DOI: 10.1002/cjoc.201280028

Preparation of Ionic Liquid-based Vilsmier Reagent from Novel Multi-purpose Dimethyl Formamide-like Ionic Liquid and Its Application

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In continuation of research to explore the applied potential of DMF-like ionic liquid, the ionic liquid version of *N*,*N*-dimethyliminiumchloride (Vilsmier reagent) has been synthesized from DMF-like ionic liquid and tested effectively for its capacity to achieve more useful organic transformations. The results show that DMF-like ionic liquid is world's first task specific ionic liquid which has catalyzed numerous diverse type of reaction and is multipurpose in its application. Thus a new term for this DMF-like ionic liquid has been coined that is DMF-like "multipurpose" ionic liquid.

Keywords novel concept, multipurpose DMF-like ionic liquid, ionic liquid-based vilsmier reagent, vilsmier reagent-catalysed reactions, TCT/DMF complex

Introduction

Task specific ionic liquid is the special class of ionic liquids in which a specific functional group is attached to imidazole ring through carbon chain of two to six carbon atoms. There are many organic molecules called organocatalysts which catalyze certain organic reactions. After the discovery of ionic liquids, some suitable functional groups were attached to ionic liquid moieties. The main object was to merge organocatalysis with ionic liquids to make organocatalysts more efficient and recyclable. Such ionic liquids infact catalyze a particular organic reaction and act as a type of organocatalyst. Task specific ionic liquids are designed and synthesized for performing a given reaction under ionic liquid conditions. A large amount of research work has been published on this topic and at this stage and thus this is no more a new concept. Many of the ordinary organocatalyzed reactions have been performed under ionic liquids conditions with extra advantages.[1] Such as Beckmann rearrangement,[2] Brönsted acidic reactions,[3] quinuclidine-catalyzed Morita-Baylis-Hillman reactions,[4] asymmetric Michael addition reactions,[5] Swern oxidation,[6] Claisen-Schmidt reaction,[7] Mannich reaction,[8] ionic liquid-supported NHPI complex.[9]

Dimethylformamide (DMF) is one of the key solvent used in organic reactions. However there are many reactions which particularly require and depend on DMF. As a solvent, it promotes the reactions involving charged intermediates or polar transition states by its aprotic polar nature. In addition to this, DMF has been used as an activator of some organic or organo-metallic reagents. Extensive literature survey reveals that there are certain reactions which produce different results when carried out without DMF,[10] such as conversion of alkyl halides into alcohols via DMF-catalyzed formyloxylation reaction with silver salt,[11] DMF-controlled chemoselective synthesis of pyrido[2,3-*d*]-pyrimidine derivatives,[12] DMF-catalyzed transformation of 2-chloroethyl amides into 2-substituted-2-oxazolines,[13] synthesis of 1,2-disubstituted-3,4-dihydronaphthalenes by DMF catalyzed cycloaddition of vinylarenes with alkynes,[14] preparation of 1,1-dioxo-7-substituted cephems using acid chloride obtained from DMF-catalyzed reaction of correspon-ding acid with oxalyl chloride,[15] DMF-trial-kylamine catalyzed dialkylation of diethyl 3,4-dihydroxy-2,5-thiophene dicarboxylate with alkyl-dibromides,[16] and DMF-facilitated *O*-alkylation of ethylene glycols and carboxylic acid to give diethers and esters respectively.[17] Apart from promoting some reactions, DMF also activates certain organic reagents and such reagents are used as coupled with DMF. For example Sasmita *et al*.[18] reported $NaIO_4$-DMF as a novel reagent for direct oxidation of variety of organic halides into corresponding carbonyl compounds. Abhishek *et al*[19] reported an efficient procedure for conversion of a variety of alcohols into the corresponding chlorides using pivaloyl chloride/DMF complex. Savita *et al*.[20] reported a direct and efficient one-pot procedure for the preparation of esters from fatty acids and hindered alcohols using $SOCl_2$-DMF as dehydrating agent. 2,4,6-Trichloro-1,3,5-triazine (cyanuric chloride,

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Received April 25, 2011; accepted September 26, 2011.

TCT) is also an organic reagent mostly used as TCT/DMF complex to accomplish large number of organic transformations.[21] DMF infact activates the TCT enabling it to give more efficient results. For instance, it has been shown that TCT can promote efficiently the carboxylic acid activation,[22] Swern oxidation,[23] Friedel-Crafts acylation,[24] Beckman rearrangement,[25] and glycosyl chlorination.[26] Giacomelli has used complex TCT/DMF to achieve a number of chemical transformations like direct conversion alcohol into corresponding alkyl chlorides,[27] Beckmann rearrangement of different oximes,[28] and selective protection of primary alcohols by a formyl residue.[29] These citations prove that TCT/DMF complex is a very powerful organic reagent.

Keeping in view the synthetic potential of the *N*,*N*-dimethylchloromethyleneiminium chloride (Vilsmier reagent), we decided to develop the ionic liquid version of Vilsmier reagent and checked few Vilsmier reagent dependent reactions. The idea consists of replacing the ordinary DMF with multipurpose DMF-like ionic liquid and treating it with TCT for converting it into ionic liquid-based Vilsmier reagent. A Vilmier reagent is highly reactive and moist sensitive electrophilic specie and is prone to facile hydrolysis. Thus it is often prepared *in situ* and subsequently used under inert atmosphere. Therefore we conceived the idea of preparing the hydrophobic Vilsmier reagent from hydrophobic multipurpose DMF-like ionic liquid with triflimide anion. This success will lead to an easy and convenient preparation and handling of water sensitive Vilsmier reagent without need of cumbersome inert atmosphere. Both hydrophobic nature and extra stability of polar Vilsmier reagent under ionic liquid solvation effects will result in efficient performance of Vilsmier reagent forming quantitative amounts of products in lesser time. Therefore the idea of developing the ionic liquid version of TCT/DMF complex as TCT/DMF-like ionic liquid seems to be promising. After synthesizing the required DMF-like ionic liquid, we will test some of the Vilsmier reagent catalyzed reactions. Such reactions include direct one pot *N*-alkylations of phthalimide,[30] direct conversion of alcohols into corresponding alkyl chlorides and bromides,[31] Beckmann rearrangement of variety of ketoximes to the corresponding amides,[32] Lossen rearrangement of hydroxamic acids into the corresponding isocyanates.[33] These are synthetically powerful reactions and much research work has already been reported about them. However most important draw backs associated with these methodologies have been ignored so far *i.e.*, use of toxic chemicals, poor yields, prolonged reaction duration, tedious work up. In order to circumvent all these draw backs in one go, there is one option left which is to try them under ionic liquid conditions.

