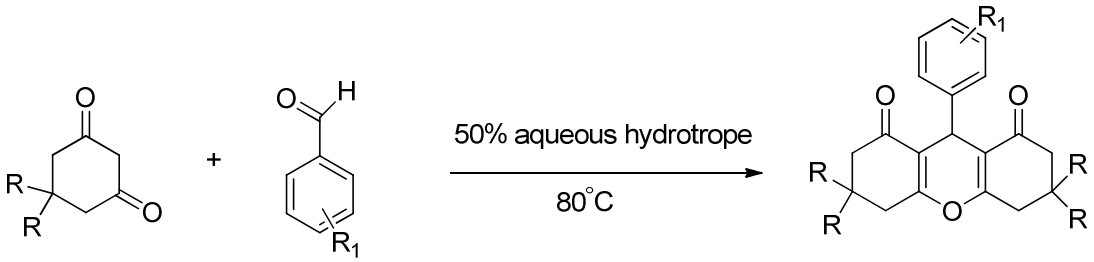
Scheme 16



Scheme 17



Scheme 18



Scheme 19

A sustainable protocol was developed for the synthesis of 1,8-dioxo octahydroxanthenes in aqueous hydrotropic solution by Kamble et al. Increase in reaction rate was observed for NaPTSA[58] (scheme-19). Short reaction time, use of water as reaction medium, recyclability and excellent yields are the advantages of developed methodology.

Ionic Liquids: Ionic liquids, a new class of non-molecular ionic solvents, have emerged as an important alternative to the volatile organic solvents[59-62].

Ionic liquids (ILs) are broadly defined as low melting salts that have melting points below 100°C[63]. They consist of an organic asymmetric cation and an anion as shown in figure-2.

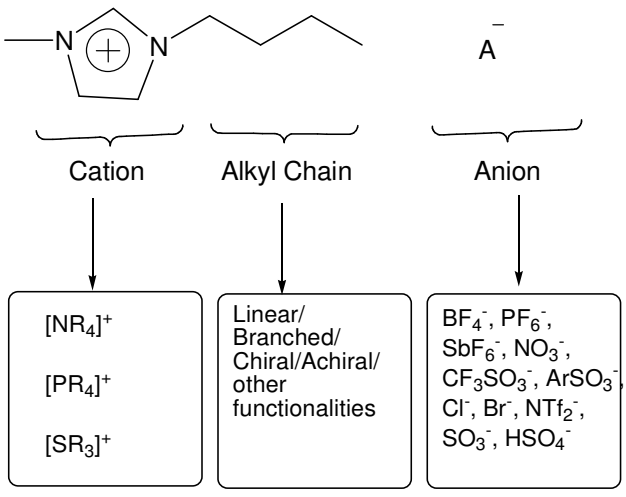
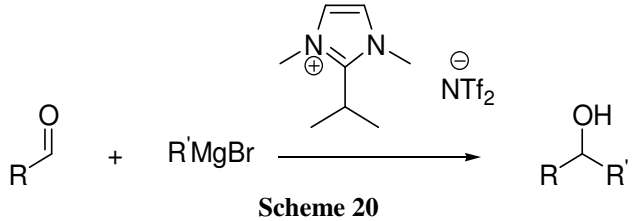


Figure-2
Diagrammatic representation of various components of ionic liquids

Ionic liquids have been described as "designer solvents" which implies that their properties can be tuned to meet the requirements of a particular reaction[64]. Properties such as melting point, viscosity, density and hydrophobicity can be modulated by simple variations in the structure of the ions[65-70].

As solvents, ionic liquids are versatile as they are reusable, increases the reactivity and selectivity of chemical transformations, simplify product isolation and facilitate the catalyst recycling[71-73]. Reaction product can be selectively extracted from the ionic liquid phase by water, organic solvent like diethyl ether, $ScCO_2$ and per-vaporation. Due to the possession of these unique properties, ionic liquids are increasingly finding applications in both academia and industry[74-77]. Ionic liquids have been used as solvents in various transition metal catalyzed reactions, multicomponent reactions, esterification, biocatalytic reactions, redox reactions and cycloaddition reactions to mention a few[78-85].

