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RESEARCH REVIEW

Recent advances in ionic liquids: green unconventional solvents of this century: part II

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In the second part of our paper, further recent developments of ionic liquids in selected name reactions of carbonyl chemistry such as Mannich, Reformatsky, Cannizzaro, Strecker, Barbier, Pechmann, etc. are described.

Keywords: ionic liquids; Mannich reaction; Reformatsky reaction; Strecker reaction; Barbier reaction; Pechmann reaction; Cannizzaro reaction

Introduction

Ionic liquids (ILs) are implicated in both experimental scientific studies and commercial production. This is necessitated because of environmental concerns specific to the present century; imposition of these concerns is manifested through enactment of various regulations/laws by various countries (1). Not only are these prohibited through legal actions but also some incentives are given in the form of awards and prizes to researchers (2–6). Organic chemists were naturally attracted to the synthesis as well as use of ILs, and significant efforts have been made in the study of major named reactions of organic chemistry; therefore, ILs have been tested for many named reactions of organic chemistry, due to their attractive properties such as: they are not volatile and therefore not harmful to environment; hence, green solvents are replacing volatile organic solvents and unsafe catalysts. They also obey the 12 principles of green chemistry such as atom economy, recyclability, safety etc., (7–21). Use of ILs at a mega/industrial scale is still a challenge, but if they are successfully produced at large scale the future of life on earth will be safe from air, water, and soil pollution. But in spite of these advantages, one question remains unanswered, namely whether the manufacture of ILs is green and whether it is in favor of ecosystems or not.

In the first part of this paper, the authors have reported developments in this direction using ILs as solvents in some selected named reactions of organic chemistry (22); some remaining ones are presented in this second part. The reactions selected here are given below, and in this paper the authors' own work is also incorporated:

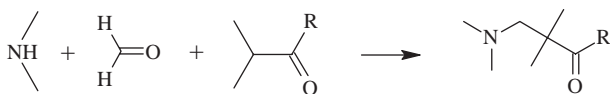
- Mannich reaction
- Reformatsky reaction
- Strecker reaction
- Barbier reaction
- Pechmann reaction
- Henry reaction
- Cannizzaro reaction

Ionic liquids, considered as alternative solvents of the present century, are discussed in the following sections as well as their role/use in major reactions.

Mannich reaction

Mannich reaction is one of the most important carbon–carbon bond-forming reaction of organic chemistry for preparation of β -amino carbonyl compounds and 1,2-amino alcohol derivatives (Scheme 1). β -Amino-carbonyl compound formed from amino alkylation of α -carbon of carbonyl group with formaldehyde and ammonia or any primary or secondary amine is known as Mannich reaction, named after its discoverer, Carl Mannich (23). Reaction of aldimines and α -methylene carbonyls also give same products, which are valuable synthetic intermediates for the synthesis of drugs and biologically active compounds (24, 25). Some green production processes/procedures in this reaction, such as microwave (26, 27) or ultrasound irradiation (28) and the use of Lewis acids (29–31) have been reported. Also, Lewis bases (32), Brønsted acids (33–35), rare metal salts (36, 37), or organo catalysts (38–40) etc., do act as promoters to catalyze Mannich-type reactions. The present authors also did contributed to a greener procedure development by using microwave irradiation (41).

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Scheme 1. Synthesis of Mannich product.

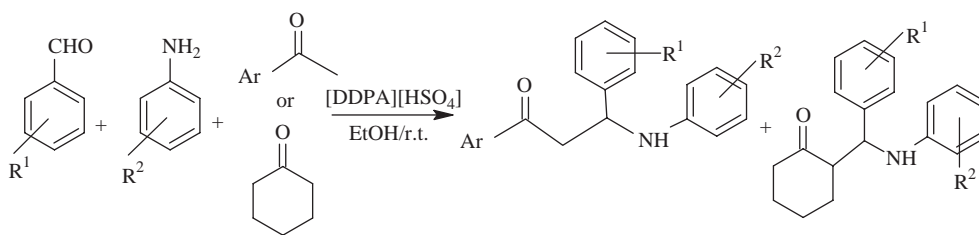
Careful examination reveals that it is a simple nucleophilic addition of an amine to a carbonyl group followed by dehydration to the Schiff base, and this Schiff base acts an electrophile which reacts in the second step in a nucleophilic addition manner to carbonyl compound containing an acidic-proton.