Hullio *et al*. gave the concept of designing synthesis and application of DMF-like task specific ionic liquid[34] and reported some of its applications in accomplishing some useful transformations.[35] In addition to those reported applications of DMF-like task specific ionic liquid to accomplish various organic transformations, some more quite diverse set of applications are being reported here. The wide scope of application of this DMF-like task specific ionic liquid is unprecedented for any task specific ionic liquids reported so far. Normally each task specific ionic liquid is reported with application of one specific reaction that is why such ionic liquids are task-specific and never beyond the reactions for which they are designed. However increasing number of applications of DMF-like ionic suggest that it is no more "task specific" rather it is "multipurpose" in its applications and numerous different tasks which it has accomplished. Thus we recommend the new term for this ionic liquid that is "multipurpose" DMF-like ionic liquid (MDIL) and it is world's first functional ionic liquid which is "multipurpose" in its applications. We reported the synthesis of DMF-like ionic liquid with structure containing *N*-methyl and *N*-formyl functionality as shown in Figure 1. It was a reasonable ionic liquid without any inherited drawbacks like viscosity.

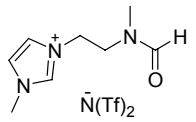

Figure 1 The conceived structure of proposed DMF-like task specific ionic liquid.

Since this ionic liquid is useful and appropriate for more than one reaction, we have coined a new term for this that is multipurpose functional ionic liquid (MPFIL).

Results and Discussions

Synthesis of DMF-like task specific ionic liquid

After the selection of structure for proposed MPFIL, a reterosynthesis was carried out to develop a facile synthetic scheme. As many synthetic routes could be foreseen, we achieved successful synthesis of required multipurpose functional ionic liquid by the strategy as shown in Scheme 1.

The synthesis started with *N*-methylation of aminoethanol (**1a**) achieved by reductive amination with paraformaldehyde to give *N*-methyl aminoethanol (**1b**) through protocol reported by Sukanta *et al*.[36] The *N*-methyl amino alcohol (**1b**) was converted to corresponding chloro derivative (**1c**) by triphenyl phosphine and tricholoroisocynuric acid.[37] At this stage *N*-formaylation was prefered over conversion of chloride (**1c**) into iodide because in that stage formamide would also facilitate the halide substitution. The *N*-formylation was achived by heating the secondry amine (**1c**) with ammonium formate to get the qauantitative yields of *N*-choloroethyl-*N*-methyl formamide (**1d**) as reported

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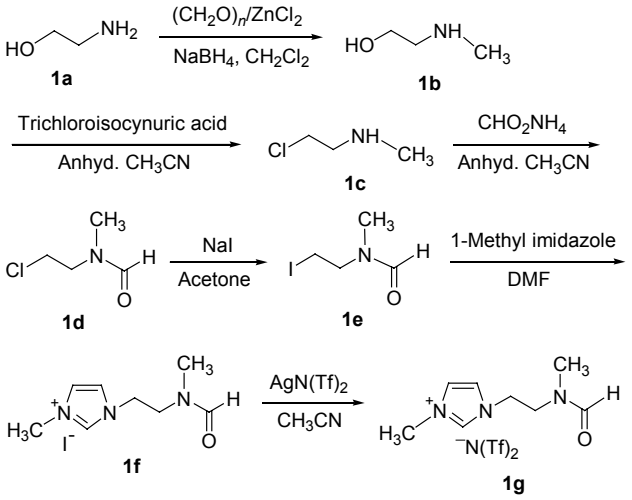
Scheme 1 Synthetic scheme of the proposed DMF-like task specific ionic liquid



by Reddy *et al*.[38] The substitution of chloro group was achieved through ordinary method of heating the **1d** with sodium iodide in dry acetone to get iodo derivative (**1e**). The *N*-alkylation of imidazole was achieved by using the methodology developed by Dupont *et al*.[39] Finally the anionic metathesis of iodide salt (**1f**) with triflimide was better achieved through the procedure used by Xun.[40] Thus the successful synthesis of desired multipurpose DMF-like ionic liquid (**1g**) was achieved.

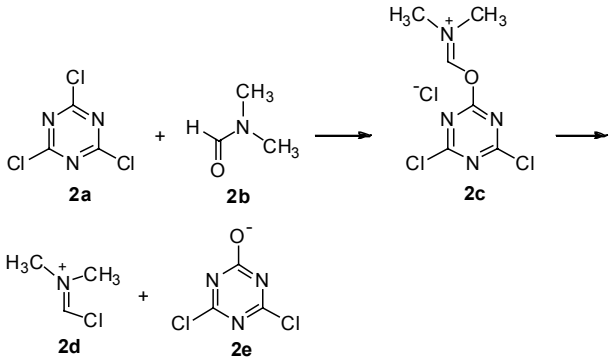
The reactions testified

Since Vilsmier reagent can be synthesized from DMF with 2,4,6-trichloro-1,3,5-triazine (TCT, cyanuric chloride) thus it is obtained from TCT/DMF complex. Many reactions pertaining to both synthesis and functional group transformations have been achieved through TCT/DMF complex. We are reporting the results of some of such reactions checked in multipurpose DMF-like ionic liquid (MDIL). Before we start discussing the results obtained, let us see how TCT/DMF complex works. Infact dimethyl formamide (DMF) reacts with 2,4,6-trichloro-1,3,5-triazine (TCT) to produce *N*,*N*-dimethyl chloro methyleneiminium (**2d**) as a catalyst promoting all of these useful transformations (Scheme 2). It is Vilsmier-type electrophilic species that reacts with different nucleophilic centres of various molecules to cause required reactions.