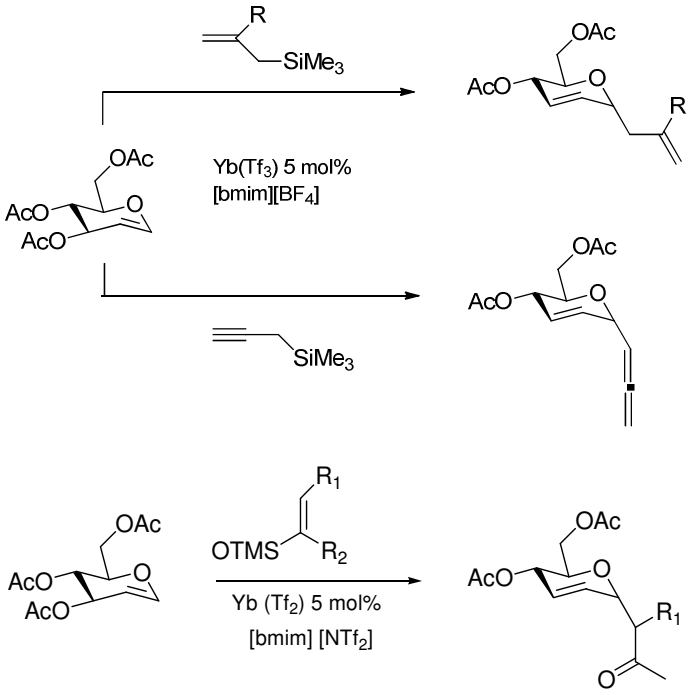
Handy prepared a base-stable imidazolium based room temperature ionic liquid which was used as a solvent for the addition of Grignard reagents to carbonyl compounds (scheme-20). Good to excellent yields of alcohols have been obtained at ambient temperature. Moreover, the ionic liquid has been recycled and reused several times without any difficulty[86].



Scheme 20

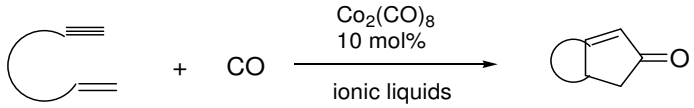
Anjaiah et al used [bmim]BF_4 and [bmim]NTf_2 as efficient, reusable solvents in ytterbium triflate catalyzed carbon-Ferrier

rearrangement of triacetyl glucal with allyl silanes, propargyl silane, and silyl enolethers[87] (scheme-21).



Scheme 21

$Co_2(CO)_8$ catalyzed intramolecular and intermolecular Pauson-Khand annelation have been efficiently carried in various imidazolium based ionic liquids under a CO pressure of 10 bar[88] (scheme-22).



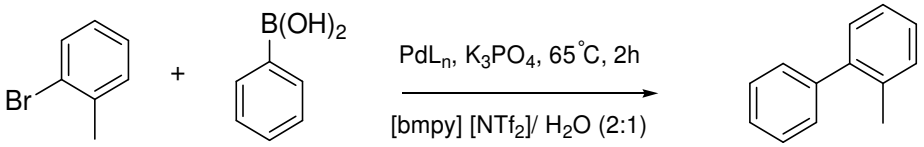
Scheme 22

Suzuki-Miyuara reaction of aryl bromides and aryl boronic acids gave good to excellent yields in pyrrolidinium ionic liquids. A pre-formed air stable and easily handled triethylammonium-tagged diphenylphosphine palladium (II) complex was used as a catalyst. The ionic liquid containing the catalyst was recycled for six times, with no appreciable loss of activity[89] (scheme-23).

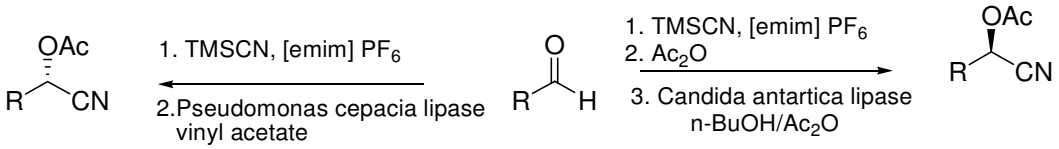
Ionic liquid has been used both as a reaction media as well as a promoter for the synthesis of optically active O- acetyl cyanohydrins via one-pot lipase catalyzed kinetic resolution of the in-situ generated racemic cyanohydrins or O-acetyl cyanohydrins by Shen and co-workers[90] (scheme-24).

