Ionic liquid assisted synthesis of six-membered oxygen heterocycles

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Abstract

Due to special properties of ionic liquids (ILs) like their wide liquid range, good solvating ability, negligible vapour pressure, non-inflammability, environment friendly medium, high thermal stability, easy recycling and rate promoters etc. they are used in organic synthesis. The investigation for replacement of organic solvents in organic synthesis is a growing area of interest due to increasing environmental issues. Therefore, ILs have attracted the attention of chemists and act as catalyst and reaction medium in organic reaction with high activity. There is no doubt that ILs have become a major subject of study for modern chemistry. In comparison to traditional processes the use of ILs resulted in improved, complimentary or alternative selectivities in organic synthesis. The aim of present review is to focus on the applications of ILs for the synthesis of six-membered oxygen heterocycles (pyrans, chromenes, coumarins and dioxanes).

Keywords Ionic liquid · Oxygen · Heterocycles

1 Introduction

Heterocyclic compounds possess many biological activities. Various natural products (hormones, vitamins, alkaloids and antibiotics), herbicides, pharmaceuticals and dyes are constituted by heterocycles [1–64]. In the past few decades, researchers have paid their much attention to explore efficient and new synthetic strategies for the preparation of heterocycles due to a wide range of applications associated them [65–97]. Among these synthetic protocols ionic liquid assisted methods gained much attention due to their short reaction times, mild reaction conditions and improved yield. More green and environmentally benign synthetic procedures are highly recommended for the organic synthesis. In the past few years, the utilization of ionic liquids in place of conventional organic solvents have much significance [98–102]. The effectiveness of synthetic route is not only measured by parameters such as yield and selectivity, but other factors like time, raw material, human resources, hazard and toxicity of the chemicals and energy consumption are also considered. The use of ionic liquids in multi-component reactions not only provided

the environmentally benign reaction medium, but ILs also act as catalyst, which is an added advantage [103–109]. Ionic liquids, due to their non-flammable, non-volatile, thermal stability, solvating potential and recyclable features, are favorable medium for chemical syntheses and have replaced traditional organic solvents [110–120].

Only ions are possessed by an IL. Room-temperature ionic liquids (RT ILs) contain asymmetric and bulky organic cations like 1-alkylpyridinium, 1-alkyl-3-methylimidazolium, ammonium ions or 1-methyl-1-alkylpyrrolidinium (Fig. 1). Ionic liquids carry a variety of anions such as simple halides, large organic anions i.e. tosylate or triflate, bis(trifluorosulfonyl)amide and inorganic anions like hexafluorophosphate and tetrafluoroborate (Fig. 2) [121–126].

Nowadays, it is known that some properties of anions influence more dramatically the intrinsic cytotoxicity of ionic liquids. Anions quite lipophilic and/or unstable were reported to play a major role. The most important function of ionic liquid is to stabilize the charged activated complex through solvent–solute-type interactions, similar (but not identical) to the interaction between polar protic/aprotic solvents and solutes [127–130].

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Fig. 1 Cations of ionic liquids

Ionic liquids are often deemed to have high thermal and chemical stability, and wide electrochemical window. However, this is not always true because the stabilities of various ionic liquids are very different. The instabilities of ionic liquids should come from the complex molecular structures. The stability of ionic liquids mainly depends on their intrinsic composition, (cation and anion), and the interactions between anions and cations. However, different types of stabilities (thermal, electrochemical, and radiolytic) follow different rules because they cause unstable or decomposition by different mechanisms [131, 132].

Reports have suggested that ionic liquids are used in many fields especially in organic syntheses. The mechanism of working of ionic liquids in organic reactions is not known and it is a point of controversy among chemists. In organic reactions the catalyst/solvent effect of ionic liquids cannot be explained on the basis of data available on properties like polarity, dielectric constants, etc. Their high polarity and the ability to solubilize both inorganic and organic compounds can result in enhanced rates of chemical processes and can provide higher selectivities when compared to conventional solvents. Given their structure and the diversity of their functionality, they are capable of most types of interactions (e.g., dispersive, π - π , n - π , hydrogen-bonding, dipolar, and ionic/charge-charge). Various single-parameter polarity scales are essentially weighted averages of all possible solute-solvent interactions. Since ionic liquids are much more complex solvent systems capable of undergoing many types of interactions, characterizing them with a single polarity term fails to encompass the broad spectrum of types and the magnitude of individual interactions that make each ionic liquid unique. Ionic liquids exhibit multiple behaviors, which explains why many ionic liquids act as polar solvents in organic reactions containing polar molecules and as less polar solvents in the presence of less polar molecules [133–139].