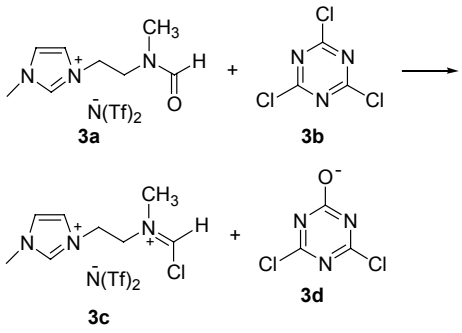
In correspondence with above observation, we propose the ionic liquid version of **2d** a dicationic highly polar intermediate acting in ionic liquid (**3c**) (Scheme 3). The TCT reacts with multipurpose DMF-like ionic liquid (MDIL) in exactly same way as with ordinary DMF to form a corresponding reactive intermediate (**3c**) and all reactions reported here proceed through this dicationic intermediate (**3c**).

Therefore the results obtained may be consistent with the mechanism depicted in Scheme 3. All four proposed chemical transformations achieved are summarized in Scheme 4.

Scheme 2 The mechanism illustrating the activation of the TCT by DMF



Scheme 3 The mechanism showing the activation of the TCT by DMF-like ionic liquid

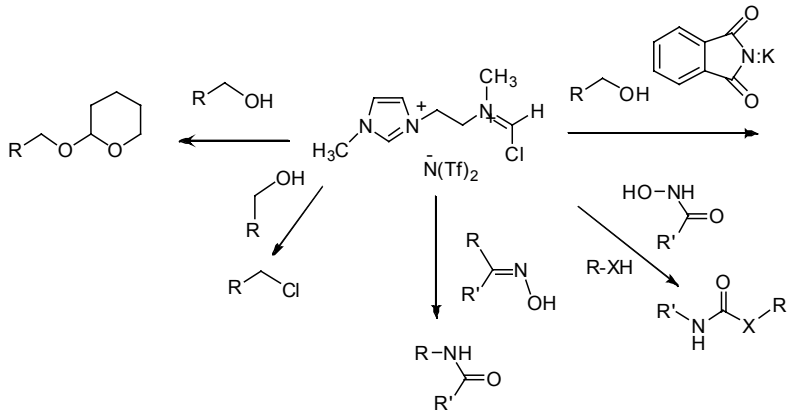


According to the reported procedures of all of these four reactions, every scheme adopted the same methodology *i.e*., initially the one equivalent mole of TCT was treated with 2.5 mol equivalents of the DMF to form the reactive complex (**2d**) (Scheme 2). Remaining desired compounds were added in required sequence. All these reactions were conducted almost under identical experimental conditions mostly including stirring at room temperature other at higher temperature under inert atmosphere. After the completion of the reactions as shown by TLC, the reactions were quenched with water followed by routine workup, specially the triazine by-products were removed by aqueous workup.

Partial tabular data reproduced here show that the products were obtained in quantitative yields. However some of the common drawbacks associated with these procedures were the prolonged reaction durations, formation of side products and tedious and laborious workup that followed. Use of large number of additional chemicals like solvents during workup rendered the procedures costly, accompanied with the generation of toxic waste which often posed environmental issues.

The use of ionic liquid version of DMF has helped circumvent a number of such drawbacks associated with normal procedures and this multipurpose DMF-like ionic liquid is proved to be instrumental in further improvement of the performance and efficiency of the TCT. The number of additional advantages discovered

Scheme 4 Summary of test reactions performed through DMF-like ionic liquid

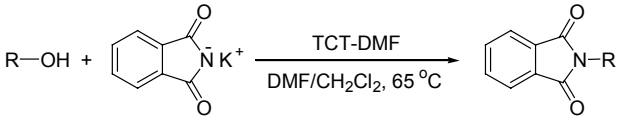


accompanying the use of DMF-like multipurpose ionic liquid include clean synthesis by minimizing the use of chemicals, rapid and quick formation of the products thus reduced reaction times and saving both the time and energy, and easy recovery of the products in each case enabling to save the labor. This observation can be rationalized with the fact that all the reactions involved polar transition states and charged reactive intermediates and the ionic liquid being highly polar in nature was able to stabilize them. The DMF-like ionic liquid has been recycled and reused with TCT without any significant loss of the efficiency. This novel methodology enjoys all green chemistry aspects as additional advantages, like other similar cases. Almost all of the reactions being tested here proceed via highly polar reactive intermediates which are stabilized by highly polar nature of the reaction conditions arising from the ionic nature of the ionic liquids used as catalyst as well assolvent. These factors overall lead to improved procedure and performance of the reactions conducted under ionic liquids conditions.

Direct *N*-alkylation of phthalimide with alcohols

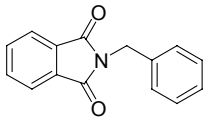
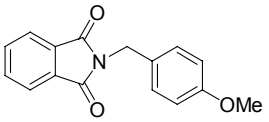
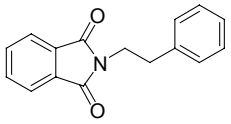
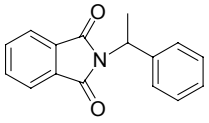
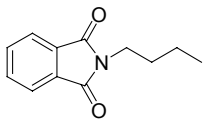
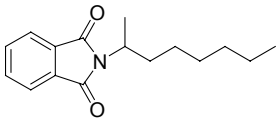
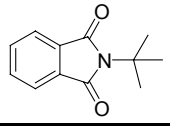
Mokhtari *et al*.[30] reported the successful use of TCT/DMF mixed reagent for one-pot direct *N*-alkylation of phthalimide by alcohols as alkylating agents (Scheme 5). According to the author the reaction proceeded via (alcoxymethylene)dimethyl ammonium chloride intermediate formed by reaction of 2,4,6-trichloro-1,3,5-triazine and dimethyl formamide. The different kinds of *N*-alkyl phthalimides obtained were reported in good-to-excellent yields (Table 1).