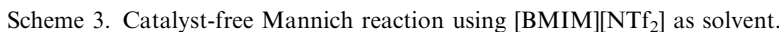
Use of IL greener solvents of present century was reported by Fang et al. in this reaction in a three-component way. So, here Mannich-type reactions of aromatic aldehydes, aromatic amines, and ketones which are catalyzed by a novel functionalized IL, 3-(N,N-dimethyldodecylammonium)propanesulfonic acid hydrogen sulfate ([DDPA][HSO₄]) at room temperature in ethanol gave various β -amino carbonyl compounds in good yields; see Scheme 2 (42). They recycled the catalyst at least six times without any catalyst activity reduction. Same groups used several ILs in this reaction to evaluate their efficacy, e.g. 3-(N,N-dimethyldodecyl ammonium) propanesulfonic acid hydrogen sulfate [DMDAPS][HSO₄] (43), 3-(N,N-dimethyldodecylammonium)propanesulfonic acid hydrogen sulfate [DDPA][HSO₄] (44), 1-butyl-3-methylimidazolium hydroxide ([bmim]OH) (45), 1-butyl-3-methylimidazolium hydroxide ([bmim]OH) (46), 3-N,N,N-trimethylammoniumpropanesulfonic acid hydrogen sulfate (47), N,N,N-trimethyl-N-butanedisulfonic acid ammonium hydrogen sulfate [TMBSA]HSO₄ (48). Invariably, these authors used these ILs in green solvents such as water and alcohol. Regarding scope reaction seems to be fairly general, as a large number of aldehydes have been used here.

Juliana and co-workers reported application of several 1-butyl-3-methylimidazolium (BMIM) salt as ILs, i.e. [BMIM][NTf₂] as solvent in the α -methylenation of carbonyl compounds at room temperature without any other catalyst (Scheme 3). This IL was reused without affecting the reaction rates or yields

over seven runs (49). Rasalkar group describes Mannich reaction, catalyzed by phosphotungstic acid (H₃PW₁₂O₄₀), a heteropoly acid in IL 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF₄) offered the best results in terms of yield of the products (50). Brønsted acidic IL containing nucleophile 1-methylimidazole and triphenylphosphine with 1,4-butane sultone and inorganic anions *p*-toluene-sulfonic acid (PTSA) and trifluoroacetic acid (TFA) catalyzed Mannich reaction smoothly to afford β -amino carbonyl compounds in excellent yield and in shorter reaction time.

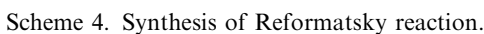
Here, IL is used as a catalyst as well as a solvent which was recycled seven times (51). Li et al. condensed aromatic aldehydes, anilines, and acetophenone and these were efficiently catalyzed by a recyclable carboxyl-functionalized IL [cmmim][BF₄] and [bmim][BF₄] in aqueous under mild conditions (52). The Mannich-type reaction of silyl enolates with aldimines proceeded smoothly with [emim]OTf as a solvent and without the addition of an activator to afford β -amino carbonyl compounds in excellent yields (53). IL media chosen by Liu and co-workers were 1-butyl-3-methylimidazolium tetrafluoroborate (BMImBF₄)/1-butyl-3-methylimidazolium dihydrogen phosphate (BMImH₂PO₄) and 1-ethylimidazolium trifluoroacetic acid (HEImTA) (54). 1,1,3,3-tetramethylguanidinium trifluoroacetate IL prepared by neutralization of 1,1,3,3-tetramethylguanidine with different acids under ambient condition and used by Gao co-workers in the synthesis of this reaction (55). In a similar way, acidic ILs as catalysts and solvents [Hmim]Tfa₂ were used by the Zhao group and they obtained Mannich adducts in excellent yields (56). A mixture of aldehyde/imine, 3-buten-2-ol and RuCl₂(PPh₃)₃ (0.005 mmol) in [bmim]PF₆ (0.3 mL) was stirred at 90 °C (57) affords the desired products in very high yields. Another group reported the use of ILs in benzene employing aniline, benzaldehyde, and acetophenone trimethylsilylenolates in solution of Yb(OTf)₃ in [bmim][PF₆]/benzene at 20 °C and stirred for 15 minutes to obtain products in excellent yields (58).

