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REVIEW

Sustainable solvents in chemical synthesis: a review

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Abstract

Almost 20 million tons of solvents are released in the nature per year. Solvents represent about 80% of the total volume of chemicals employed in chemical synthesis. Solvents are often flammable or toxic, calling for the replacement of conventional solvents by sustainable solvents. Recent sustainable solvents can be recovered and reused easily, and can efficiently support catalysts. Here we review key synthetic procedure using supercritical liquid CO_2, polyethylene glycol, glycerol, ionic liquids and deep eutectic solvents.

Keywords Green solvents · Supercritical fluids · Ionic liquids · PEG · Glycerol · Deep eutectic solvents

Abbreviations

CMRs	Carcinogenic, mutagenic, reprotoxic substances
WHO	World Health Organization
IARC	International agency for research on cancer
CFC	Chlorofluorocarbons
ILs	Ionic liquids
$scCO_2$	Supercritical carbon dioxide
DESs	Deep eutectic solvents
DMF	*N*,*N*-dimethyl formamide
DMSO	Dimethylsulfoxide

Introduction

Organic solvents used in various chemical processes contribute hazardous impact on the environment and increase economic cost. Some of them pose adverse effect on the human health and increase environmental cost (Agata 2017). Organic solvents are flammable, toxic, form smog and released hazardous waste. To reduce the use of harmful organic solvents and search for better substitute to them is the prime aim of green chemistry. Almost 20 million tons of volatile organic solvents is released in the nature per year, and most of them are employed in organic synthesis (Wu et al. 2019). Chemical and pharmaceutical industries contribute significant chemical waste due to high requirement of solvents for the production of complex compounds and conversion of raw material into active pharmaceutical ingredients (APIs) approximately 85% solvent by mass (Abou-Shehada et al. 2016; Sheldon 2005). In this context, the replacement of conventional toxic and volatile solvents by sustainable solvents could improve chemical processes, reduce the economical cost and decrease the processing steps (Rama Koteswararao et al. 2014; Welton 2015) with a lower environmental impact, including their regeneration and recycle, process intensification, atom efficiency. These are the safe and basic tools that must be taken into account while designing new clean chemical synthesis (García-Verdugo et al. 2015). Chemists have recently developed sustainable solvents can be recovered and reused easily and efficiently supported to catalysts. In this respect, ionic liquids, supercritical fluids and polyethylene glycols possess all the characteristics of green solvents and are evolving non-aqueous solvents, also named neoteric solvents, which have received most attention worldwide (Li and Anastas 2012).

In organic chemistry, solvents play a crucial role in molecular interaction of substrate species and reagents, such as alcohol, acetone, hydrocarbons, CH_2Cl_2, DMSO, DMF, THF and benzene. Most of them are found to be harmful to mankind and pose adverse effects on the environment, such as depletion of ozone layer, toxic to living organisms

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and agent of greenhouse effect. To overcome these disadvantages of organic solvents, organic chemists developed a new concept 'reaction in green medium' (Clarke et al. 2018) (Table 1).

Legislative and regulatory measures of World Health Organization (WHO) and International Agency for Research on Cancer (IARC) evaluation usually restricted the used of various hazardous solvents such as benzene, dichloromethane, chloroform which was recognized as carcinogen as well as hepatotoxic (Sanni and Mutta 2014; WHO 2015)*; toluene was suspect to damage organs and unborn child. According to European regulation* 'Registration, Evaluation, Authorisation and Restriction of Chemicals'(REACH) poses restriction on use of toluene, dichloromethane, chloroform with certain condition (Byrne et al. 2016). Solvents contribute around 80% of total volume of chemicals used in chemical processes, and most of them are found to be a volatile and toxic to human health and environment (Hackl and Kunz 2018).

In recent years, Ionic liquids, water, supercritical fluids, liquid polymers evolved as green solvents for the chemical processes (Agata 2017; Parvulescu and Hardacre 2007). Their remarkable features such as high efficiency, safe, non-ecotoxic, low hepatotoxic, recyclable, thermally stable do not form smog, etc. accessibility and the possibility of reuse as well as great efficiency. An ideal green solvent would also mediate reactions, separations or catalyst recycling and significantly increases the outcome of the process (Li and Trost 2008; Constable et al. 2007). In typical chemical reaction, solvents are required to dissolving reactants, influencing chemical reactivity, for extracting or washing the resultant and for separation product. Most of organic solvents were large number of advantages associated with them, but generally toxic for human health, animals and plants and also volatile, flammable explosive. Uses of volatile and hazardous organic solvents in the chemical reaction were causes of mass consumption and their recovery capacity far from acceptable limits and contribute to more environmental pollution (Anastas 2003; Horvath and Anastas 2007).

The ideal reaction can be performed which will proceed through green chemistry tool to achieve more convenient, efficient and sustainable routes in an order to carry out organic synthesis in an environmentally and economically beneficial manner. Significant work is in progress in several important research fields in organic synthesis, such as catalysis, the development of renewable feedstock and the design and use of safer chemicals, reagents and environmentally benign solvents (Bose et al. 2002). Synthetic chemists are skilled to design and develop processes and routes with a clear perception for environmental impact. The synthetic chemistry is to develop new procedures which will be the ideal synthesis that achieves safety, environmental benign, reduced waste, economic, simple or the waste should be useful (Trost 1991, 2002; Larhed and Olofsson 2006; Mason 1999; Wender et al. 2006; Nuchter et al. 2004).

Green chemistry is based on the principle to use supplementary compounds or solvent substances should be innocuous and these substances should enhance the speed and yield of the reaction (Anastas and Williamson 1998). The hazardous and toxic properties of various solvents, mainly hydrochloro-carbons, create concerns for environmental safety with the contamination of water savage and atmospheric emissions. Therefore, it is recommended that the use of non-conventional solvents as substitute for environmentally harmful established solvents can decrease waste solvent and therefore created environment-friendly environment to great extent (Adams et al. 2004). The basic principles involved for the green synthesis of organic compounds are given in Table 2.

Table 1 Classical solvents and their hazards (Joshi and Adhikari 2019)

Solvents	Hazards
Carbon tetrachloride (CCl_4)	Carcinogenic, toxic, ozone layer depleter
Dimethoxyethane	Carcinogenic, toxic
Benzene (C_6H_6)	Carcinogen (cmrs category 1), toxic to humans and environment
Chloroform ($CHCl_3$)	Carcinogenic
Dichloroethane	Carcinogenic
Dimethylformamide (DMF)	Toxic
Pyridine	Carcinogenic/mutagenic/reprotoxic

CMRs carcinogenic, mutagenic, reprotoxic substances

Supercritical liquid CO_2

Super critical liquids such as liquid CO_2 are found to be a better substitute to the organic solvents because it meets various characteristics of green mediums (Hyatt 1984; Beckman 2004; Rayner 2007). It is non-flammable, non-toxic, non-ecotoxic, abundant, renewable, recyclable, does not form smog and more easy to prepare and isolate from the products. Supercritical liquids possess properties of gases and liquids in an intriguing manner, which offers wide range of applications in synthetic chemistry. Supercritical CO_2 used to conserve energy and reduce waste is found to be an important alternative to organic solvents. Hence, it was termed as green solvent (Branch and Bartlett 2015; Nalawade et al. 2006). Supercritical CO_2 has numerous advantages such as recyclable, easily available, non-corrosive, non-expensive, eco-friendly, non-explosive, low surface tension and non-viscous which make it ideal solvents in green chemistry (Blanchard et al. 1999; Zhang et al. 2005; Zhang and Han 2013) (Fig. 1).

Table 2 Basic and important principles of green chemistry (Tang et al. 2005)

Important principles of green chemistry	
Waste prevention	Prioritize the prevention of waste, rather than cleaning up and treating waste after it has been created. (Tang et al 2005)
Atom economy	Reduce waste at the molecular level by maximizing the number of atoms from all reagents that are incorporated into the final product. (Wagare et al. 2017)
Less hazardous chemical synthesis	Design chemical reactions and synthetic routes to be as safe as possible (Adams 2004).
Designing safer chemicals	Minimize toxicity directly by molecular design (Joshi and Adhikari 2019)
Safer solvents and auxiliaries	Choose the safest solvent available for any given step (Biglari et al 2019)
Design for energy efficiency	Choose the least energy-intensive chemical route
Use of renewable feedstocks	Use chemical which are made from renewable sources rather than other equivalent chemicals originating from petrochemical sources (Shaikh et al. 2019)
Reduce derivatives	Minimize the use of temporary derivatives such as protecting groups
Catalysis	Use catalytic instead of stoichiometric reagents in reactions (Szyling et al. 2017)
Design for degradation	Design chemicals that degrade and can be discarded easily.
Real-time pollution prevention	Monitor chemical reactions in real-time as they occur to prevent the formation and release of any potentially hazardous and polluting substances
Safer chemistry for accident prevention	Choose and develop chemical procedures that are safer and inherently minimize the risk of accidents.