Scheme 5 TCT/DMF complex promoted direct *N*-alkylation of phthalimide with alcohols



The one mole equivalent of benzyl alcohol with large excess of potassium phthalimide in the presence of TCT/DMF complex produced *N*-benzylphthalimide at 65 ℃. Under similar conditions, potassium phthalimide was alkylated with a wide variety of primary and secondary alcohols. The results obtained are reproduced in Table 1. When similar reactions with same mole ratio were performed in TCT/MPFIL complex in DMF-like ionic liquid with acetonitrile co-solvent, some new notable findings were seen. Same yields of the product

Table 1 Comparison of *N*-alkylations of potassium phthalimides in both reported and new methodology

Entry	Product	Time[a]/ h	Yield[a]/ %	Time[b]/ h	Yield[b]/ %
1		3.0	93	2.0	95
2		2.5	96	1.35	96
3		3.5	83	2.5	88
4		5.0	69	4.25	75
5		5.0	76	4.0	82
6		5.5	61	4.30	73
7		Nil	Nil	3.40	78

[a] Time and yield (GC analysis) under reported conditions; [b] time and yield (GC analysis) under ionic liquid conditions.

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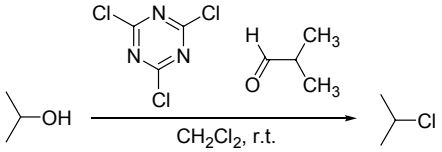
were obtained, time duration reduced to almost one half of the reported time under normal conditions. The reactivity pattern was found to be similar *i.e*., aromatic ring with electron donating groups furnished better yields. However the time duration of the reaction was found to be reduced. The interesting hydrophobic and lipophobic nature of our ionic liquid made the workup quite simplified *i.e*., the used triazine byproduct was simply extracted with water and required organic product was formed as separate layer. The data is compared in Table 1. As in case of reported normal conditions, the DMF-like ionic liquid exhibited the same trend of reactivity *i.e*., the primary benzylic alcohols were effectively converted into corresponding alkylphthalimides in excellent yields. On the other hand, the yields of the *N*-alkylphthalimides from the secondary alcohols were lower than primary ones. However, contrary to the reported procedure the tertiary alcohols gave successful alkylation of phthalimide along with some chloroalkyl byproducts. Reason for this observation can be attributed to the highly polar nature of the reaction media where life of tertiary carbocation is increased sufficiently to allow the phthalimide to attack.

An efficient route to alkyl chlorides from alcohols

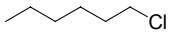
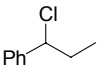
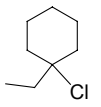
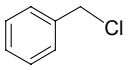
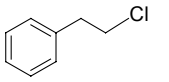
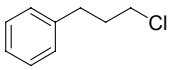
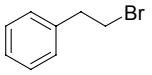
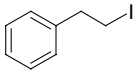
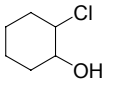
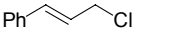
Giacomelli *et al*.[31] used TCT/DMF complex for efficient conversion of different alcohols and *β*-amino alcohols to the corresponding alkylchlorides. The procedure involved preparation of TCT/DMF complex and then treating it with 1 mole equivalent of alcohol in dichloromethane at 25 ℃ (Scheme 6).

Scheme 6 TCT/DMF complex promoted direct conversion of alcohol into alkyl chloride



Under this methodology a variety of alcohols with structural diversity were converted to the corresponding alkylchlorides requiring the reaction time from 10—15 min to 4 h. The procedure was also found efficacious for special cases of sterically hindered alcohols and diols. The sterically bulkier alcohols, such as borneol and neopentyl alcohol took longer time. The diols gave monochloro product using 1 mole equivalent of the diol, and the conversion to dichloride was complete only using its 0.5 mol equivalent. The results obtained in case of TCT/MPFIL in DMF-like ionic liquid with acetonitrile co-solvent furnished comparable yields (Table 2). Although variation in yields obtained in both conditions was not much significant except in few cases, nevertheless few procedural advantages of new method made it superior to the reported one. These include rapid completion of the reaction, the easy recovery of product and minimal use of organic solvents and recycling of ionic liquid. Apart from achieving the alkyl bromides from alcohol by adding sodium bromide, as in case of reported method, we obtained significant amount of alkyl iodides under the new protocol by using sodium iodide in large excess unlike reported procedure.

Table 2 Comparison of aliphatic alcohols into the corresponding alkyl halides in both reported and new methodology

Entry	Product	Time[a]/min	Yield[a]/%	Time[b]/min	Yield[b]/%
		15	96	15	96
2		60	98	45	98
3		240	98	150	98
4		15	98	15	98
5		15	97	15	97
6		15	99	15	99
7		15	97	15	88
8		15	97	15	81
9		15	98	15	98
10		15	92	15	93

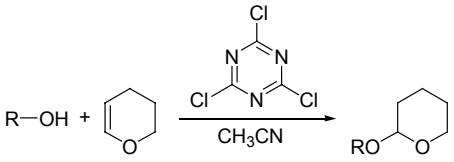
[a] Time and yield (GC analysis) under reported conditions; [b] time and yield (GC analysis) under ionic liquid conditions.

Tetrahydropyranylation of phenols and alcohols

Akhlaghinia[32] tested the ability of 2,4,6-trichloro-[1,3,5]triazine without DMF for the protection of hydroxyl groups with 3,4-dihydro-2*H*-pyran and reported the successful tetrahydropyranylation of primary, secondary and tertiary alcohols and phenols (Scheme 7).