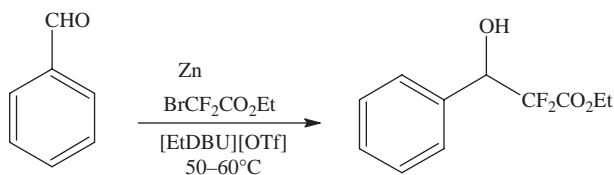
Scheme 2. IL: [DDPA][HSO₄] catalyzed Mannich-type reaction.



Asymmetric version of this reaction is reported by Liu and co-workers who used amide ILs (AILs)/L-proline in synergy catalyzed Mannich reaction and reactants isovaleraldehyde, methyl ketones, aromatic amines, and products are obtained in moderate to high yields (up to 96%) with high stereo selectivities (>99% e.e.). The authors claim the process to be fairly general, and the catalyst system was recyclable at least thrice without significant loss of efficiency (59). Same asymmetric synthesis was carried out by the Liu group under mild conditions using amide-task-specific ILs (AILs)/L-proline to obtain products in high yields and good enantioselectivities (72–96%, 28–99% ee) (60). Barbas et al. observed that Mannich reactions, in the presence of 5 mol% of L-proline, were 4–50 times faster in [bmim]BF₄ than in organic solvents. It is of interest to note that both the diastereoselectivities and the enantioselectivities of the reactions were excellent (*dr* 19:1, 99% ee; Scheme 3). The catalyst in IL was used over four consecutive reaction cycles with only a slight decrease in yields and constant enantioselectivity was observed. The authors also noted a poor performance of hydroxyacetone in Mannich reactions in ILs (61). A catalytic amount of RuCl₂(PPh₃)₃, a cross-coupling of 3-buten-2-ol with aldehydes and imines was developed via a tandem olefin migration aldol Mannich reaction in bmim[PF₆] proposed by Yang. With In(OAc)₃ as a co-catalyst, α-vinylbenzyl alcohol and aldehydes underwent similar coupling reactions. Compared with aqueous and other organic solvents, complementary diastereoselectivity was observed with IL as the solvent. The IL/catalyst system could be reused at least five times without any significant loss of activity (62). The Chen group developed another highly asymmetric Mannich-type reaction catalyzed by InCl₃ or In(OTf)₃ using [bmim][BF₄[−]] ILs; the reactions proceeded smoothly at room temperature and gave high diastereoselectivities and

Historically, alpha amino nitriles is the oldest multicomponent reaction reported by Strecker, which employs aldehydes, amines, and sodium cyanide/potassium cyanide to afford α -amino nitriles (72).





Scheme 5. [EtDBu][OTf] catalyzed Reformatsky reaction.

This involves addition of cyanide to C=N bond, a common strategy to obtain α -amino nitriles, which serve as important synthons in organic chemistry for preparation of a variety of heterocycles. These nitriles can be conveniently converted into a variety of amino acids (73) and several nitrogen heterocycles like thiadiazoles, (74) imidazoles, (75) and other biologically significant compounds such as saframycin A (76).

Invariably on mixing aldehyde and amine, Schiff's bases are produced which are used *in situ* and TMSCN addition occurs. Evidently this process requires polarization of C=N bond to facilitate nucleophilic attack of cyanide from TMSCN and is achieved by using suitable Lewis acid and other additives; see Scheme 7 (77–81). The present authors also tried to replace the catalysts used with greener ones, i.e. milder ones in this reaction (82, 83). Certainly, the authors were successful in using non-waste producing additives.

Mojtahedi et al. demonstrated the first efficient and environmentally friendly use of 1-butyl-3-methyl-1H-imidazolium perchlorate [bmim][ClO₄] IL as the catalytic recyclable media for three-component conversion of aldehydes, amines, and TMSCN to α -aminonitriles at room temperature in excellent yields in one-pot procedure with short reaction times, and IL used was reusable several times (84). Another IL 1-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF₄ is reported for this process (85).