Some researchers have described that ionic liquids served as organocatalysts. This organocatalysis occurred through hydrogen bonding interactions; the results have

demonstrated that they have a huge impact on organo-catalysis. The use of ionic liquids in most powerful way is their use as a combination of catalyst and solvent in catalysis. The new solvent is employed as a catalyst if the change of solvent results in fast rate of reaction. Based on this idea the same solvent is kept in case of accelerated reaction. The features of ionic liquid solvents are studied in many studies. Different methods have provided a much data on properties of ionic liquids like polarity and dielectric constants. The ionic liquid, whose anion or cation acts as a catalyst activator, catalyst, or co-catalyst in a chemical reaction, is significant. In recent literature, the ionic liquid is prepared so that its one of the ion can act as a catalyst and reaction medium in reaction [140–151].

The purpose of this review is to discuss the recent and current applications of ionic liquids as solvents, catalysts and reaction media for the synthesis of six-membered oxygen heterocycles (pyrans, chromenes, coumarins and dioxanes).

2 Ionic-liquid assisted synthesis of six-membered oxygen heterocycles (pyrans, chromenes, coumarins and dioxanes)

2.1 Synthesis of six-membered one oxygen containing heterocycles

Song and co-workers [152, 153] synthesized 4*H*-pyrans in aminofunctionalized ionic liquids via catalytic protocol. A higher loading capacity was achieved when the reactions were conducted in homogeneous solutions because of lower molecular weight of the functionalized IL. The intermediates were purified by simple extraction. Due to hydrogen bonding, the miscibility and solubility properties of ionic liquid [2-aemim][PF₆] (1-aminoethyl-3-methylimidazolium hexafluorophosphate) are different than those of conventional ionic liquids. The ionic liquid (solvent) and reactant were utilized in a molar ratio of 1:3

Fig. 2 Anions of ionic liquids and common ionic liquids

and it was reused seven times without any much decrease in yield. A variety of structurally diverse aldehydes were used to increase the scope of this method. The 4*H*-pyrans were obtained from both electron deficient and electron-rich aromatic aldehydes [154] (Scheme 1).

Peng and Song [155] utilized a three-component strategy for the synthesis of 4*H*-pyrans derivatives under microwave irradiation in the presence of a recyclable and environmentally benign reaction medium i.e. the mixture of catalytically active 1-methyl-3-(2-aminoethyl)

Scheme 1 Synthesis of 4*H*-pyrans **Scheme 2** Synthesis of 4*H*-pyrans

imidazolium hexafluorophosphate and water (Scheme 2) [156].

Polyfunctionalized 4*H*-pyrans exhibit a wide range of pharmacological properties [157, 158]. The pyran rings are building blocks due to the inherent their reactivity [159]. The arylidenemalonitriles and activated methylene compounds were reacted in organic bases to synthesize 2-amino-4*H*-pyrans [160, 161]. Song and co-workers [162] treated malononitrile with aryl aldehydes, and 1,3-dicarbonyl compounds for the preparation of 2-amino-4*H*-pyrans in the presence of ionic liquid soluble support. The TMG-[bmim][BF₄] (1,1,3,3-tetramethylguanidine 1-butyl-3-methylimidazolium tetrafluoroborate) was used in this reaction in a molar ratio of 1:3 (reactant/IL). The ionic liquid was recovered and reused up to five times without any appreciable decrease in activity. The electronic effects of

phenyl ring substituents have shown that electron-withdrawing groups favored the reaction while electron-releasing groups not. For higher reaction rates and yields the ionic liquids solvent was found to be superior than ethanol (yields 60–80%) [154] (Scheme 3).