The benzyl alcohol was converted into benzyl tetrahydropyranyl ether after 20 min in quantitative yield using 1∶1∶1 mole ratio of alcohol, pyrane, and

Scheme 7 TCT promoted direct conversion pyranylations of alcohol and phenols



R: primary, secondary, tertary, alkyl, phenyl

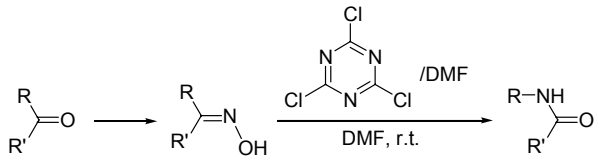
triazine. As shown in Table 3, this method is very suitable for the protection of various types of alcohols and phenols. This method exhibited the selectivity for primary alcohols in presence of secondary and tertiary alcohols. On performing the same reactions with similar mole ratios in our novel multipurpose functional ionic liquid (MFIL), some of the superior procedural advantages were found. Almost same level of yields were achieved with reduced reaction time. All types of aliphatic alcohols and aromatic alcohols underwent successful pyranylations. As in case of other reactions tested under this methodology, easy recovery of product and clean synthesis were achieved. In all schemes only selected compounds were tested depending upon the requirement for illustrating the effectiveness of the proposed methodology. The comparison of tabular data suggests that the new method is proved to be much more efficient than the one reported.

Beckmann rearrangement of different oximes to amides and nitriles

Giacomelli *et al*.[27] used TCT/DMF complex to achieve quantitative conversion of ketoximes into the corresponding amides and aldoximes to nitriles (Scheme 8).

This reaction was also selected for its scope in new multipurpose functional ionic liquid and it was found to be superior to the reported one from many aspects. The reaction duration was narrowed, no side products

Scheme 8 TCT/DMF complex promoted conversion of ketoximes into corresponding amides

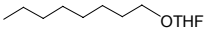
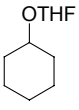
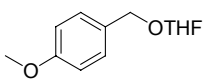
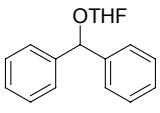
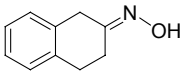


what-soever were formed, and only one of the two possible amides was isolated (Table 4). The trend in tabular data shows that electron-donating groups especially at *ortho-para* positions on the aromatic ring seem to reduce the reaction rate. Usually, an aryl group has greater migratory aptitude as compared to that of an alkyl group. However, in the case of both *tert*-butyl phenyl ketone oxime and the oxime of 3,3-dimethylbutan-2-one the rearrangement gives rise to migration of the *tert*-butyl group. Under new protocol, the results obtained with the oximes of cyclic ketones proved to be much more efficient, convenient and simple to obtain the commercially useful lactams. Especially the conversion of the cyclohexanone oxime is rapid under the conditions reported and pure ε-caprolactam is recovered in a quantitative yield.

Aldoximes apparently show different reaction trend, forming corresponding nitriles rapidly and quantitatively under the same conditions (Scheme 9).

We performed Beckmann rearrangement according to both the reported procedure as well as new methodology and results are shown in Table 5. The differences in outcomes of both methodologies are self explanatory. Under the new protocol 1 mole equivalent of different oximes were added to TCT/MFIL. The reaction was stirred at room temperature until all reactants were found to have been consumed as indicated by TLC. Theevaluation and comparison of the data in Table 5, reveals the superiority of the new methodology over the one with which it is being compared. For every entry,

Table 3 Comparison of preparation of THP ethers in both reported and new methodology

Entry	Product	Time[a]	Yield/%[a]	Time[b]	Yield/%[b]
1		8 h	90	5 h	93
2		44 h	97	32 h	95
3		35 min	96	30 min	95
4		28 h	90	16 h	90
5		34 h	68	26 h	73

[a] Time and yield (GC analysis) under reported condition; [b] time and yield (GC analysis) under ionic liquid conditions.

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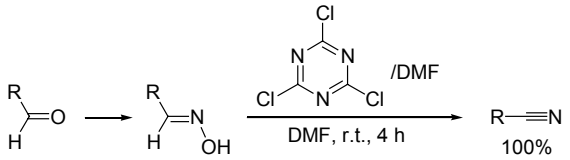
Scheme 9 TCT/DMF complex promoted conversion of aldoximes into corresponding nitriles



enhanced yields in lesser time duration is quite vivid. The compatibility of new methodology with structural diversity is amply evident from the starting substances. The essential reason for the better yields and lesser time duration lies in highly polar nature of the reactions conditions arising from the ionic nature of the ionic liquids used as catalyst as well as solvent. All of these reactions involve polar intermediates and charged species formed in almost every cases reported here, which are highly stabilized by powerful polar solvation by the ionic liquids. This stability results in higher yields coupled with lower reaction time.

The Lossen rearrangement

Hamona *et al*.[34] reported a TCT-promoted Lossen rearrangement of hydroxamic acids to form isocyanates which were subsequently *in situ* trapped with different nucleophiles (R^2XH) to form carbamates and thiocarbamates in a one-pot procedure (Scheme 10).

As a model reaction, the phenylcarbamic acid ethyl ester was prepared directly from benzohydroxamic acid. According to the reported procedure, the best results were obtained by using 0.4 equiv. of TCT in the presence of an excess of *N*-methylmorpholine (2 equiv.) in dichloroethane under stirring the mixture at 0 ℃ for 90 min. Two equivalents of EtOH were then added at 0 ℃ and the reaction mixture was refluxed overnight to afford carbamate in 87% yield. With other nucleophiles including alcohols, thiols, and amines the corresponding carbamates, thiocarbamate, and ureas, respectively, were obtained in good to excellent yields (73%—99%).