The room temperature ionic liquid [bmim]PF_6 has been used as an efficient and recyclable medium for highly chemoselective synthesis of 2,2-dimethyl-6-substituted 4-piperidones *via* a L-proline catalyzed tandem Mannich reaction of ammonia, aldehydes and acetone. Both aryl and alkyl aldehydes gave good yields in this reaction[91] (scheme-25).

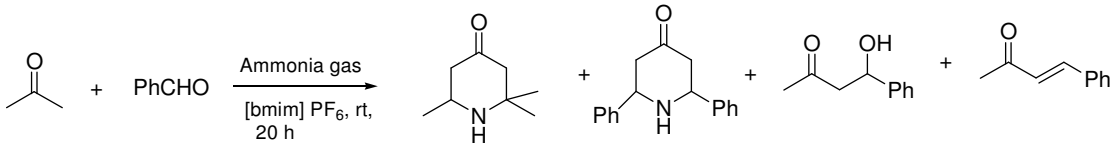
Singh et al reported an efficient synthesis of selenoesters from acyl chlorides catalyzed by CuO nanopowder using onic liquid as a recyclable solvent. This methodology exhibits high efficiency than the previous protocols due to non-residual methodological design[92] (scheme-26).



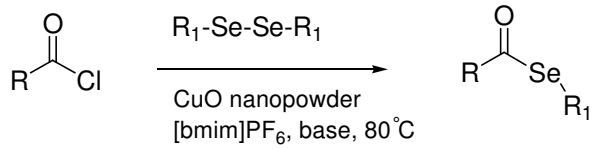
Scheme 23



Scheme 24



Scheme 25



Scheme 26

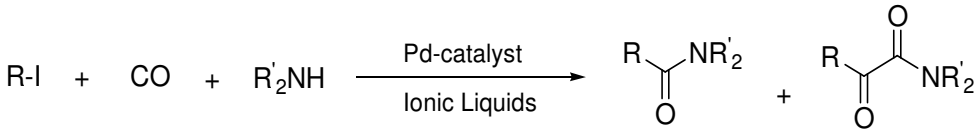
Ionic liquids have been used as reaction media for the atom transfer carbonylation reaction using a variety of alkyl iodides catalyzed by a palladium-carbene complex. The palladium catalyst and ionic liquid were recycled[93] (scheme-27).

[bmim] BF_4 has been used as a solvent for the efficient oxidation of benzylic alcohols to aldehydes and ketones using N-chlorosuccinimide/$AlCl_3.6H_2O$ as catalytic system[94] (scheme-28).

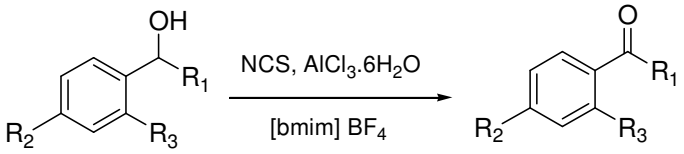
Alkene copolymerization with carbon monoxide has been carried out in a number of N-alkyl pyridinium, 1,3-dialkylimidazolium, tetraalkylammonium, and tetraalkyl phosphonium based [NTf_2] ionic liquids and catalyzed by palladium complexes[95] (scheme-29).

Singh et al efficiently carried out Mizoroki-Heck and Sonogashira reaction in an ammonium based ionic liquid [TMBA] NTf_2 using an ammonium tagged palladacycle and its clay hybrid[96] (scheme-30, 31). The catalytic system, which includes palladacycles and ionic liquid, was found to be recyclable upto seven cycles.

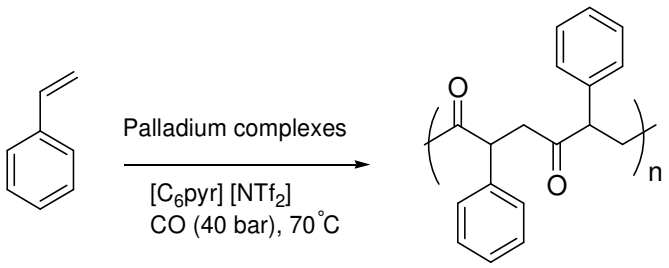
Phan and Collegues used chitosan as a heterogeneous catalyst in ionic liquid solvent to execute Knoevengeal condensation[97] (scheme-32). The catalytic system could be efficiently recycled several times.