Various natural products possess 4*H*-pyran and therefore have attracted the attention of chemists [163, 164]. The preparation of oxygen containing heterocyclic compounds is slightly more complex, because to affect the final ring-closing step only reduced numbers of suitable oxygen nucleophiles were available. The 4*H*-pyran derivatives have high reactivity and are used as synthons for the construction of more complex species. Addition of malononitriles, aromatic aldehydes, and β-dicarbonyl was performed in [bmim][BF₄] and 1,1,3,3-tetramethylguanidine catalyst to afford highly substituted 4*H*-pyrans (Scheme 4) [165, 166].

The *exo*-methylene five- and six-membered lactones were synthesized selectively in high yields by an intramolecular alkoxy carbonylation of alkynols with the aid of Pd(II)/PyPh₂P complexes immobilized in (BMI)PF₆ or (BMI)BF₄ [167]. Catalyst recycling and product isolation was done in the same way as that of carbonylation of aryl halides [168] (Scheme 5).

The unexpected product methyl 6-(4-methoxyphenyl)-2*H*-pyran-3-carboxylate was obtained in 80% yield by mixing (*Z*)-methyl 5-chloro-3-hydroxy-5-(4-methoxyphenyl)-2-methylenepent-4-enoate (1.0 mmol) with NaNO₃ (1.1 mmol) at 80 °C in ionic liquid [hmim]HSO₄ for 12 h (Scheme 6) [169].

Various aldehydes and homoallylic alcohols underwent Prins cyclization at room temperature in Et₄NF·5HF. The fluorinated tetrahydropyrans were obtained with high

Scheme 3 Synthesis of 2-amino-4*H*-pyrans

Scheme 4 Synthesis of 4*H*-pyrans **Scheme 5** Synthesis of 4,5-dimethyl-3-methylenetetrahydro-2*H*-pyran-2-one **Scheme 6** Synthesis of methyl 6-(4-methoxyphenyl)-2*H*-pyran-3-carboxylate**Scheme 7** Synthesis of tetrahydropyrans

stereoselectivity (cis products were formed exclusively) in excellent yields by Prins cyclization of an alicyclic aldehyde, an aliphatic aldehyde and an aromatic aldehyde with a homoallylic alcohol [170, 171]. The expected products were observed in a same way, irrespective of the substituents at para position of benzaldehyde. The 2,4,6-trisubstituted tetrahydropyrans were obtained in quantitative yields reacting 1-substituted homoallylic alcohols with aldehydes. No or quite low reactivity was reported for ketones. Sabitha and co-workers [172] reported Prins cyclization of many ketones with homoallylic alcohols in the presence of trimethylsilyl iodide (TMSI). The protons of $\text{Et}_4\text{NF} \cdot 5\text{HF}$ have low capacity to activate the carbonyl groups as indicated by these results. However, the spiro product was only obtained by reacting cyclic ketone (Scheme 7) [173].

The photo-oxygenation of furans was carried out in ionic liquid reaction media using singlet oxygen [174]. The [bmim] BF_4 and [emim]Br (1-ethyl-3-methylimidazolium bromide) ionic liquids were utilized and the obtained

results were compared with those of acetonitrile and water. Acetonitrile (10% v/v, to dissolve the solid salt) and water (50% v/v, to ensure solubility of substrates) were used as co-solvent with [emim]Br because at room temperature [emim]Br is not a liquid. Methylene blue and rose bengal were employed as sensitizers and a halogen lamp was utilized for irradiation. The influence on the fate of the *endo*-peroxide was investigated using a number of substituents (Scheme 8).

This procedure was utilized for concise synthesis of ($\pm$)-centrolobine to ensure the feasibility of intramolecular hydroalkoxylation in Bronsted acidic ionic liquids (Scheme 9). The stem of *Brosimum potabile* in the Amazon forest and heartwood of *Centrolobium robustum* contain an antiprotozoal natural product (–)-centrolobine [175–177]. For the synthesis of tetrahydropyran skeleton there is no example that involved an intramolecular hydroalkoxylation as a key step. The tetrahydropyran skeleton was produced by an atom economical method from alkenyl alcohol in the presence of Bronsted acidic