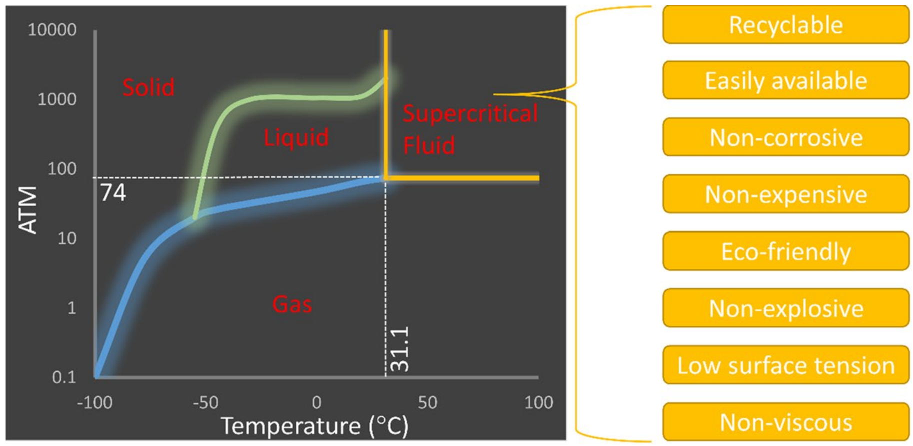
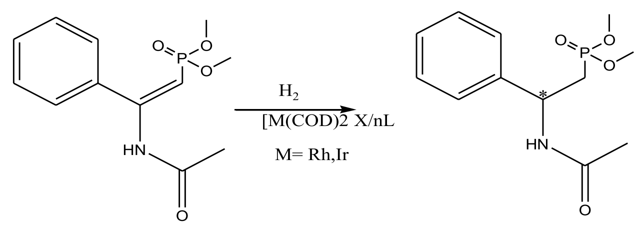


Fig. 1 Phase diagram of carbon dioxide and its advantages at supercritical conditions. This phase diagram for CO_2 shows at what pressures and temperature the material is solid, gas and liquid. The transition line indicates where it goes from one phase to another. At 5.2 bar and −56 °C, however, CO_2 is at its triple point, the temperature and pressure at which it can exist in equilibrium in the liquid, solid and gaseous states. The temperature above 31 °C and pressure above 74 bar for CO_2 create a supercritical phase, neither liquid nor gas but a combination of both properties. High diffusion like a gas but with the solvation (ability to dissolve substances) of a liquid. Here, ATM is refers to atmospheric pressure

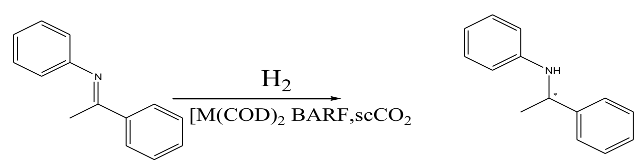
Supercritical liquids can progress the reaction, which is difficult or nearly impossible to achieve by organic solvents. Physical properties of supercritical CO_2 are density:1 g/cm^3, diffusion: below 10-5, the more praise property of supercritical CO_2 is very low viscosity (10^{-2} g cm S) and negligible surface tension, (Han and Poliakoff 2012), it has more dissolving power toward many non-polar compounds, and it can dissolve into condensed phase drastically by reducing the viscosity and surface tension of the condense phase making processing highly viscous material easily. Moreover, it does not cause harm to ozone layer like chlorofluorocarbons which were used in synthesis of polymer. Supercritical CO_2 is a right choice as a solvent for the processing of pharmaceuticals, biomolecule separation and heat-sensitive phenomenon because of its easily recoverable, low value of critical temperature (Knez et al. 2019). various organic compounds soluble in supercritical CO_2 such as amoxicillin (Ahmadi Sabegh et al. 2012), ketoprofen, piroxicam and nimesulide (Macnaughton et al. 1996), isoniazid (Heryanto et al. 2010), 2,20-bipyridine and 4,40-dimethyl-2,20-bipyridine (Bai et al. 2007), polynuclear aromatic hydrocarbons (fluoranthene, chrysene and triphenylene) (Barna et al. 1996), artemisinin (Xing, et al. 2003), cholesterol, some fat-soluble vitamins A, D, E, K (Johannsen and Brunner 1997), phenols and pyrocatechols (García-González et al. 2001; Reshi et al. 2020).

Hydrogenation

Lyubimov et al. (2010) reported the asymmetric hydrogenation of (*E*)-dimethyl-2-acetamido-2-phenylvinylphosphonate was performed in CH_2Cl_2 and supercritical CO_2 with the participation of Rh and Ir complexes with chiral phosphite-type ligands (Scheme 1). Similarly, iridium-catalyzed asymmetric hydrogenation of imines was successfully carried in supercritical CO_2 using phosphite-type ligands (Lyubimov et al. 2011) (Scheme 2).



Scheme 1 Asymmetric hydrogenation of (E)-dimethyl-2-acetamido-2-phenylvinylphosphonate. COD is 1,5_cyclooctadiene

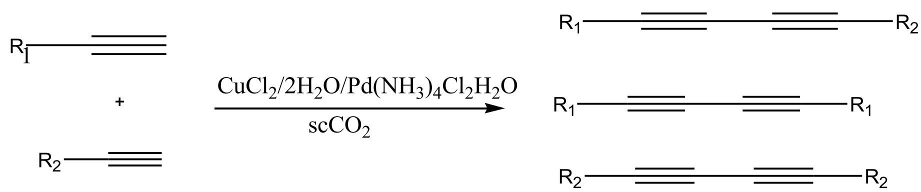


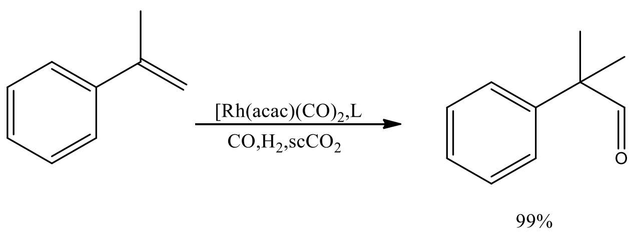
Scheme 2 Enantioselective hydrogenation of N-(1-phenylethylidene) aniline. COD is 1,5_cyclooctadiene, and BARF is (tetrakis[3,5_bis(trifluoromethyl)phenyl]borate), scCO_2 (supercritical carbon dioxide)

Cross-coupling reactions

Wang et al. (2018) designed a new protocol to prepare the unsymmetrical 1,3-diynes in supercritical carbon dioxide

Scheme 3 Cross-coupling reaction in $scCO_2$. $scCO_2$ is supercritical carbon dioxide





Scheme 4 Hydroformylation reaction in $scCO_2$. Here, acac (acetyl acetone), $scCO_2$ (supercritical carbon dioxide), L = tri(2,4-di-tert-butylphenyl) phosphite

($scCO_2$) as the solvent. The direct coupling of two terminal alkynes was catalyzed by a bimetallic catalyst, $CuCl_2 \cdot 2H_2O/Pd(NH_3)_4Cl_2 \cdot H_2O$, where tetramethylethylenediamine (TMEDA) was used as a base (Scheme 3).

Hydroformylation

In hydroformylation reaction, most valuable precursor aldehyde has been synthesized from olefins by using syngas. Koeken and Smeets (2013) developed an efficient route to convert disubstituted alkenes to aldehydes selectively with excellent yield (97%) (Scheme 4).

Unimolecular nucleophilic SN¹ reaction

Thais Delgado-Abad et al. (2016) reported the ethanol inhibits SN^1 reactions of alkyl halides which does not give ether as product in supercritical carbon dioxide ($scCO_2$). They observed surprising behavior of alcohols in the alkyl halides reaction with 1,3-dimethoxybenzene in $scCO_2$ with different parameters described in terms of Lewis and Brønsted base–acid equilibria of reagents, intermediates, additives and products in a singular solvent analyzed by: (i) CO_2 does not behave as a proton sink due to its weak Lewis base character; (ii) the strong quadrupole and Lewis acid characteristics of carbon dioxide inhibit SN^2 paths by solvation of basic solutes; (iii) the compressible behavior of $scCO_2$ enhances the preferential solvation impact on the availability of carbon dioxide for determining solvent-demanding rate (Scheme 5).

Diels–Alder reactions

Better diasteroselectivity on optimizing temperature and pressure can be obtained while performing cycloaddition reactions in $scCO_2$. Aza–Diels–Alder reaction between Danishefsky's diene and imine is derived from different perfluorinated sulfonic acids in the presence of metal salts to give large reaction yields and catalyst solubility (Scheme 6) (Shi et al. 2004).

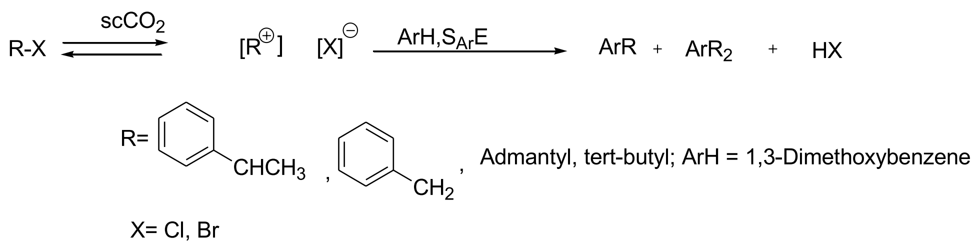
Catalytic hydroboration

Szyling et al. (2018) reported green synthesis of unsaturated organoboron compounds from the internal alkynes and hydroboration of terminal in supercritical CO_2. This method allows to obtain borylsubstituted olefins with high selectivity up to the 16th catalytic cycle using $Ru(CO)Cl(H)(PPh_3)_3$ an efficient catalyst (Scheme 7). The self-dosing catalyst process was utilized that gradually released to the reaction mixture with supercritical conditions in the individual batch.