Barbier reaction

This reaction was discovered by P. Barbier in 1899 (86). Classically, it is a reaction between an alkyl halide and a carbonyl group in the presence of suitably activated metal zinc; later on several organic halides and metals were shown to participate in this

reaction, such as aluminum, zinc, indium, tin, etc. Usually, this reaction is restricted to allyl halides and *in situ* allylic metal systems are formed which add on to carbonyl group to afford secondary or tertiary alcohols (see Scheme 8).

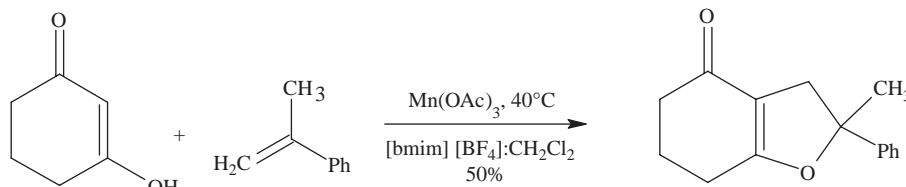
From time to time, improvements have been made to make this reaction also environmentally benign and here also the present authors have made some contributions using metals like bismuth, cadmium and tantalum (87, 88). The introduction of ILs in organic synthesis also prompted researchers to use these in this reaction as well. So, Zhao et al. reported Barbier allylation in one-pot manner using (un)substituted benzaldehydes, allylbromide, and phenols in IL (BuPyCl/SnCl₂·2H₂O) to directly synthesize 4-(2-hydroxyphenyl)-4-[(un)substituted phenyl]but-1-ene which finally led to the synthesis of 4-(substituted phenyl)-chromans *via* intramolecular cyclization reactions. This IL was recycled more than four times and it does not affect the yields of products (89). Same group also synthesized 4-arylchromans *via* Barbier allylation through intramolecular hydroalkoxylation of aromatic aldehydes, allylbromides, and phenols in an IL (BPyX-SnCl₂·2H₂O). They represent intramolecular hydroalkoxylation of 4-aryl-4-(2-hydroxyphenyl)-but-1-enes can be promoted using the Lewis acid ZnCl₂ in an IL (90).

Pechmann reaction

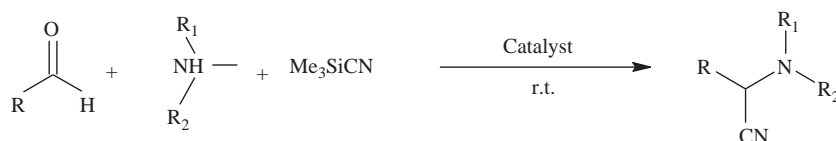
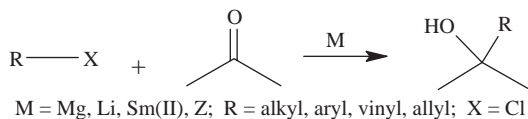
Classically, the Pechmann reaction (91) refers to the condensation of β -ketoesters with phenols in the presence of excess of acid catalysts to produce 4-substituted heterocyclic compounds i.e. coumarins, involving tandem hydroxyalkylation, transesterification, and dehydration. Esterification/transesterification followed by attacking the activated carbonyl ortho to the oxygen to generate the new ring *via* dehydration, as in the case of aldol condensation (92, 93). A plausible mechanism is also shown here (Scheme 9 and Scheme 10).

Mechanism of Pechmann reaction

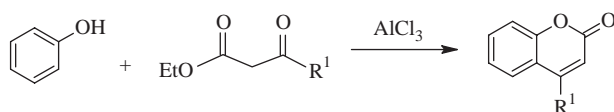
Evidently, the Lewis acids used here are very strong and several others of the same type are used. So, for



Scheme 6. Manganese acetate catalyzed Reformatsky reaction.

Scheme 7. Synthesis of α -amino nitriles *via* Strecker reaction.