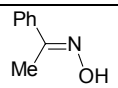
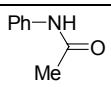
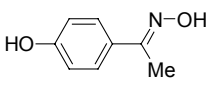
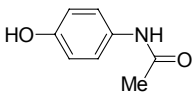
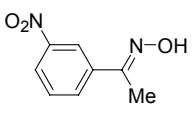
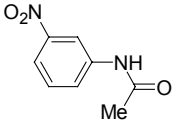
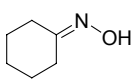
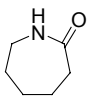
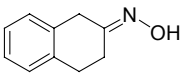
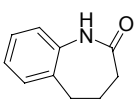
The execution of this last test reaction under our new procedure produced the same trend and observations as evident from the Table 6. The better performance of the novel strategy in this case verifies the multipurpose nature of the proposed ionic liquid. The every hydroxamic acid and *N*-methylmorpholine was treated with TCT/MFIL complex dissolved in acetonitrile in reported mole ratio and stirred at room temperature under nitrogen for required time. The reaction mixture was stirred at higher temperature after addition of suitable nucleophile like alcohol, amine or thiol. The results obtained were much better as shown in Table 6 due to the same reasons as described earlier.

Experimental Section

General

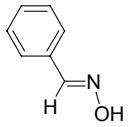
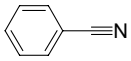
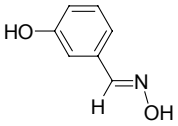
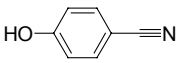
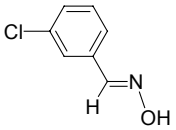
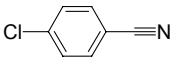
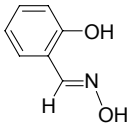
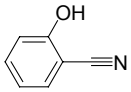
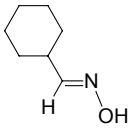
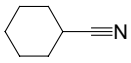
All the reagents and solvents were pure and of analytical grade chemicals purchased from Aldrich and were used without further purification. Melting/boiling points were determined with a Buchi 510 melting point apparatus (Flawi/SG, Switzerland) and are uncorrected. Electron impact (EIMS) mass spectra were determined with a Finniggan MAT-312 (Bremen, Germany), Vrain MAT-112 (Bremen, Germany) double focusing mass spectrometer connected to a PDP 11/34 (DEC) computer system. The ^{1}H NMR spectra were recorded in

Table 4 Comparison of conversion of ketoximes into amides in both reported and new methodology

Entry	Oxime	Amide	Time[a]/h	Yield[a]/%	Time[b]/h	Yield[b]/%
1			6	100	3	100
2			6	80	2.5	80
3			12	80	8	80
4			3	100	2	100
5			12	83	7.5	83

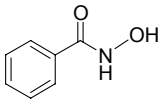
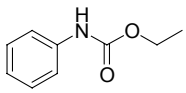
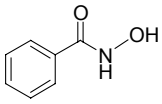
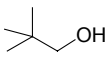
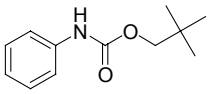
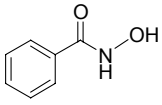
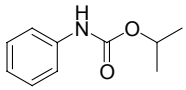
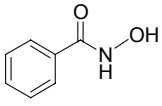
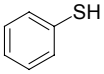
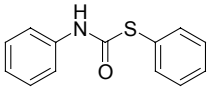
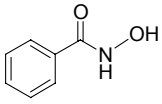
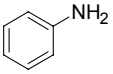
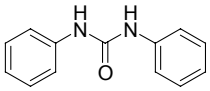
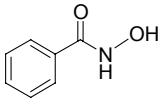
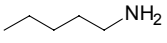
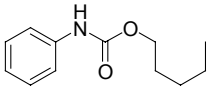
[a] Time and yield (GC analysis) under reported conditions; [b] time and yield (GC analysis) under ionic liquid conditions.

Table 5 Comparison of conversion of aldoximes to corresponding nitriles in both reported and new procedure

Entry	Oxime	Nitrile	Time[a]/h	Yield[a]/%	Time[b]/h	Yield[b]/%
1			4	85	2.0	88
2			6	89	2.5	94
3			5	92	2.5	92
4			5.5	94	2.5	94
5			6	96	3.0	96

[a] Time and yield (GC analysis) under reported conditions; [b] time and yield (GC analysis) under ionic liquid conditions.

Table 6 Comparison of hydroxamic acids rearrangement to isocyanates and its further reaction in both reported and new methodology

Entry	$R^1CONHOH$	R^2XH	$R^1NHCOXR^2$	Yield[a]/%	Yield[b]/%
1				87	94
2				84	92
3				81	88
4				73	85
5				99	99
6				88	94

[a] Yield (GC analysis) under reported conditions; [b] yield (GC analysis) under ionic liquid conditions.

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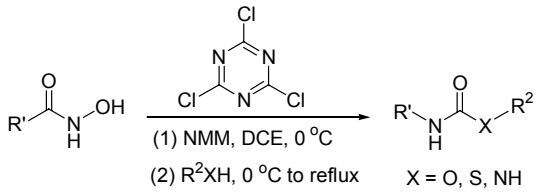
Scheme 10 TCT/DMF complex promoted Lossen rearrangement of hydroxamic acids and *in situ* capturing isocyanates with different nucleophiles



CD_3OD and $CDCl_3$ with Bruker AM 300 and 400 spectrometers (Rheinstetten-Forchheim, Germany) operating at 300 an 400 MHz, respectively. The purity of the products was checked on TLC plates (Merck, Darmstadt, Germany), coated with silica gel PF_{254} and the spots were characterized with UV light at 254 and 366 nm and by spraying with ninhydrin and iodine tank.