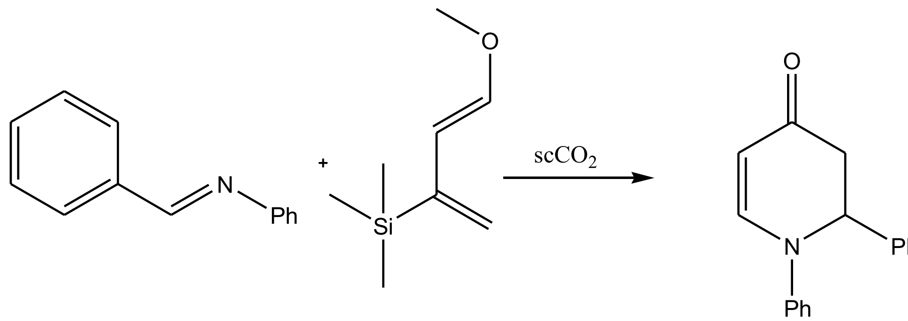
Synthesis of organic semiconducting material

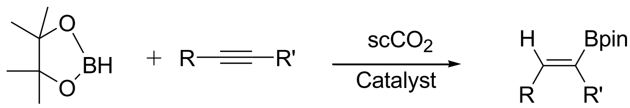
Hirase et al. (2018) studied the synthesis and purification of 5, 5‴-bis(tridecafluorohexyl)-2,2′:5′,2″:5″,2‴-quaterthiophene (BFH-4 T, n-type organic semiconducting material) in ($scCO_2$) green solvent. BFH-4T was collected with better selectivity and higher yield by TDAE/PdCl2-effectively used as a catalyst for the reductive coupling reaction of 5-bromo-50-(tridecafluorohexyl)-2,20-bithiophene in scCO2 (Scheme 8).

Scheme 5 Reaction of alkyl halides with 1,3-dimethoxybenzene in $scCO_2$. Here $S_{Ar}E$ is aromatic electrophilic substitution, $scCO_2$ (supercritical carbon dioxide)



Scheme 6 Diels-alder reaction in $scCO_2$; $scCO_2$ (supercritical carbon dioxide)





Scheme 7 Synthesis of organoboranes in $scCO_2$; $scCO_2$ (supercritical carbon dioxide)

Carbon–hydrogen bond functionalization

Sarmiento et al. (2019) reported the selective catalytic alkane functionalization process in supercritical carbon dioxide ($scCO_2$). The functionalization of carbon–hydrogen bonds of alkanes transforms the $CHCO_2Et$ group from N_2CHCO_2Et (ethyl diazoacetate, EDA) which was driven by a silica supported copper complex containing an N-heterocyclic carbene ligand. They resulted that, in neat hexane, about 3% of the primary C–H bonds (where ethyl heptanoate was the product) was functionalized, and the identical reaction was obtained in $scCO_2$ resulted in a 30% yield in this linear ester (Scheme 9).

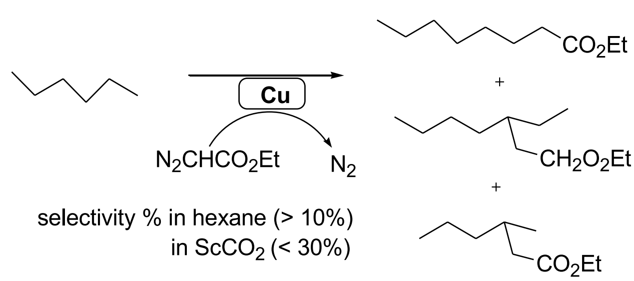
Hydrosilylation of alkynes

Stefanowska et al. (2017) investigated hydrosilylation of a various alkynes with four structurally different silanes performed in supercritical CO_2 ($scCO_2$). They developed different protocol for the preparation and isolation of more than forty silyl ethenes. Synthesized products were characterized by different techniques such as ^{1}H, ^{13}C, ^{29}Si NMR, EA and GC–MS. Further, the molecular structures of (E)-triethyl(2-(triphenylsilyl)vinyl)silane and (E)-3-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)-2,5-dimethylhex-3-ene-2,5-diol were investigated by the X-ray crystallography (Scheme 10).

Polyethylene glycol

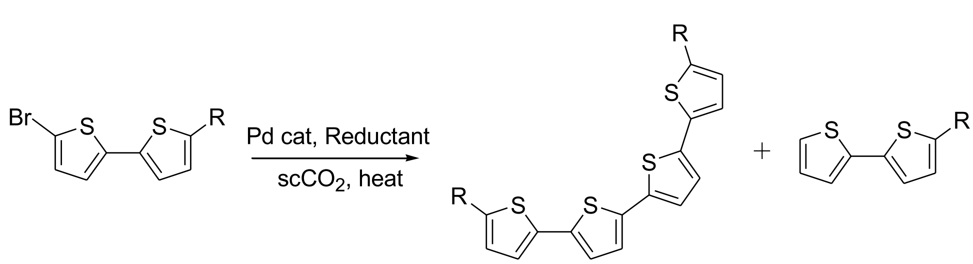
Polyethylene glycol (PEG) has attracted great attention of organic chemist as an environmentally benign, non-volatile, recyclable and inexpensive medium as well as acts as an appreciable phase transfer catalyst in organic transformations (Chen et al. 2005). PEGs are stable at high temperature and can be used in acidic and basic reaction conditions as well as for oxidation and reduction reactions [Guo et al. 2002; Chen et al. 2004).

In recent years, polyethylene glycols and its aqueous solutions emerge in green medium in organic synthesis, especially for solvent replacement, as compared to other green solvent systems such as supercritical CO_2, micellar systems and different ionic liquids. PEGs are soluble in

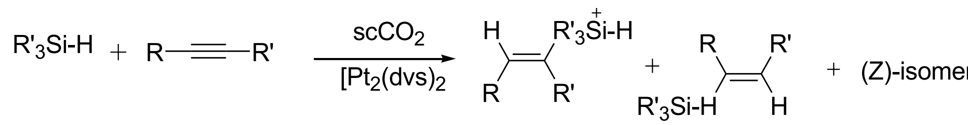


Scheme 9 C-H functionalization reaction in $scCO_2$. $scCO_2$ (supercritical carbon dioxide)

Scheme 8 Palladium-catalyzed reductive coupling reaction of aryl bromide in $scCO_2$. $scCO_2$: supercritical carbon dioxide



Scheme 10 Hydrosiliation reaction in $scCO_2$. $scCO_2$ (supercritical carbon dioxide)



water, and their solubility increases in water with increasing molecular weight and these are also soluble in various organic solvents such as alcohol, propan-2-one, acetonitrile, toluene and dichloromethane but insoluble in hydrocarbons such as n-hexane, cyclohexane or ethers (Jawale et al. 2010). PEG aqueous solutions could usually substitute for costly and infrequently hepatotoxic phase transfer catalyst and ionic liquids. PEG is environmentally benign, flexible, recyclable, inexpensive and biodegradable polymer used as reaction medium in various reactions like Suzuki, Heck, Baylis–Hillman (Moritz et al. 2009), Tandem alkylation, Bignelli, etc. (Wang and Alper 1986). Ethylene glycol and sugarcane waste are sustainable sources of PEG (Zhu et al. 2016; Reichardt 2007). It is estimated that the global market for ethylene glycol is around 20 billion/year, whereas only around 15 million tons/year is produced, and thus, sustainable sources of ethylene glycol are of great interest. In recent, liquid polymers such as bio-based compounds (glycerol) and PEG have emerged as green alternatives for overcoming drawbacks associated with the use of conventional organic solvents (Fig. 1) (Kerton and Marriot 2013). Due to the high dissolving tendency for different kinds of organic compounds such as significant phase extraction potential, non-toxic and biodegradable behavior, they have a large number of applications in medicinal chemistry field (Kostić and Divac 2019).

Multicomponent reactions in PEG-400

Wagare et al. (2017) developed one-pot efficient synthesis of 4-aryl-2-aminothiazoles, imidazo[1,2-a]pyridines (Wagare et al. 2016a), 4-phenylfuro[3,2-c]Coumarins (Wagare et al. 2016b), imidazothiadiazoles (Wagare et al. 2019) in PEG-400 and water. In all these reactions, lachrymatric phenacyl bromides were prepared in situ from the selective monobromination at alpha position of aromatic ketones in PEG-400 (Scheme 11). Aqueous-phase PEG was successfully employed for the synthesis of these heterocyclic compounds. Alireza Hasaninejad developed four-component synthesis of novel asymmetrical bisspirooxindole from the reaction of N-alkyl isatin, alkylmalonates and C–H activated carbonyl compounds (Hasaninejad and Beyrati 2018) (Scheme 12).

Synthesis of heterocyclic compounds

Shaikh et al. (2019a, b, c) studied the preparation of novel Schiff bases 4-((1,3-diphenyl-1H-pyrazol-4-yl)methyleneamino)-5-(pyridin-4-yl)-4H-1,2,4-triazole-3-thiol using condensation reaction of pyrazolyl carbaldehyde and triazole in PEG-400 (Scheme 13).

Gupta et al. (2019) described the preparation of anticancer isatin-linked chalcones and their 3-hydroxy precursor in PEG-400. They reported that isatin-linked chalcones can show potential anticancer activity and act as versatile substrates and at the same time key intermediates for the preparation of a various bioactive spirooxindoles (Scheme 14).