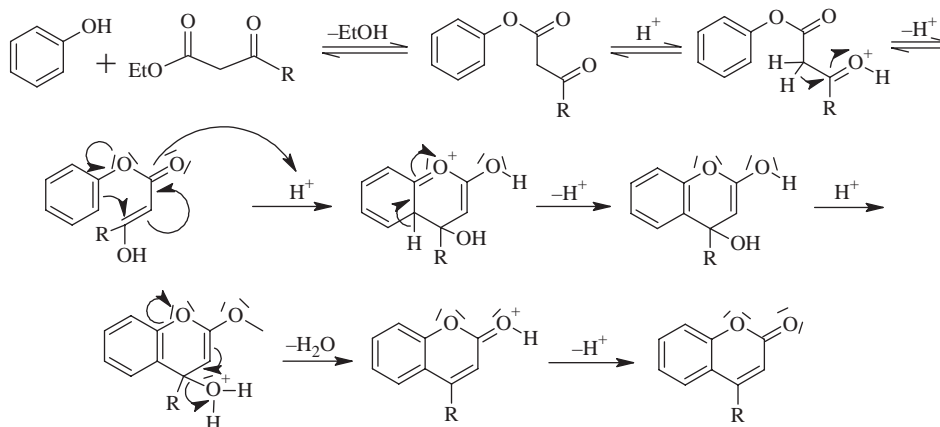
Scheme 8. Classical synthesis of Barbier reaction.

Scheme 9. AlCl_3 catalyzed synthesis of coumarins.

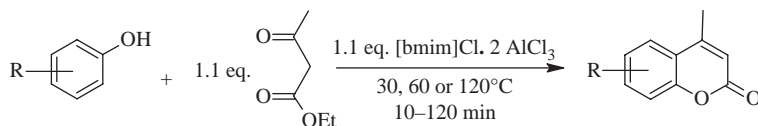
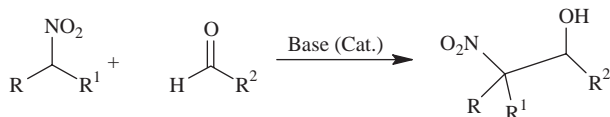
greener process several mild procedures are reported including our own (94). As usual ILs here also had prominent place and were used in this reaction (see Scheme 11).

1-Butyl-3-methylimidazolium chloroaluminate, [bmim] $\text{Cl} \cdot 2\text{AlCl}_3$ IL was the first IL (Scheme 11) which was used as an alternative to conventional acid catalysts in the Pechmann condensation of phenols with ethyl acetoacetate leading to the formation of coumarin derivatives by Potdar (95). Similar chloroaluminate IL was used by Khandekar and Khadilkar for the synthesis of substituted coumarins to obtain coumarins in good yields, and they employed 1-Butylpyridinium chloroaluminate IL as a solvent cum catalyst for this condensation (96). But these chloroaluminated ILs are very sensitive to hydrolysis; traces of water can change the composition of the melt and the concentration of protons. As a result, it

is difficult to accurately control the acidity of these ILs. Another disadvantage with these is that they cannot be stored for a long time and should be prepared freshly. So these problems enthruse chemists to search new green ILs solvents as well as catalysts. Some efforts are discussed in the following paragraphs. An efficient and easy method for preparation of (1-butyl-3-methyl-imidazolium hydrogen sulphate) IL using sodium bisulphate in place of concentrated sulphuric acid by microwave irradiation was developed by Singh, and this acidic room temperature IL has been exploited for the synthesis of coumarins under microwave irradiation and solvent-less conditions reducing time and increasing yields (97). Another four non-chloroaluminate acidic ILs have been used by Gu et al. as catalysts for this Pechmann condensations of phenols under solvent-free conditions. These were SO_3H -functionalized trifluoromethane sulfonate imidazolium IL and they proved to be the most effective catalyst (98). Other variation was carried out using 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim] PF_6) IL by Potdar and his group (99). Similarly, several ILs are reported, claiming one advantage or the other; these are 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim] BF_4) and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim] PF_6) (100), 1-butyl-3-methylimidazolium chloride with NbCl_5 (101), anhydrous FeCl_3 with ILs [MoeMim][Tf_2N] and [BMim][Tf_2N] (102), and N,N,N-trimethyl-N-propanesulfonic acid ammonium hydrogen sulfate [TMPSA][HSO_4] (103).



Scheme 10. Plausible mechanism for the Pechmann reaction.

Scheme 11. [bmim]Cl·2AlCl₃ catalyzed Pechmann reaction.

Scheme 12. Base catalyzed synthesis of Henry reaction.