Various biological activities are possessed by naturally occurring flavones [202–204]. The flavones were synthesized by different protocols such as Allan–Robinson synthesis [205], the use of chalcones [206] and the Wittig reaction [207, 208]. The Baker–Venkatraman rearrangement was most common procedure for the synthesis of flavones. The 2-phenyl-4*H*-chromen-4-ones were furnished in high yield in short reaction time from substituted 1-(2-hydroxyphenyl)-3-phenyl-1,3-propane diones under MW irradiation in the presence of [EtNH₃]⁺NO₃[−] ionic liquid. The benzoyl ester was formed from 2-hydroxyacetophenone. The formed benzoyl ester provided 1,3-diketone in base (pyridine/KOH). The flavones were produced from cyclization of 1,3-ketones under strongly acidic conditions [209]. The flavones were synthesized from various substituted diketones under microwave irradiation in

Scheme 9 Synthesis of tetrahydropyran

Scheme 10 Synthesis of 2-phenylchroman-4-one

the presence of an ionic liquid catalyst, ethyl ammonium nitrate ($[\text{EtNH}_3][\text{NO}_3]$) without the formation of any side product except water (Scheme 11). The ionic liquid was utilized in a molar ratio of 1:2 (reactant/IL), and it was recovered and reused two times with only little decrease in activity. The simplicity in procedure and work up, mild reaction conditions and good yields were benefits of this

reaction. The flavone derivatives were formed in 82% yield when the reaction was carried out under acidic conditions (HCl) in a molecular solvent (acetic acid) by reflux of 14 h [210]. This is not clear whether it was the microwave irradiation or the ionic liquid that increased the efficiency of reaction. The ionic liquid was good alternative to a molecular solvent [211, 212]. The ionic liquid $[\text{EtNH}_3]$

NO_3 was synthesized as described in literature [198–200]. The 1,3-diketones were irradiated in a domestic microwave oven in ionic liquid $[\text{EtNH}_3][\text{NO}_3]$ for a specified time period. Pure flavones were observed in 80–90% yield after completion of the reaction and extraction with organic solvent followed by aqueous work-up. Due to the water solubility of ionic liquid, it goes into the aqueous layer. The ionic liquid (about 90%) was left behind after distilling the aqueous layer under vacuum at 80 °C to remove water [154, 156, 213–215].

The important derivatives of benzopyrans i.e. coumarins were prepared by Wittig reactions (Scheme 12) in the presence of acidic or basic catalysts [216].

Tetrahydrobenzo[*b*]pyran derivatives can be synthesized by a multi-component reaction of an aromatic aldehyde, dimedone and malonitrile in the presence of both acidic as well as basic catalysts. Recently, Peng and Song [153] carried out this multi-component reaction (MCR) by replacing dimedone by β -ketoester and synthesized new derivatives of pyrans by employing a mixture of water and ionic liquid, while for the same purpose Babu et al. [217] used a heterogeneous strong basic Mg/La mixed oxide catalyst in methanol (Scheme 13) [218].

The coumarins were synthesized using an acid catalyzed Pechmann reaction by condensing phenols with

β -ketoesters. Many reagents, such as sulfuric acid [219], phosphorus pentoxide [220], aluminium chloride [221], and trifluoroacetic acid [222], have been employed in this reaction. Environmentally benign and gentle reagents (oxalic acid, SnCl_2 , silica triflate, alum ($\text{KAl}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$) and iodine [223–228]) were preferably used in this reaction. Pechmann condensation for the coumarin synthesis was promoted in both neutral [229] and acidic [230–232] ionic liquids. Singh and co-workers [233] combined microwave irradiation and an ionic liquid for this reaction. The Bronsted acidic $[\text{bmim}][\text{HSO}_4]$ ionic liquid was used as a catalyst under conventional reflux conditions and it was observed that less yields of coumarins in much more times were reported in comparison to microwave conditions (Scheme 14).

The 5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran was synthesized with dimedone (1,3-dicarbonyl source) in $[\text{hmim}][\text{BF}_4]$ (1-hexyl-3-methylimidazolium tetrafluoroborate), $[\text{bmim}][\text{BF}_4]$, $[\text{omim}][\text{PF}_6]$ (1-octyl-3-methylimidazolium hexafluorophosphate), $[\text{omim}][\text{BF}_4]$ (1-octyl-3-methylimidazolium tetrafluoroborate) and $[\text{DMIM}][\text{PF}_6]$ (3-methylimidazolium hexafluorophosphate). No additional catalyst was needed and the reactions completed in 2–6 h in yields ranging from 52 to 98% [234, 235]. The group of Fang et al. [236] developed a modified condensation of malononitrile