Synthesis of bis-(2-pyridyl)diselenides in PEG-400

A series of bis-(2-pyridyl) diselenide derivatives **62** have been prepared (100:0) from 2-chloropyridines **61** and selenium species generated in situ reductively (Scheme 15) (Peglow et al. 2017). The reaction was promoted by the *p*-TsOH, where PEG-400 was used as a reaction medium; such synthetic approach has enabled the synthesis of bis-(3-amino-2-pyridyl) diselenides.

One-pot synthesis of 1,2-disubstituted benzimidazoles

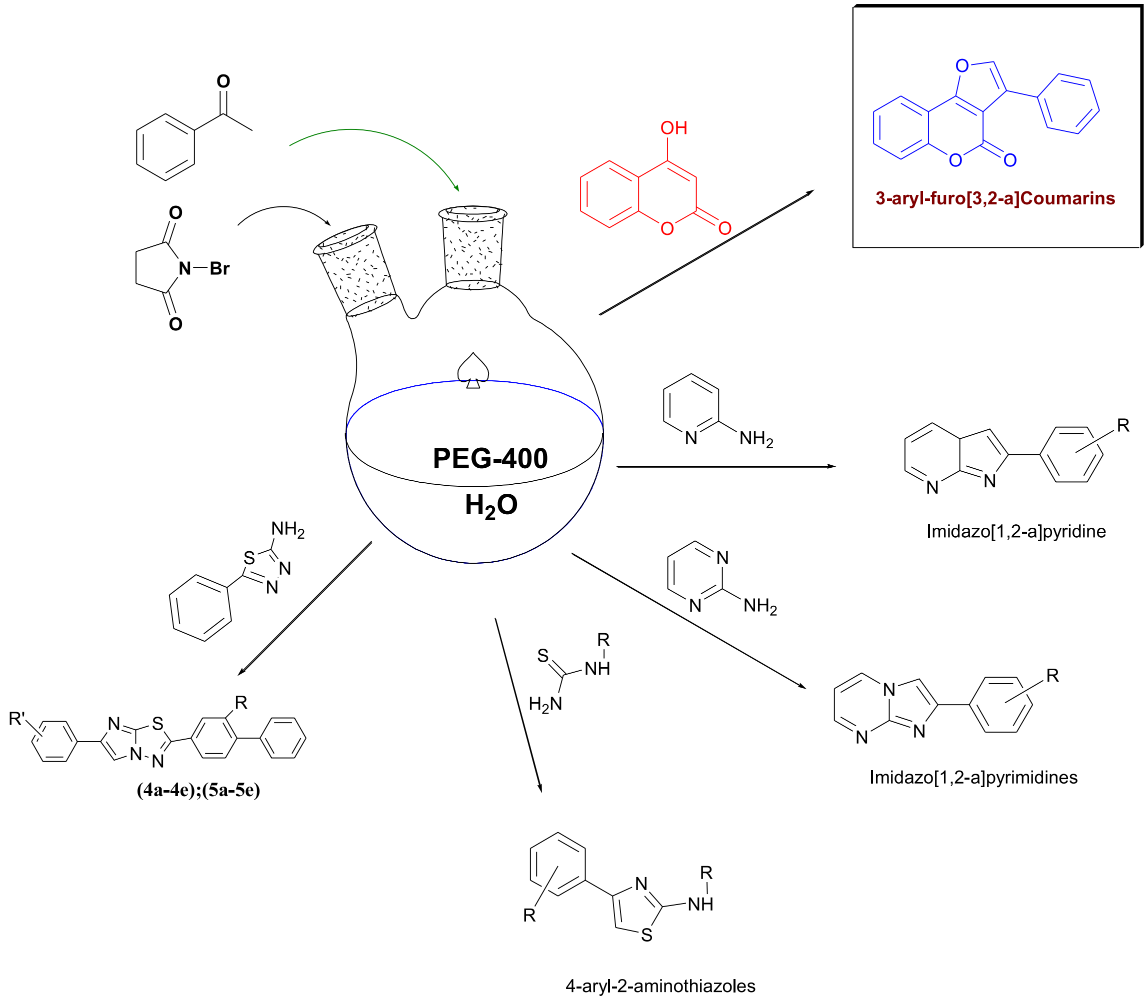
Mekala et al. (2015) used polyethylene glycol (PEG-400) for the one-pot synthesis of 1,2-disubstituted benzimidazoles which shows higher yield quantity. Here, low-cost, recyclability, environment-friendly, low cost, high yields and recyclability of the PEG-400 were the vital characteristics of this protocol (Scheme 16).

Synthesis of isoxazolyl pyrroles

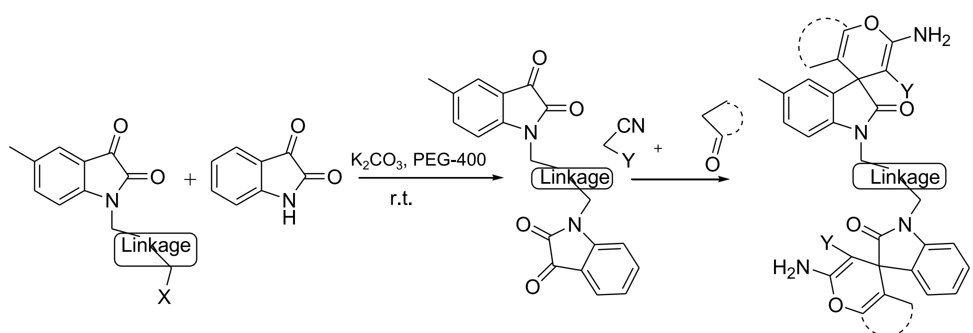
The preparation of novel isoxazolyl pyrroles was described by a one-pot reaction of nitroolefins and isoxazolyl enamino esters using polyethylene glycol (PEG-400) as a promoter and H_2O as a reaction medium (Ponduri et al. 2018). Such approach revealed an efficient, simpler and green route since it has metal/base free, fast reaction time, higher yields, various substrates scope and PEG-400 can be recovered and reused (Scheme 17).

Synthesis of unsymmetrical thiosulfonates

Peng et al. (2018) reported a green and practically feasible approach between disulfides and sulfonyl hydrazides was reported to prepare unsymmetrical thiosulfonates assisted



Scheme 11 One-pot synthesis of various biologically active heterocycles in aqueous PEG-400



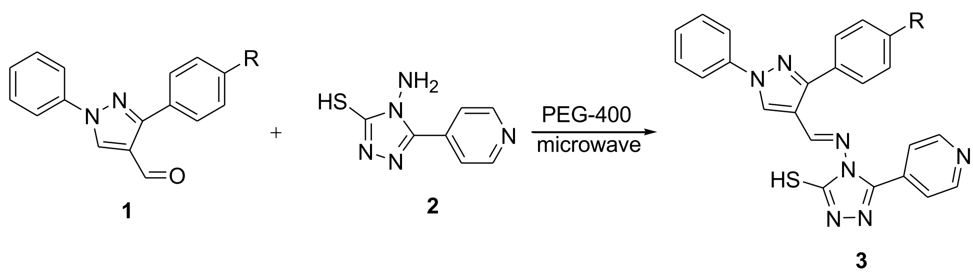
Scheme 12 Preparation of novel asymmetrical bis-spirooxindoles **6** via the reaction between N-alkyl isatin **1**, isatin derivatives **2**, alkyl malonates **4** and carbonyl compounds **5** in the presence of K_2CO_3 in PEG-400 at 300 K

by H_2O_2 in PEG-400 that released H_2O and N_2 byproducts. Such a compatible and efficient method was assumed to be useful in the absence of metallic catalysts via radical mechanism analyzed by EPR (electron paramagnetic resonance) characterization (Scheme 18).

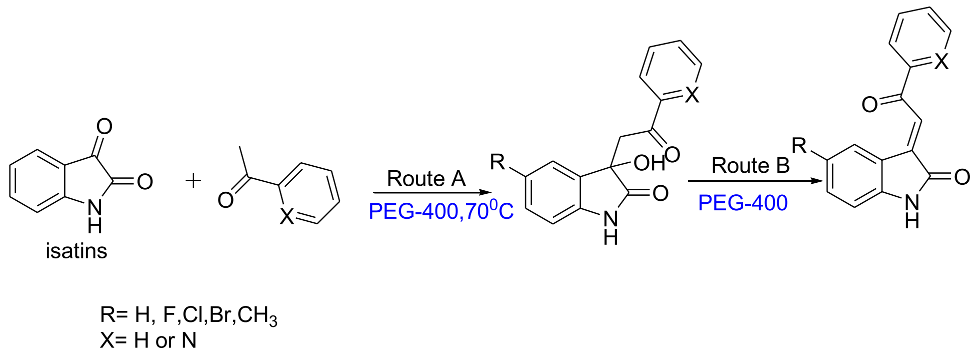
Glycerol as a green reaction medium

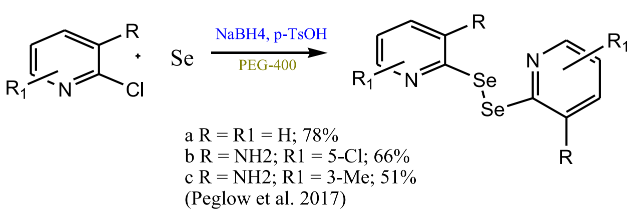
Glycerol or glycerin or 1,2,3-propanetriol is a viscous liquid, colorless, odorless having sweet taste (Díaz-Álvarez et al. 2014). Hence, the synthesis of organic molecules