Synthesis scheme of DMF-like ionic liquid

***N*-Methyl 2-aminoethanol (1b)** In 200 mL round bottom flask, a mixture of amino ethanol (30 g, 0.491 mol), zinc chloride (133.85 g, 0.982 mol), paraformaldehyde (29.49 g, 0.982 mol), in dichloromethane (150 mL) was stirred at room temperature for 1 h under dry atmosphere. Sodium borohydride (37.14 g, 0.982 mol) was then added and resulting mixture was stirred for 18 h. The progress of the reaction was monitored by TLC using ninhydrin reagent. The reaction mixture was then quenched by addition of aqueous ammonia (200 mL, 2 mol•L^{-1}), stirred for 10 min and the organic layer was separated. The aqueous part was extracted with dichloromethane (25 mL×1), the combined organic extracts were concentrated *in vacuo* after drying over anhydrous Na_2CO_3. The crude product was purified by the flash chromatography over neutral alumina using hexane∶diethyl ether (3∶1) as the eluent to yield 51 g (72%) of pure *N*-methylaminoethanol as a colorless liquid product; b.p. 150—155 ℃.

Spectral data: ^{1}H NMR ($DCCl_3$, 400 MHz) δ: 2.35 (d, $^4J_{3,5}$=0.63 Hz, 3H, H-5), 2.60 (dd, 2H, $^3J_{2,3}$=5.5 Hz, $^4J_{3,5}$=0.63 Hz, H-3), 3.54 (t, $^3J_{2,3}$=5.5 Hz, 2H, H-2), 3.64 (s-broad, 1H, H-1); ^{13}C NMR (300 MHz, $CDCl_3$) δ: (36.05, CH_3), (54.30, CH_2), (60.30, CH_2); MSEI *m*/*z* (%): 75 (M^++40), 74 (49), 73 (10), 44 (100), 31 (15); HRMS (ESI) calcd for C_3H_9NO (M^+) 75.110, found 75.108.

***N*-(2-Chloroethyl)-*N*-methyl amine (1c)** Ph_3P (267.5 g, 1.02 mol) was disolved in 200 mL anhydrous acetonnitrile in a 300 mL round-bottom flask. Then 83.7 g (0.36 mol) of tricholoroisocynuric acid was added slowly over about 30 min. The reaction mixture was stirred and heated at 60 ℃. Then *N*-methylaminoethanol (51 g, 0.68 mol) was added to the mixture, and the reaction was stirred for 3 h. On completion of the reaction 10 mL water was added to quench the reaction. Most of the acetonitrile was removed by rotary evaporator and residue was extracted with 100 mL (25 mL×4) diethylether. The organic layers were combined, concentrated and dired over Na_2SO_4. The product was further purified with flash chromatography to give 44.51 g (70%) 2-chloro, *N*-methyl ethylamine as cololess liquid with b.p. 109—111 ℃.

Spectral data: ^{1}H NMR ($DCCl_3$, 400 MHz) δ: 2.54 (d, $^4J_{3,2}$=0.63 Hz, 3H, H-2), 2.72 (d, $^3J_{4,3}$=6 Hz, 2H, H-3), 2.96 (s-broad, 1H, H-1), 3.50 (t, $^3J_{4,3}$=6 Hz, 2H, H-4); ^{13}CNMR ($CDCl_3$, 300 MHz) δ: (34.93, CH_3) (42.34, CH_2) (57.55, CH_2); HRMS (ESI) calcd for C_3H_8ClN (M^+) 93.555, found 93.550.

***N*-(2-Chloroethyl)-*N*-methyl formamide (1d)** To a solution of *N*-methyl-2-chloroethyl amine (44.51 g, 0.48 mol) in dry acetonitrile (500 mL) was added anhydrous ammonium formate (45.36 g, 0.72 mol) and the resulting mixture was heated at 95 ℃ (bath temperature) for 15 h. Acetonitrile was removed under reduced pressure. The residue was diluted with ethyl acetate (200 mL) and washed with distilled water (50 mL×4). The organic layer was concentrated and dried over anhydrous Na_2SO_4 and then further purified by flash chromatography to yield (51.84 g, 90%) colorless liquid formamide.

Spectral data: ^{1}H NMR ($DCCl_3$, 400 MHz) δ: 3.22 (s, 3H), 3.58 (t, $^3J_{6,5}$=6.68 Hz, 2H, H-6), 3.92 (t, $^3J_{6,5}$=6.68 Hz, $^4J_{5,2a}$=0.63 Hz, $^4J_{5,4}$=0.63 Hz, 2H, H-5), 8.02 (s, 1H, H-2a); ^{13}C NMR ($CDCl_3$, 300 MHz) δ: 31.99 (CH_3), 44.62 (CH_2), 59.58 (CH_2), 165.06 (CHO). HRMS (ESI) calcd for C_4H_8ClNO (M^+) 121.565, found 121.568.

***N*-(2-Iodoethyl)-*N*-methyl formamide (2e)** A solution of *N*-(2-chloroethyl)-*N*-methyl formamide (**iii**) (51.84 g, 0.24 mol) in 25 mL of anhydrous acetone was added dropwise to a stirred solution of NaI (37.5 g, 0.25 mol) in 250 mL of anhydrous acetone over a period of 45 min at room temperature. The stirring was continued for 20 h. The precipitate formed was collected by filtration and washed with 100 mL of acetone. The combined filtrate was evaporated and residue was distilled to give colourless oil. And it was further purified by flash chromatography to give 66.34 g, 73% yield.

Spectral data: ^{1}H NMR ($DCCl_3$, 400 MHz) δ: 3.24 (s, 3H, H-4), 3.60 (t, $^3J_{6,5}$=7.77 Hz, 2H, H-6), 4.00 (t, $^3J_{6,5}$=7.77 Hz, $^4J_{5,4}$=0.63 Hz, $^4J_{5,2a}$=0.63 Hz, 2H, H-5), 7.79 (s, 1H, H-2a); ^{13}C NMR ($CDCl_3$, 300 MHz) δ: −0.60 (CH_2), 32.59 (CH_3), 56.10 (CH_2), 164.39 (CHO); HRMS (ESI) calcd for C_4H_8INO (M^+) 213.017, found 213.016.