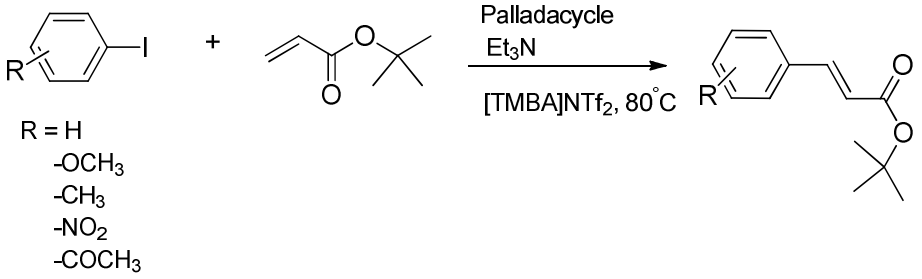
Scheme 27



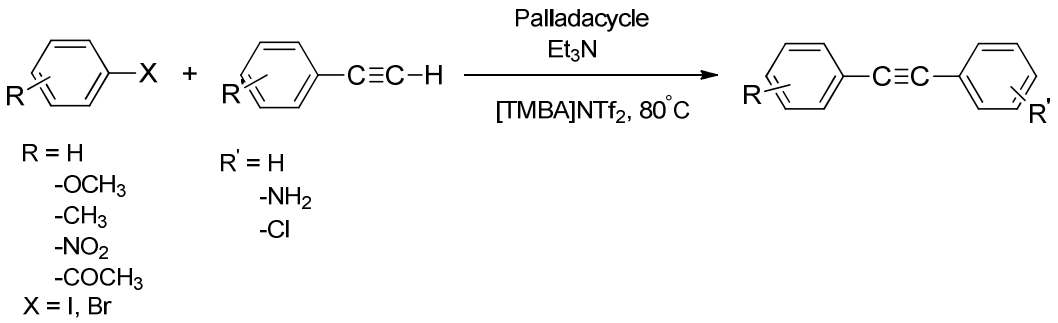
Scheme 28



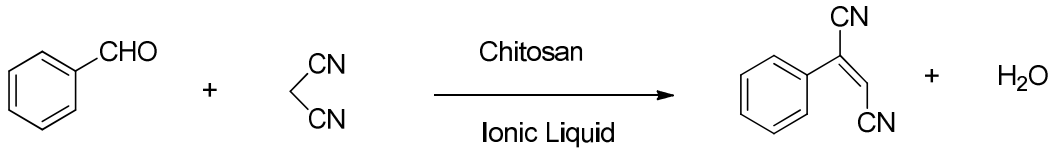
Scheme 29



Scheme 30



Scheme 31



Scheme 32

Schenzel et al developed a sustainable protocol for transesterification of cellulose using [bmim]Cl as solvent, DMSO as co-solvent. The developed methodology is quite versatile as promising results are obtained for aromatic, aliphatic and fatty acid cellulose esters[98]. [bmim]Cl-DMSO mixture can be recycled and reused thereby avoiding the use of volatile organic solvents.

Not only in laboratories, ionic liquids have paved their way into industries too[99-101]. BASF pioneered the application of ionic liquids on a commercial scale with a number of BASIL (Biphasic Acid Scavenging utilizing Ionic Liquids) processes. One of these processes replaced triethyl amine with 1-methylimidazolium ion as an acid scavenger of HCl, thereby, facilitating the work-up greatly[102]. Rogers and Seddon reported that, for one particular BASIL process, the productivity had been increased by 80,000 compared to the conventional methodology[103]. Similarly, Degussa has commercialized the usage of ionic liquids as secondary dispersive agents in paints, thereby, minimizing the use of hazardous volatile organic solvents[104]. Though ionic liquids possess numerous advantages still owing to their high cost, the number of industrial processes using them is. Research efforts, now a day, are focused on the development of cheap and easily biodegradable ionic liquids for commercial purposes.

Conclusion

The review is focused on the use of non-conventional reaction media for organic synthesis which is a pre-requisite for making chemistry green. Applications of supercritical fluids, Ionic liquids, water and fluorous media in organic reactions have been discussed in detail. Choice of solvent is, indeed, decided by the nature of reaction. Combination of these non-conventional solvents can be used in reactions requiring bi-phasic conditions. As solvents constitute a major part of industrial processes so using an appropriate non-conventional solvent can improve the economy as well as green attributes of commercial processes.

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