Scheme 13 Synthesis of 4-((1,3-diphenyl-1H-pyrazol-4-yl)methyleneamino)-5-(pyridin-4-yl)-4H-1,2,4-triazole-3-thiol



Scheme 14 Synthesis of 3-hydroxy-2-oxindoles and 3-methylene-2-oxindoles

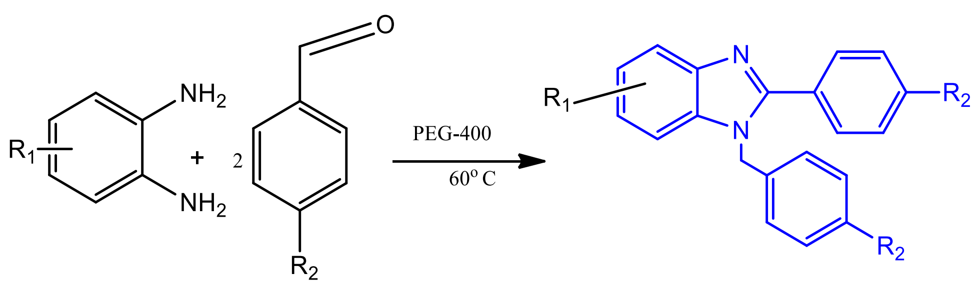




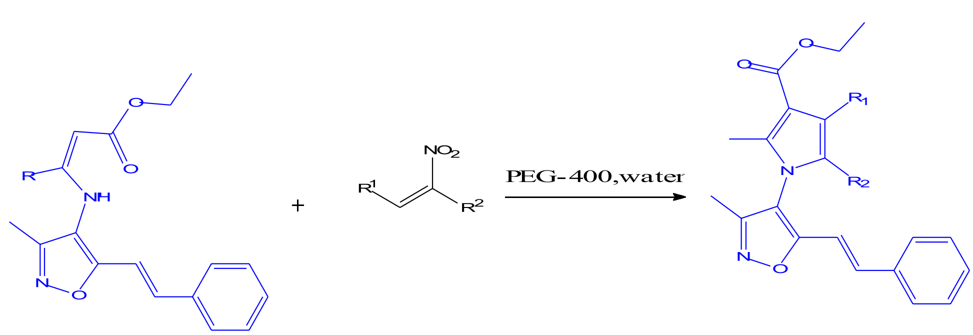
Scheme 15 Synthesis of bis-(2-pyridyl) diselenide

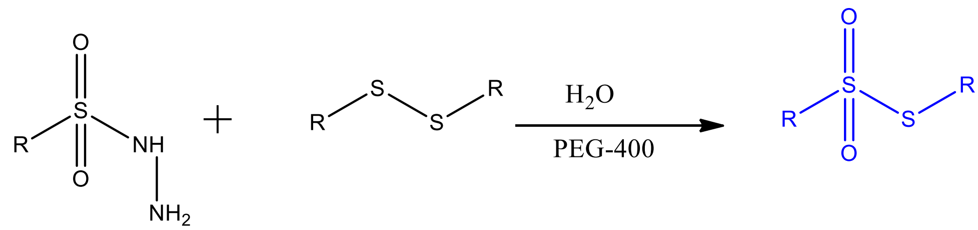
through green media is becoming the need of researcher and glycerol, PEG were the best choices. The epichlorohydrin hydrolyzed to give glycerol, acrolein and propylene oxide is giving glycerol (Yu 2014). Glycerol is a waste product, on large-scale production of biodiesel from fats (Christoph et al. 2006). Therefore, preparation method of glycerol is not cost-effective. Continuous research is focusing to convert glycerol to synthetic precursors, viz. epichlorohydrin and acrolein (glycerol).

Scheme 16 Synthesis of 1,2-disubstituted benzimidazoles



Scheme 17 Synthesis of isoxazolyl pyrroles





Scheme 18 Synthesis of unsymmetrical thiosulfonates in PEG-400

Glycerol also termed as "organic water" is readily available, cheap, polar, non-toxic, biodegradable and easily form strong networks of hydrogen bond. Glycerol has a wide range of solubilities for inorganic and organic compounds, such as transition metal catalysts (Pagliaro and Rossi 2008). The peculiar physical and chemical properties of glycerol (Table 3) are non-volatile solvent, low toxicity, easily prepared from renewable feedstocks (Loren et al. 2010) and high boiling point, easily removed from reaction matrix. Glycerol is widely use as a green medium in various organic transformation like, cross-coupling reactions (Wolfson and Christina 2009) include Suzuki cross-couplings, acid-base promoted condensations, asymmetrical reduction (Quan et al. 2011) and multicomponent reactions (Rao and Vijaya 2006; Gouin 1994).

Glycerol is used as a solvent in beverages and foods. Glycerol may help preserve foods and is also used as sweetener. It serves as thickening agent in liqueurs and as filler in low-fat foods (like, cookies). Glycerol–water can be used to preserve various kinds of plant leaves (Wolfson et al. 2007). Glycerol is categorized by the Academy of Nutrition and Dietetics for their use in food by labeling E number E422. It is added into ice (frosting) to keep it porous which preventing them for becoming hard. Similar to table sugar, glycerol has a caloric density but lower glycemic index and within the body different metabolic pathway. Glycerol is medically allowed as an additive while using in polyol sweeteners (Ichthyosis 2013). Glycerol is also usable in personal care, medical treatment, pharmaceutical drug preparations, providing lubrication and generally as a means of smoothness improvement. Xerosis and Ichthyosis have been relieved by the topical use glycerin (Mark et al. 2017; Glycerin Enema 2017). It is used in cough syrups, skin care allergen immunotherapy's, elixirs, mouthwashes, toothpaste, expectorants, shaving cream, soaps, hair care, personal lubricants, etc. Glycerol is applicable as a "tablet holding agent" in solid dosage forms like tablets. To preserve red blood cells from freezing, glycerol is also used in blood banking. Glycerol is one of the components in glycerin soap where essential oils are included for fragrance. It prevents skin dryness and skin irritation due to its moisturizing properties; hence, it is used by people as a kind soap. It prevents excessive drying of skin layers and draws moisture up. Glycerol can be used as a laxative and mucosa and induces a hyperosmotic (Glycerin 2012). Glycerol is taken orally since it is generally mixed with fruit juice to reduce its sweetness. It can cure internal pressure of eye rapidly for short period of time and thus can be a first aid for the emergency treatment of eye pressure (Hudgens et al. 2007).

Previously, ethylene glycol is used as an anti-freeze automotive applications which is now take over by glycerol as it has a lower freezing temperature around −36 °F (−38 °C) corresponding to 70% glycerol in water, due to its hydrogen bonding attraction, that avoids the formation of ice. Further, glycerol is a non-toxic and hence is applicable in automotive applications (Proposed ASTM 2012; Emma et al. 1996). Glycerol can be stored at temperatures < 0 °C for enzymatic reagents because of its reduced freezing temperature. Nitroglycerin is produced by glycerol which is an essential ingredient of various explosives such as gelignite, dynamite and propellants like cordite.

Glycerol along with water generally is used in order to stop the drying out area rapidly and to maintain the wetness (Ildon et al. 1976). Glycerin–water is used in proportion of 1:99 to generate a smoky/foggy environment. Glycerol is a precursor for the preparation of phospholipids and triacylglycerols in the adipose tissue and liver. Fatty acids and glycerol can be released into the bloodstream, since body

Table 3 Advantages of glycerol

Easily recoverable and Reusable	Glycerol easily recovered from reaction matrix and reused without purification (Shaikh et al. 2019a, b, c)
Non-corrosive	Does not harm to the skin
Inexpensive	Prepared from renewable feedstock
Eco-friendly	Safe to human and environment
Non-explosive	High boiling point and non-explosive solvent (Loren et al. 2010)
Water soluble	Easily soluble and extensively use with water (Wolfson et al. 2007)
Non-toxic	Non-poisonous nature term it as "organic water" (Shaikh et al. 2019a, b, c)

employs to store fat as an energy source. The glycerol is used as a component in the glycolysis pathway directly, and it is converted to glucose through gluconeogenesis. The glycerol entered into pathways which is converted into enzyme glycerol kinase presented in the kidneys, liver, muscle, brain and other body tissues (Newsholme and Taylor 1969; Jenkins and Hajra 1976).

Multicomponent reactions in glycerol

Shaikh and co-workers developed multicomponent synthesis of 2-aminothiazoles, (Scheme 19) (Shaikh et al. 2017) pyrazolyl-thiazole Schiff bases (Scheme 20), (Shaikh et al. 2017) pyrazolyl-4-thiazolidinone (Scheme 21) (Shaikh et al. 2019a, b, c) in glycerol and water.

One-pot synthesis of 3,4-dihydro-2*H*-naphtho[2,3-*e*][1,3]oxazine-5,10-diones

Gupta et al. (2016) reported eco-friendly one-pot synthesis of 3,4-dihydro-2*H*-naphtho[2,3-*e*][1,3]oxazine-5,10-diones by employing glycerol as a green medium. 3-aryl-3,4-dihydro-2H-naphtho[2,3-e][1,3]oxazine-5,10-diones have been prepared using the condensation of 2-hydroxy-1,4-naphthoquinone, aromatic amines and formaldehyde in glycerol at 50 °C with 85–95% yields. The glycerol–water layer was extracted after separation of product by using ethyl acetate, and the dried glycerol layer was successfully reused several times (Scheme 22).