Scheme 11 Synthesis of 2-phenyl-4*H*-chromen-4-ones

Scheme 12 Synthesis of coumarins

Scheme 13 Synthesis of tetrahydrobenzo[*b*]pyran

(or ethyl cyanoacetate), aromatic aldehyde, and dimedone (or 1,3-cyclo-hexanedione) for the generation of more highly substituted 5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyrans with acidic ionic liquids like [TBPSA][HSO₄], [TEBSA][HSO₄], [EDPSA][HSO₄] in water (Scheme 15). The products were obtained in good yields (86 to 94%) [164, 237–240].

Zhou and co-workers [241] reported the microwave-assisted intramolecular Stetter reaction of 3-ethyl-5-(2-hydroxyethyl)-4-methylthiazolium bromide using imidazolium-type room temperature ionic liquids (RT ILs) as solvents. The reaction conditions were optimized by intramolecular Stetter reaction of (*E*)-methyl 4-(2-formylphenoxy) but-2-enoate in the presence of butylmethylimidazolium tetrafluoroborate [bmim]⁺[BF₄][−] solvent. The salts of many heterocycles, including imidazolium salts, were utilized as catalysts. The ionic liquids played the role of solvent as well as of catalyst, although it is less active than thiazolium salts, and furnished poor yields of the expected product. The yield was improved to 96% on increasing the quantity of thiazolium salt from 5 to 15 mol%. A number of aromatic substrates undergo the intramolecular Stetter reaction under microwave irradiation with thiazolium salts

and Et₃N catalysts in imidazolium-type room temperature ionic liquids as solvents. The reactions were completed in 5–20 min and good to excellent yields of products were observed under these conditions, usually higher than those obtained under conventional heating conditions. The ionic liquid and thiazolium salts catalyst were recyclable and reusable (Scheme 16).

Many 2-alkyl-substituted chromanones were synthesized in basic ionic liquid catalyst. Two consecutive reactions were comprised in one-step by using basic ionic liquid, [bmim]OH. The ortho-acylphenols were condensed with terminal alkynoates in [bmim]OH as a catalyst, followed by intramolecular cyclization. The remarkable features of this synthetic protocol are green reaction conditions and reusability of catalyst with good yields. The chromanone was prepared by coupling of orthohydroxy acetophenone and ethyl propiolate in the presence of basic ionic liquid [bmim]OH to optimize the reaction conditions (Scheme 17). This reaction occurred in two steps: in the first step hydroxyl group of phenol was protected, in second step 2-alkyl substituted chromanone derivative was synthesized by cyclization. Authors tried to prepare

Scheme 14 Synthesis of coumarins

Scheme 15 Synthesis of 5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran

Scheme 16 Synthesis of methyl 2-(7-chloro-4-oxochroman-3-yl)acetate

Scheme 17 Synthesis of 2-alkyl-substituted chromanones

Scheme 18 Synthesis of coumarin

Scheme 19 Synthesis of ethyl 2-oxo-2H-chromene-3-carboxylate

Scheme 20 Synthesis of 4H-benzo[b]pyran

2-alkyl substituted chromanone derivative in a single step using [bmim]OH ionic liquid catalyst. This indicated the efficiency of [bmim]OH catalyst [242].

The Knoevenagel condensation of many ketones, aromatic and aliphatic aldehydes with active methylenes was efficiently catalyzed by basic ionic liquid [bmim]OH (1-butyl-3-methylimidazolium hydroxide) under solvent-free conditions at room temperature. The coumarin was furnished in very high yields by one-pot condensation of an aromatic *o*-hydroxy aldehyde with ethyl acetoacetate or diethyl malonate (Scheme 18) [243, 244].

The Knoevenagel condensation between aldehydes or ketones with active methylene compounds was performed with EDDA (ethylenediammonium diacetate) catalyst in ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF₄. Solvent and catalyst are recyclable [245] (Scheme 19).