1-[2-(Formylamino)ethyl]-3-methyl-1*H*-imidazol-3-ium iodide (2f) Freshly distilled *N*-methyl imidazole (19.7 g, 0.24 mol) and 66.34 g (0.31 mol) of *N*-(2-iodoethyl)-*N*-methyl formamide (**2e**), were added to 100 mL of acetonitrile (CH_3CN) and brought to reflux with stirring under nitrogen at 80 ℃ for 24 h. After completion of reaction as evident from TLC analysis the reaction mixture was cooled to room temperature. A solid compound was collected during cooling process. The acetonitrile was removed by rotary evaporator un-

der vacuo. The resulting white solid was washed with ethyl acetate, dried under reduced pressure at 30 ℃ for 6 h to afford imidazolium iodide (**2f**) (46.56 g, 89%).

Spectral data: ^{1}H NMR (CD_3OD, 400 MHz) δ: 3.16 (s, 3H, H-11), 3.92 (t, $^3J_{6,7}$=6.63 Hz, $^4J_{2,6}$=0.6 Hz, $^5J_{4,6}$=0.3 Hz, $^4J_{5,6}$=0.4 Hz, 2H, H-6), 4.19 (t, $^3J_{6,7}$=6.63 Hz, $^4J_{7,9a}$=0.63 Hz, $^4J_{7,11}$=0.63 Hz, 2H, H-7), 7.40 (s, 1H, H-5), 7.70 (s, 1H, H-4), 7.98 (s, 1H, H-2), 7.75 (s, 1H, H-9a); ^{13}CNMR ($CDCl_3$, 300 MHz) δ: 32.26 (CH_3), 37.20, 46.97 (CH_2), 51.27 (CH_2), 116.41 (CH), 123.30 (CH), 140.28 (CH), 161.49 (CHO); HRMS (ESI) calcd for $C_8H_{14}N_3O$ (M^+) 168.216, found 168.219.

1-[2-(Formylamino)ethyl]-3-methyl-1*H*-imidazol-3-ium triflimide (2g) To a solution of 1-[2-(formylamino)-ethyl]-3-methyl-1*H*-imidazol-3-ium iodide (46.56 g, 0.16 mol) in dry acetonitrile (20 mL) was added silver triflimide (62.08 g, 0.16 mol). The mixture was stirred for 2 h in the dark under nitrogen. The mixture was filtered to remove the light yellow salt and the filtrate was evaporated by rotary evaporation under vacuum and dried *in vacuo* to generate the product **2g** as a clear liquid with a very light brown color (67 g, 100% yield).

Spectral data: ^{1}H NMR (400 MHz, CD_3OD) δ: 3.16 (s, 3H, H-12), 3.75 (s, 3H, H-11), 3.82 (t, $^4J_{2,6}$=0.6 Hz, $^5J_{4,6}$=0.3 Hz, $^4J_{5,6}$=0.4 Hz, $^3J_{6,7}$=6.63 Hz, 2H, H-6), 4.08 (t, $^3J_{6,7}$=6.63 Hz, $^4J_{7,9a}$=0.63 Hz, $^4J_{7,12}$=0.63 Hz, 2H, H-7), 7.75 (s, 1H, H-9a), 8.40 (s, 1H, H-5), 8.65 (s, 1H, H-4), 8.47 (s, 1H, H-2); ^{13}CNMR ($CDCl_3$, 300 MHz) δ: (32.26, CH_3) (37.20, CH_3) (46.97, CH_2) (51.27, CH_2) (116.41, CH) (123.30, CH) (140.28, CH) (161.49, CHO), (108.84, 116.71, 124.59, 132.46, CF_3); HRMS (ESI) calcd for $C_8H_{14}N_3O$ (M^+) 168.216, found 168.218

General reported procedure for testing of reactions in multi-purpose functional ionic liquid (MPFIL)

For each run of test reactions, the activated complex of TCT-MDIL was prepared by mixing the Trichloro-1,3,5-triazine (0.183 g, 1.0 mmol) and ionic liquid (1.06 g, 2.5 mmol) by stirring both at 25 ℃ in 10 mL acetonitrile as co-solvent to reduce the viscosity. After preparation of Vilsmier reagent, each of reaction was tested by running the required number of test. For each test of a given type of reaction, required mole ratio of the reactants were introduced in the activated complex in acetonitrile. The resulting reaction mixture was stirred at required temperatures until the TLC showed the completion of reaction. After completion of reactions the consumed cyanuric chloride was extracted with water and product was extracted with diethyl ether, organic layer was concentrated and dried with Na_2SO_4. After evaporation of the solvent the product was further purified by flash column chromatography using ethyl acetate/*n*-hexane (1/10) as the eluent. The products were characterized by comparing their m.p., IR, ^{1}H NMR, ^{13}C NMR and elemental analysis with those reported for the authentic samples. Spectral data for some representative compounds are available.

Recycling efficiency

The proposed ionic liquid system was tested for its recycling potential with different type of reactions. Each cycle was tested with fresh DMF-like ionic liquid and recycling was found to be fairly consistent for four times. The results found are shown in (Table 7).

Table 7 Recycling efficiency of the DMF-like ionic liquid

No. of recycles	1	2	3	4
Product yield[a]/%	95	93	92	89
Product yield[b]/%	98	97	95	94
Product yield[c]/%	95	92	91	90
Product yield[d]/%	100	98	97	95

The recycling studies were performed with *N*-benzylation of phthalimide[a], benzyl alcohol to benzyl chloride[b], pyranation of 4-methoxy benzyl alcohol[c], acetophenone oxime to phenyl acetamide[d]. Yield[a-d] (GC analysis) of products.

Conclusions

A stable and hydrophobic ionic liquid based Vilsmier reagent has been prepared from multipurpose DMF-like ionic liquids. It has been shown to be more stable and efficient organocatalyst as compared to Vilsmier reagent prepared from ordinary DMF for some useful organic transformations. The successful execution of all these reaction proves that our DMF-like ionic liquid is a multipurpose ionic liquid.

Acknowledgment

The authors thankfully acknowledge the Higher Education Commission (HEC) of Pakistan for financial support and H.E.J International Centre for Chemical and Biological Research, Karachi for provision of spectroscopic facilities.

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