Henry reaction

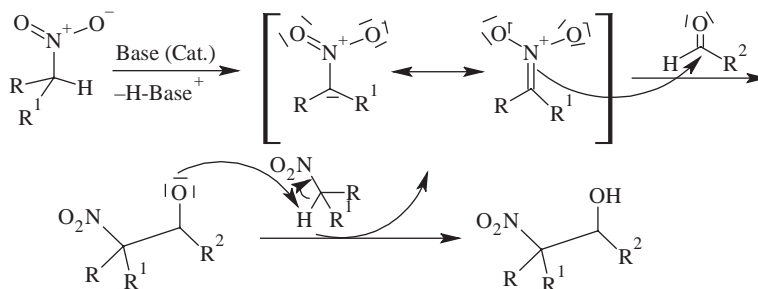
Henry reaction (104) is a base-catalyzed carbon–carbon bond-forming reaction (105–107) between nitroalkanes and aldehydes or ketones like aldol condensation and also referred to as the nitroaldol reaction (Scheme 12 and Scheme 13). If acidic protons are available (i.e. when R = H), the products tend to eliminate water to give nitroalkenes. Therefore, only small amounts of base should be used if the isolation of the β-hydroxy nitro-compounds is desired.

Base-catalyzed nitroaldol reaction is associated with various competitive reactions (108–112) such as aldol condensation, Cannizzaro reaction, Tishchenko reaction, and Nef-type reaction.

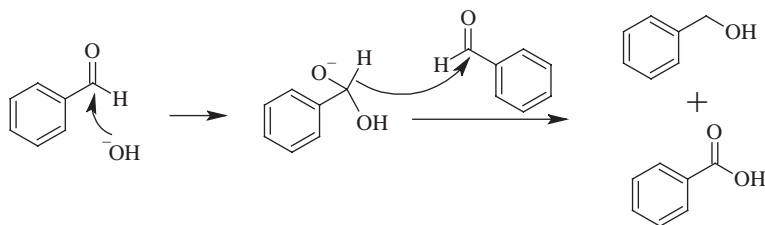
Mechanism of the Henry reaction

Researchers in pursuit of green processes and ILs being attractive used these in this well-known reaction also. Qian et al. (113) were the first to employ these in this reaction and they obtained β-Nitroalkanol in good yields, employing 1-ethyl-3-methylimidazolium tetrafluoroborate in this condensation at room temperature with DBU. Another report was published using 1,1,3,3-tetramethyl guanidine (TMG)-based IL by Jiang group. In this protocol, the catalyst could be recycled more than 15 times. This TMG-based IL is shown to be fairly general and is applicable to

aliphatic carbonyls (114). Another protocol was disclosed by Khan in this reaction at room temperature IL [bmim]BF₄ using Na₂CO₃ as base. The 2-nitroalcohols have been obtained in good yields, and the IL was reusable. However, the diastereoselectivity of the reaction is not very high. When benzaldehyde is used it gives a 35:65 mixture of *syn*:*anti* nitroalcohols and in case of nitrobenzaldehyde 44:56 of *syn*:*anti* nitroalcohols were obtained (115). Kumar and Pawar accelerated the Henry reactions in chloroaluminate room temperature ILs. The chloroaluminates with higher compositions of organic species of the chloroaluminates prove to be more efficient rate promoters than the ones with lower organic species in catalyzing Henry reactions, involving both aliphatic and aromatic carbonyl compounds. The ILs can be recycled five times to offer good yields. It should be pointed out that the IL used by Jiang et al. and others are better than this chloroaluminate IL with regard to its recyclability, as they noted a decrease in the yields after five cycles, while their IL was active up to 15 cycles (116). Chiral guanidinium chloride salts were synthesized by Wu et al. from 1,3-dimethyl-2-imidazolidinone and (S)-1-phenylethylamine; these ILs are likely to be better potential catalysts for asymmetric Henry reaction (117). Burguete and co-workers reported the preparation of new solid base catalysts with suitable mechanical stability for their application for continuous-flow processes. These catalytic systems are based on basic anions immobilized by metathesis onto supported IL-like phases (SILLPs) and have been applied for batch and continuous nitroaldol reaction. This approach synergically combines the advantages of supported ILs as a “supported liquid solvent”, those of an immobilized base as a “green” catalyst, and those of



Scheme 13. Plausible mechanism for the Henry reaction.