The described method has the merits of simple operation, environmentally benign, convenient workup, good yields and economic efficiency. The 4H-benzo[b]pyran derivatives were synthesized by a clean, simple and environment friendly three-component reaction in basic ionic liquid [PhCH₂Me₂N⁺CH₂CH₂NMe₂]Cl[−] (*N,N*-dimethyl aminoethylbenzyltrimethylammonium chloride) as an efficient catalyst without the need of solvent (Scheme 20). The excellent yields of desired products in good purity were obtained under solvent-free condition when a number of aromatic aldehydes were condensed with malononitrile and 5,5-dimethylcyclohexane-1,3-dione (dimedone) [244, 246].

The green, efficient and one-pot formation of tetrahydrobenzo[b]pyran derivatives was promoted by basic ionic liquid, [bmim]OH (Scheme 21). The role of reaction medium as well as catalyst was played by ionic liquid.

Scheme 21 Synthesis of tetrahydrobenzo[*b*]pyran

The ionic liquid can be used for up to five times without decrease in productivity [244, 247].

The condensation of salicylaldehyde or its derivatives with ethyl acetoacetate was promoted by L-proline in neutral ionic liquid [emim]BF₄. The ionic liquid containing L-proline was recyclable and can be reused many times without loss in activity. All reactions provided high yields under mild reaction conditions. The L-proline-[emim]BF₄ system contributed to the development of inexpensive and environmentally benign methods in organic syntheses. The efforts began with salicylaldehyde and ethyl acetoacetate in ionic liquid [emim]BF₄ at room temperature without L-proline. The catalytic activity of L-proline for these reactions was investigated, and no reaction took place in ionic liquid in 24 h in the absence of L-proline. When 5 mol% L-proline was added, the reaction yield was 85%, and when 40 mol% L-proline was added, the reaction yield increased to 95%. However, using 50 mol% L-proline resulted in lower yield. The amount of ionic liquid used in the reaction was also optimized, and the results show that the yield increased as the amount of ionic liquid increased from 0.5 ml to 1 ml; however, the yield began to decrease as ionic liquid increased to 1.5 ml. Therefore, the best result was observed when 40 mol% L-proline was used as a promoter in 1 ml ionic liquid. The reaction gave almost no products in CH₃CN, tetrahydrofuran (THF), and CH₂Cl₂, and yielded a low level of dimethyl sulfoxide (DMSO) in the presence of L-proline when the reaction time was prolonged to 48 h. In summary, both L-proline and [emim]BF₄ had an important effect to the reaction: without one of the two, the reaction would not take place. Since the L-proline and ionic liquid [emim]BF₄ are soluble in water, they were extracted with water and the solid material was filtered off to give high purity products. The water solution containing L-proline was distilled under a reduced pressure,

and the remaining ionic liquid containing L-proline was recycled and reused at least five times without noticeably decreasing the productivity. Compared with conventional methods, the L-proline-[emim]BF₄ system offers a clean, efficient, eco-friendly protocol for the synthesis of coumarins, with a high yield and a simple work-up procedure, and also a recyclable reaction medium [248] (Scheme 22).

In 1995 Cignak and co-workers [249] described the first detailed investigation of the intramolecular Stetter reaction using achiral triazolium salts. A year later, Enders et al. [250] reported the first asymmetric example of the intramolecular Stetter reaction using triazolium (Scheme 23). The 4-chromanone products are obtained in good yield and moderate enantioselectivity.

Various chromones were obtained in very good yields by this selective and efficient ligand-free cyclocarbonylation reaction of *o*-iodophenols and terminal acetylenes with the help of palladium catalyst under atmospheric CO pressure. The efficiency of the cyclocarbonylation reaction was increased when phosphonium salt ionic liquid was utilized as a reaction medium [251] (Scheme 24).

The activity of metal triflates was dramatically improved using hydrophobic ionic liquids. The Friedel–Crafts alkylations of aromatic compounds with various alkyl- and aryl-substituted alkynes were conducted in the presence of metal triflates [252] (Scheme 25).