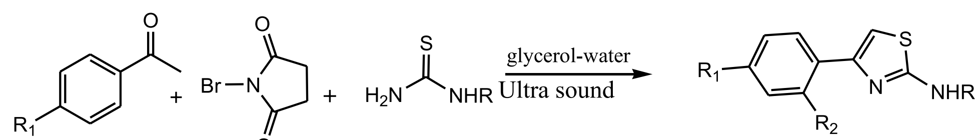
Synthesis of 4-aryl-7,7-dimethyl-5-oxo-3,4,5,6,7,8-hexahydrocoumarin

4-aryl-7,7-dimethyl-5-oxo-3,4,5,6,7,8-hexahydrocoumarin derivatives were synthesized by one-pot multicomponent reaction of Meldrum's acid with benzaldehyde, and cyclohexanedione in glycerol (Wang et al. 2017) (Scheme 23)

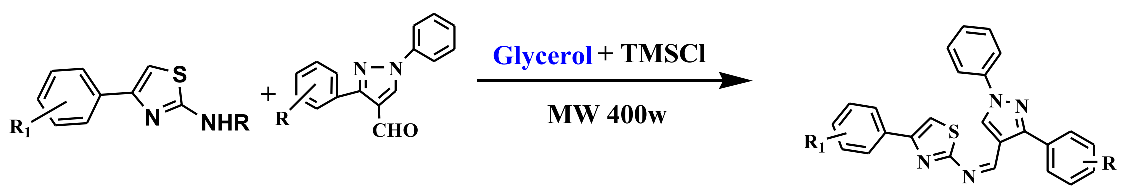
Ionic liquids as a green solvent

Ionic liquids (ILs) are a composition of heterocyclic cations and a variety of anions having sole properties such as non-flammability, non-volatility and extensive temperature choice for liquid phase. The term 'ionic liquids' currently

Scheme 19 Synthesis of 2-aminothiazoles



1 2 3 4a-4h

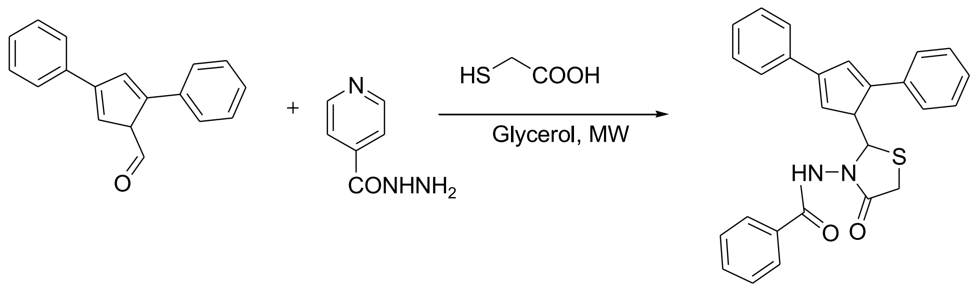


1 2 3a-k

(*Z*)-4-phenyl-*N*-((1,3-diphenyl-1*H*-pyrazol-4-yl)methylene)thiazol-2-amine

Scheme 20 Synthesis of pyrazolyl-thiazole Schiff bases

Scheme 21 Synthesis of *N*-(2-(1,3-diphenyl-1*H*-pyrazol-4-yl)-4-oxothiazolidine, MW (microwave)



refers to liquids collected entirely of ions that are fluid. The increased attention in ionic liquids by researcher clearly is because of the effectiveness of ionic liquids as solvents for rate of reaction in chemistry, as well as catalytic reactions (Hu et al. 2019). The craving for green solvents for manufacturing processes is responsible, but also many researchers now become conscious that ionic liquids offer some exceptional properties as solvents. In addition, the ionic liquids have the outlook for convention design of the solvent to meet precise requirements for a scrupulous reaction type. Some of ionic liquids initially most commonly was used there were BF_4^-, $AnlCl_4^-$, (CF_3SO_2) $N^- = Tf_2N^-$), PF_6^- (Wilkes et al. 1982). The degree of effectiveness of ionic liquids as solvents in organic reactions and catalysis has been reviewed (Olivier-Bourbigou and Magna 2002; Wasserscheid and Welton 2003). Some ionic liquids can be liquid at low temperatures as − 96 °C, and some liquids are at over 400 °C. In addition, room temperature ionic liquids are normally fluid, colorless and easy to handle. Ionic liquids and deep eutectic solvents are extensively used in the synthesis of selenides molecules (Kostić and Divac 2019).

Bio-based ionic liquids act efficient absorbent for both hydrophobic and hydrophilic volatile organic compounds (Fahri et al. 2020). Moreover, ionic liquids also capture CO_2 and decreased emissions of greenhouse gases (Lu et al. 2019). Ionic liquids serve as environmentally benign solvent to remove toxic metals (Rajadurai and Anguraj 2020).

Synthesis of thiazoles in ionic liquids

Potewar et al. (2007) reported that the reaction of phenacyl bromide, thiourea or thioacetamide in 1,3-di-n-butylimidazoliumtetrafluoroborate [bbim]BF4 can be resulted into thiazole after stirring at ambient temperature (Scheme 24).

Synthesis of azetidine

Xie et al. (1999) reported this reaction by using imine and EDA in ionic liquid [BMIM][PF6] for 5 h (Scheme 25).

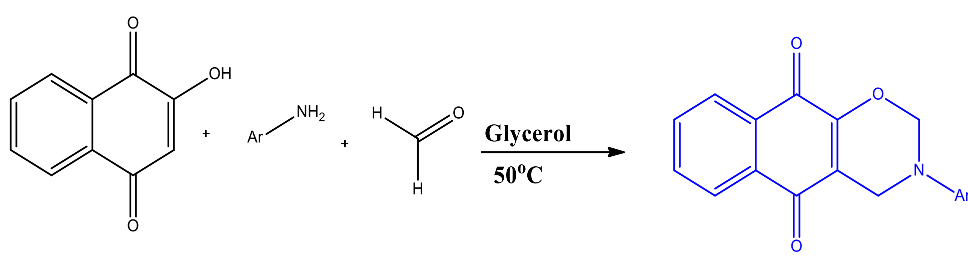
Synthesis of quinoxaline

Zare et al. (2010) reported the synthesis of quinoxaline by using the mixture of 1,2-diamine and 1,2-diketone in a microwave vessel, in which [bmim]Br was added and mixed thoroughly. The as-obtained mixture was then irradiated and stirred in a microwave oven at 500 W (Scheme 26).

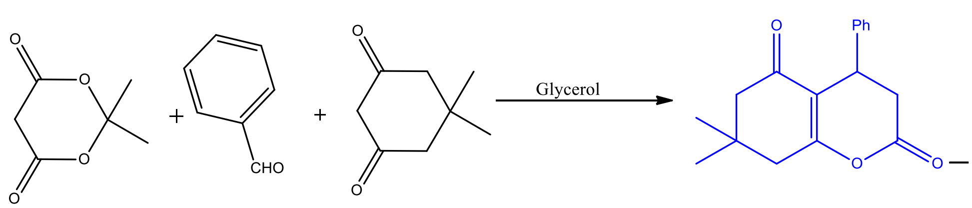
Synthesis of dihydropyrano [2, 3-c] pyrazoles

Julio A. Seijas et al. reported that a mixture of aromatic benzaldehyde, malononitrile, hydrazine hydrate and ethyl acetoacetate was diluted into [Et3NH][HSO4]. This mixture was stirred continuously at ambient temperature and was then quenched with ice. Thereafter, the mixture

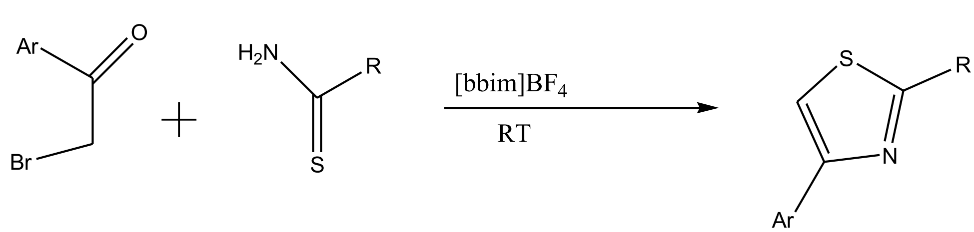
Scheme 22 One-pot multicomponent synthesis of 3,4-dihydro-2*H*-naphtho[2,3-e] [1,3] oxazine-5,10-diones



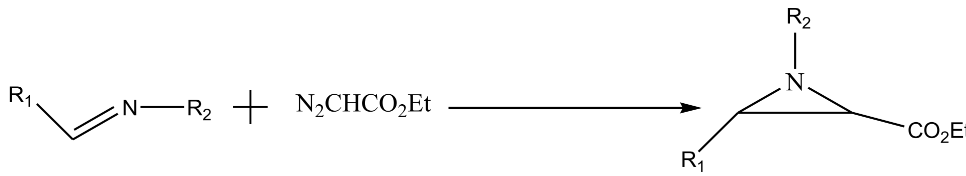
Scheme 23 One-pot synthesis of 4-aryl-7,7-dimethyl-5-oxo-3,4,5,6,7,8-hexahydrocoumarin