Scheme 14. Preparation of Cannizzaro product.

solvent-free reactions with the advantages of a continuous flow process, easy product separation, and catalyst reuse (118). Chinese chemists catalyzed Henry reaction using basic IL 1-methyl-3-butylimidazolium hydroxide ([bmIm]OH) with good yields in short time at room temperature. This strategy is general and works over a broad range of aldehydes. The recovered [bmIm]OH can be recycled with consistent activity (119). Yadav and Rai developed a convenient three-component coupling reaction of nitromethane, aromatic aldehydes, and trimethylsilyl cyanide (TMSCN) or ammonium thiocyanate for an expeditious synthesis of b-nitrocarbonitriles or b-nitrothiocyanates, respectively, *via* C–C and C–S bond-forming reactions. The synthetic protocol strategically involves a one-pot sequential Henry reaction and a Michael addition efficiently promoted by the same IL [bmim]OH. The main advantages of the present approach include use of inexpensive simple substrates and an IL as an efficient reaction promoter for the mild synthesis in a one-pot procedure (120). Blay et al. discussed enantioselective Henry (nitroaldol) reaction between nitromethane and an aromatic aldehyde, and this was successfully catalyzed by copper complexes of chiral iminopyridine, prepared from camphorsulfonic acid. High yield and good enantioselectivity were achieved (121). Henry reaction of benzaldehyde with nitromethane using methoxyl propylamine acetate IL as catalyst is investigated by Wang. Effects of experimental conditions on Henry reaction are studied. Main factors included molar ratio between benzaldehyde and nitromethane, amount of ILs, reaction time, and reaction temperature. Methoxyl propylamine acetate IL is an effective catalyst for Henry reactions under solvent-free conditions. The product separated easily with high yields. Catalyst recycled readily and reused to produce almost identical results (122).

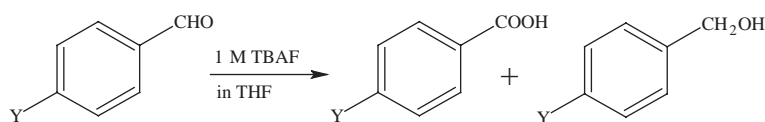
Cannizzaro reaction

This is also named after its discoverer S. Cannizzaro (123) in 1853. Classically, this reaction includes the use of caustic alkali, and one molecule of aldehyde is oxidized to acid and the other is reduced to corresponding alcohol (124–127) (Scheme 14). In this reaction normally employed bases were strong caustic alkalies like NaOH and KOH etc. In recent years, as in other reactions, development of green processes was attempted, and milder alkalis and solvent-free reactions were reported. In a typical case under solvent-free conditions, KOH pellets were grinded with benzaldehyde to obtain the expected acid and alcohol (128). Here, present authors used NaOH under solvent-free condition which effectively catalyzed the reaction in the cross version, i.e. cross-Cannizzaro reaction employing aromatic aldehydes with paraformaldehyde also this reaction could be conducted to obtain oxidized and reduced products in excellent yields when basic alumina is used in place of caustic alkalis (129).

In pursuit of further greener versions organo-catalyst has been used employing LiBr along with triethyl amine (130) Also, another exciting organo-catalyst based on guanidines is reported in recent years (131).

Regarding the utility of ILs in this reaction, there does not seem to be extensive literature available, rather it is scanty and indirectly ILs is used coupled with TBAF/[bmim][PF₆] as shown below (132) (Scheme 15).

To conclude this account it is worthwhile to state that the entire set of synthetic reactions of organic chemistry is attracting much attention from chemists for developing greener reactions; and in chase of this ILs are abundantly used as discussed and some of the ILs are used along with other additives and even in presence of water. It is certainly hoped that all these

Scheme 15. TBAF/[bmim][PF₆] catalyzed Cannizzaro reaction.

efforts of reducing waste, avoiding VOCs would certainly help in sustaining the environment. Authors have tried to bring in this article the recent developments in these discussed named reaction and if any important work of any author is left out, it is sincerely regretted.

Acknowledgements

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