Flavones were produced from substituted 1-(2-hydroxy phenyl)-3-phenyl-1,3-propane diones with the help of *n*-butyl-3-methyl-imidazolium tetrafluoroborate ionic liquid. The reaction of 1,3-diketones was studied in 1-*n*-butyl-3-methyl imidazolium tetrafluoroborate [bmim]BF₄ at 100 °C in model reaction. The aqueous work-up after the completion of reaction gave pure flavones in high yields. Many substituted diketones were synthesized by this well known protocol to see its synthetic utility [62]. The

Scheme 22 Synthesis of coumarins

Scheme 23 Synthesis 4-chromanone

Scheme 24 Synthesis of chromones

Scheme 25 Synthesis of 4-methyl-2H-chromen-2-one

Scheme 26 Synthesis of 2-phenyl-4H-chromen-4-one

flavones possessing Cl, NO_2 , hydroxy and methoxy groups in the aromatic rings were obtained cleanly in high yields without any undesirable side reaction. This method has advantages such as fast reaction rate, simple and easy procedure, excellent yields and mild reaction conditions. The ionic liquid was recovered and reused many times with no loss in productivity [253–257] (Scheme 26).

The 4H-benzo[b]pyrans are biologically important. The excellent yields (77–95%) of 4H-benzo[b]pyrans were obtained after stirring at ethanol reflux for 30–50 min. The $[\text{bmim}][\text{OH}]$ ionic liquid was employed as a catalyst in this synthetic protocol [144, 164] (Scheme 27).

The reaction was performed with another active methylene compound, 4-hydroxycoumarin, in place of 1,3-cyclohexanedione or dimedone. The benzaldehyde, 4-hydroxycoumarin and urea were condensed using TMSCl (trimethylsilyl chloride) catalyst in $[\text{bmim}]\text{BF}_4$. However, according to spectral data and melting point surprisingly the isolated product was found to be 3,3'-benzylidenebis-(4-hydroxycoumarin), and unreacted urea was observed in reaction mixture. Simple heating of aldehyde and 4-hydroxycoumarin at 60–70 °C in ionic liquid in the absence of catalyst provided biscoumarins. Under similar conditions, a range of aromatic,

heteroaromatic and aliphatic aldehydes were condensed with 4-hydroxycoumarin. Excellent yields of biscoumarins were obtained from all aldehydes (Scheme 28) [258].

2.3 Synthesis of six-membered two oxygen containing heterocycles

The olefins were condensed with aldehydes via acid-catalyzed Prins reaction for carbon–carbon bond formation in organic synthesis [259]. The main products of the classical Prins reaction are 1,3-dioxanes, 1,3-diols, unsaturated alcohols and the products of acid-catalyzed polymerization of olefins [260, 261]. Many bioactive natural products were obtained from 1,3-diol building blocks [262, 263]. The olefins were added to paraformaldehyde in acid catalysts for the synthesis of 1,3-diols. This transformation was promoted in Bronsted acids or Lewis acids in both stoichiometric and catalytic amounts [264–271]. Yadav et al. [272] employed catalytic amount of indium tribromide in [bmim][PF₆] for the preparation of 1,3-dioxanes. The 1,3-dioxanes were obtained in excellent yields when a number of styrenes were reacted smoothly with

paraformaldehyde. The reactions occurred efficiently in all cases with high selectivity at 25 °C. The best results were reported when the reactions were conducted for 3.5–6.5 h at room temperature in 10% indium tribromide in ionic liquids (Scheme 29). The ionic liquid was used in a molar ratio of 1:5 (reactant/IL), and it was recovered and reused three times without any much loss in yield. The improved yields, enhanced reaction rates and high selectivity were the major benefits of using ionic liquids in comparison to conventional solvents. The 4,5-diphenyl-1,3-dioxane was obtained in 90% yield with trans selectivity when *trans*-stilbenes were reacted with paraformaldehyde for 5.5 h in 10 mol% indium tribromide in [bmim][PF₆] whereas the product was observed in 70% yield as cis and trans isomers in a molar ratio of 2:8 by same reaction for 8.0 h in dichloromethane [154, 273, 274].

Although the acetal product formed quickly, it was presumed that acetal formation would be reversible, and with this in mind the one-pot cascade reaction was examined. However, no desired Stetter product was observed. All attempts to overcome the acetal formation failed to provide the desired product [275] (Scheme 30).

Scheme 27 Synthesis of 4H-benzo[b]pyrans

Scheme 28 Synthesis of biscoumarins

Scheme 29 Synthesis of 4-methyl-4,5-diphenyl-1,3-dioxane

Scheme 30 Synthesis of dimethyl 2-(1-(4-hydroxy-6-phenethyl-1,3-dioxan-2-yl)-4-phenylbutan-2-yloxy)maleate

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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