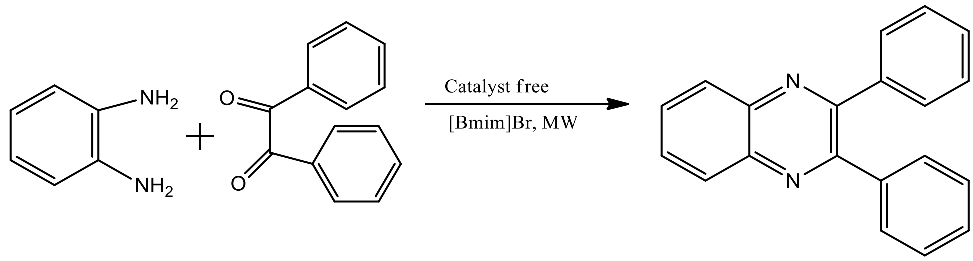
Scheme 24 Synthesis of thiazole in ionic liquids. Here, RT is room temperature



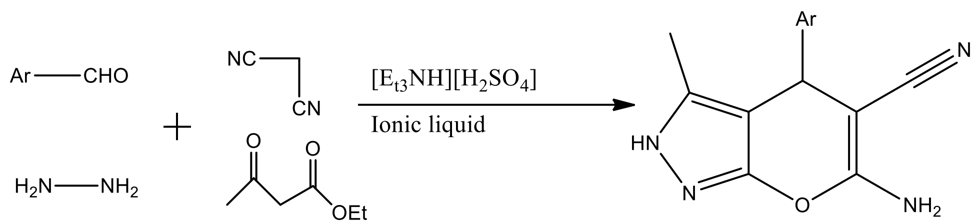
Scheme 25 Synthesis of azetidine in ionic liquids



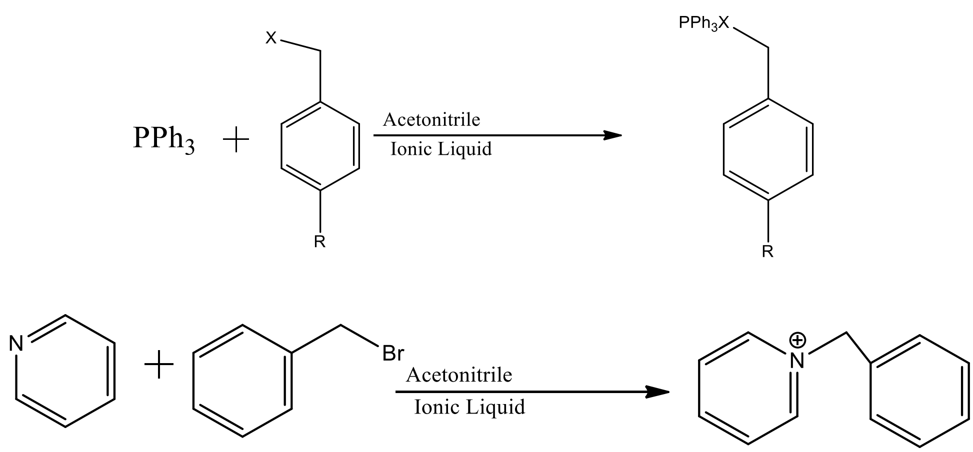
Scheme 26 Synthesis of quinoxaline. MW (microwave)



Scheme 27 Synthesis of dihydropyrano [2, 3-c] pyrazoles



Scheme 28 SN^2 reactions in ionic liquid



was extracted with ethyl acetate (Nimbalkar et al. 2017) (Scheme 27).

SN^2 reactions in ionic liquid

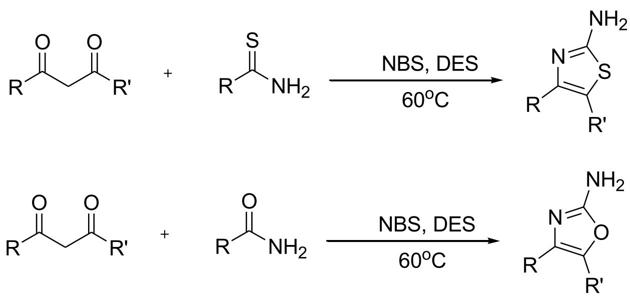
Schaffarczy et al. (2018) have reported two scheme (Scheme 28) with ionic liquid. Scheme 1 bimolecular nucleophilic substitution reaction among triphenylphosphine 5. Benzyl derivatives produced the salts which was inspected in reaction mixtures consisting the ionic liquid. In Scheme 2, the bimolecular nucleophilic substitution reaction between benzyl bromide and pyridine to produce the pyridinium salt, which was inspected in reaction mixtures consisting the ionic liquid (Scheme 28).

Deep eutectic solvents (DESs)

Deep eutectic solvents evolved as a sustainable and convenient alternative to the organic solvents. They are mainly mixture consisting of a hydrogen bond acceptors such as phosphonium salts, quaternary ammonium salts, choline chlorides and hydrogen bond donor such as alcohols, amides, organic acids and amides.(Abbott et al. 2004). DESs are low melting mixture. DESs have various advantages over

Table 4 Classifications of deep eutectic solvents (Smith et al. 2014; Al-Murshedi et al. 2019)

Type	Composition	General formula
Type I	Organic salt + metal salts	Y = metal salt MCl_x (M = Zn, Sn, Fe)
Type II	Organic salts + hydrated metal salts	Y = metal salt MCl_x, y H_2O (M = Cr, Co, Cu, Ni, Fe)
Type III	Organic salts + hydrogen bond donors	Y = hydrogen bond donor RZ (Z = COOH, OH, $CONH_2$)
Types IV	Metal salts + hydrogen bond donors	Y = hydrogen bond donor and the cation is replaced by a salt such as $ZnCl_2$



Scheme 29 One-pot synthesis of thiazole and oxazoles in DESs. Here DESs are deep eutectic solvents and NBS is N-bromosuccinimide

conventional organic solvents such as easy to prepare, inexpensive, highly stable, non-poisonous and inert to water and air (Fernández et al. 2018; Smith et al. 2014). Deep eutectic solvents efficiently used as green absorbents of toxic and volatile organic pollutants and carbon capture technologies (Moura et al. 2017; Krishnan et al. 2020).

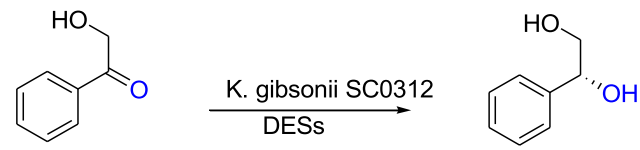
Recently, researcher had growing interest to prepare natural deep eutectic solvents (NADESs) because of their non-toxic and highly biodegradable nature (Li, et al. 2016). DESs are classified on the basis of complexing agent largely in four types with the general formula: $Cat^+ X^- z$ (Table 4).

Synthesis of aminothiazoles and aminoxazoles

Azizi et al. designed one-pot synthesis of 2-aminothiazole and 2-aminoxazoles from 2-aminothiazole and 2-aminoxazole derivatives using deep eutectic solvent. Choline chloride is used as a hydrogen bond acceptor and urea used as a hydrogen bond donor to furnished deep eutectic solvent (Azizi et al. 2015) (Scheme 29)

Biocatalytic reduction

Choline chloride/1,4-butanediol (ChCl/Bd) showed excellent biocompatibility and suitably increased the cell membrane permeability while having a little impact on the structure of DNA. K. gibsonii SC0312 catalyzed reduction of 80 mM 2-hydroxyacetophenone in the choline chloride/1,4-butanediol furnished (R)-1-phenyl-1,2-ethanediol in 80% yield with optical purity > 99% at 30 mg/mL wet cells (Peng et al. 2018) (Scheme 30)



Scheme 30 Biocatalytic reduction in DESs

Multi-component synthesis of tetrahydrobenzo[b] pyran and pyrano[2,3-d] pyrimidinone

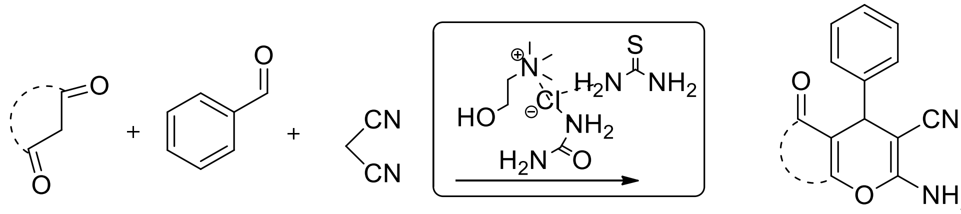
Biglari et al. reported three component synthesis of tetrahydrobenzo[*b*]pyran and pyrano[2,3-*d*]pyrimidinone (thione) from the reaction of aldehydes, malononitrile and active methylene compounds using green deep eutectic solvents (Scheme 31). New deep eutectic solvent made of choline chloride (hydrogen bond acceptor), urea and thiourea (hydrogen bond donor) (Biglari et al. 2020a, b).

Synthesis of indeno[2,1-*c*]quinolones

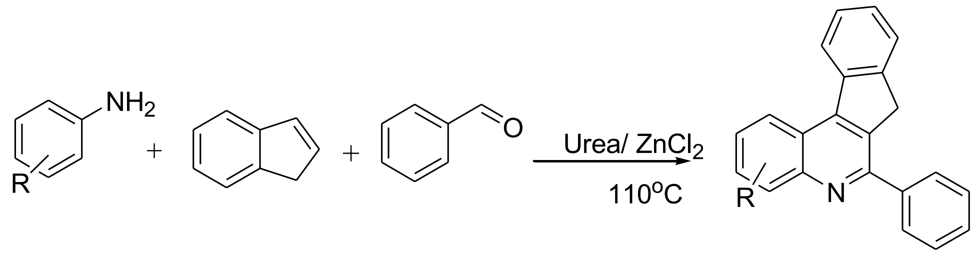
Solórzano et al. prepared the low melting eutectic solvent from urea–zinc chloride and characterized by IR, RAMAN and TGA techniques (Scheme 32). This deep eutectic mixture of urea–zinc chloride is used for three component Povarov reaction between benzaldehydes, anilines and indene to obtained indeno[2,1-*c*]quinolines in high yields (Peña-Solórzano et al. 2020).

Multi-component synthesis of pyrano[2,3-d]pyrimidinone (thione), hexahydroquinoline, and biscoumarins

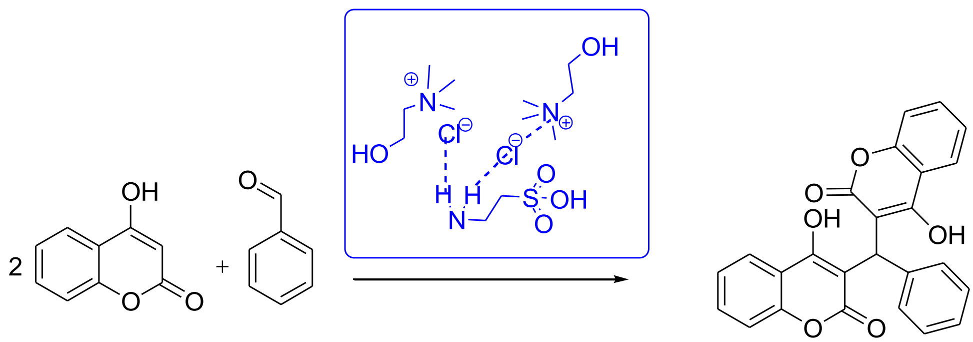
Biglari et al. (2020a, b) synthesized taurine/choline chloride deep eutectic solvent and characterized and used as an eco-compatible catalyst in the synthesis of biscoumarin (Scheme 33), pyrano[2,3-d]pyrimidinone (thione) (Scheme 34) and hexahydroquinoline derivatives (Scheme 35) (Biglari et al. 2020a, b).



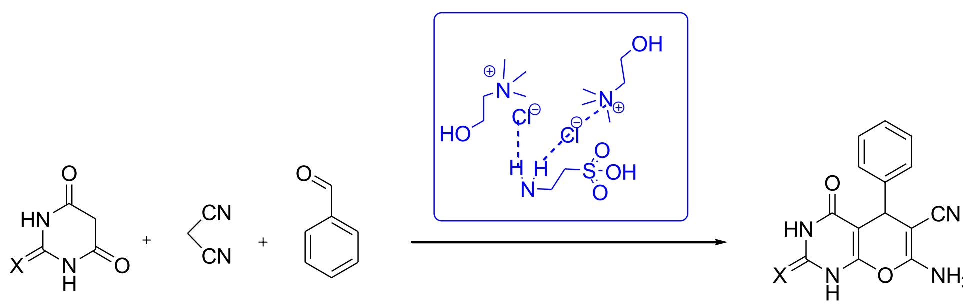
Scheme 31 Synthesis of tetrahydrobenzo[b]pyran



Scheme 32 Synthesis of indeno[2,1-*c*]quinolones in DES



Scheme 33 Synthesis of bis-coumarins



Scheme 34 Synthesis of pyrano[2,3-d]pyrimidinone

Synthesis of 2-benzimidazolones and 2-imidazolones

Aghapoor et al. reported synthesis of 2-benzimidazolone and 2-imidazolone derivatives by employing zinc chloride:urea (1: 3.5) type IV eutectic mixture under mild reaction conditions. (Aghapoor et al. 2019) (Scheme 36)

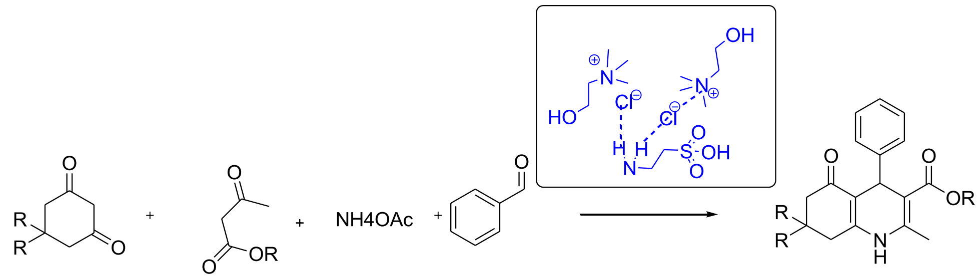
Synthesis of *α*-amino nitriles via Strecker reaction in deep eutectic solvents

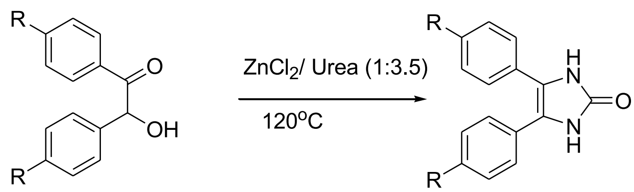
Choline chloride/urea used as a deep eutectic solvent for Strecker reaction for the synthesis of *α*-amino nitriles that contain a thiazole moiety (Scheme 37) (Bahrani and Karimi-Jaberi 2019).

One-pot synthesis of hydrazinyl-4-phenyl-1,3-thiazoles

Foroughi Kaldareh et al. developed one-pot synthesis of hydrazinyl-4-phenyl-1,3-thiazoles from the reaction of reaction of ketones or aldehydes, phenacyl chloride and thiosemicarbazide by employing choline chloride/urea as a deep eutectic solvent (DES) (Foroughi Kaldareh et al. 2019) (Scheme 38).

Scheme 35 Synthesis of hexahydroquinoline





Scheme 36 Synthesis of 2-imidazolone derivatives using $ZnCl_2$/urea deep eutectic solvent

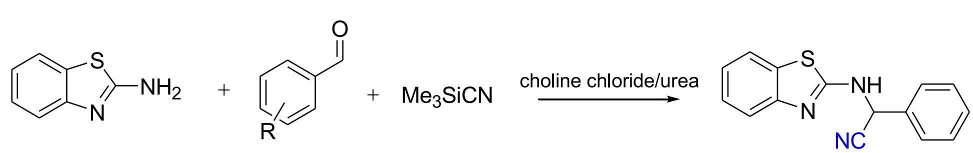
Conclusion

This review has concluded that promising applications are reported from the natural source as well as synthetic origin. Apart from trailing the principles of green chemistry as direction, sustainable chemistry is now motivating a comprehensive way by securing future advancement through optimizing the supply chain. Such a mindset has developed as an intrinsic component of the alternative solvent community. The green principles directed the use of "switchable water" experiences that increase the ionic strength while exposing to CO_2. Thus, the use of solvents may be restricted wherever possible. This protocol is important for large-scale processing where chloroform or hexane is the reaction solvents.

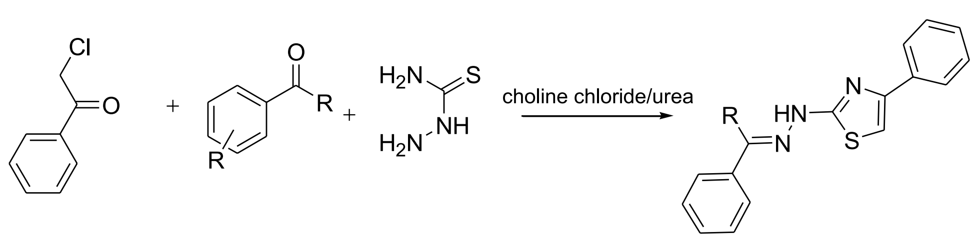
Further, the advancement in the green chemical approach may rely on the application of novel integrated reaction/separation systems, which should be effective, simpler and sustainable as well. Nature offers us a key to the most advanced toolbox containing catalysts to execute selective, clean, environmentally friendly and sustainable transformations. The technological applicability of enzymes can be greatly improved while using them in non-aqueous solution instead of using them in natural aqueous reaction medium due to the enlargement in the repository of enzyme-catalyzed transformations. The virtue of hydrophobic ionic liquids to arrange proper micro-environments for chemical synthesis was reinforced by the phase nature of ionic liquids based on cations with long alkyl chains. The unique characteristics of ionic liquids promote the advancement of green and simple approach for precisely splitting a hydrophobic organic compound (e.g., flavors esters) from a homogeneous ionic liquid/organic compound solution via cooling and centrifugation approach.

There is large scope to synthesize new deep eutectic and neoteric solvents which will be better substitute to organic and harmful solvents mostly employed in chemical synthesis.

Scheme 37 Synthesis of *α*-amino nitriles



Scheme 38 One-pot synthesis of hydrazinyl-4-phenyl-1,3-thiazoles



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