Iranian Journal of Catalysis 1(2), 2011, 79-86

IRANIAN JOURNAL OF CATALYSIS

Application of multipurpose dimethyl formamide-like task specific ionic liquid as a recyclable reagent for direct iodination of alcohols

Ahmed Ali Hullio*, G.M Mastoi

Dr. M.A Kazi Institute of Chemistry, University of Sindh Jamshoro-76080 Sindh, Pakistan

Received 1 Nov 2011; received in revised form 25 Nov 2011; accepted 30 Nov 2011

ABSTRACT

A direct and an efficient conversion of a wide range of primary, secondary even tertiary alcohols to the corresponding iodides have been achieved under ionic liquid conditions. The method involves preparation of ionic liquid-based iminium chloride intermediate from DMF-like ionic liquid then stirring it with alcohol in present of sodium iodide. The higher yields of alkyl iodides were obtained within minimum time with simplest operational procedure. The DMF-like ionic liquids could be recycled.

***Keywords**: DMF-like ionic liquid, Iminium chloride, Vilsmier reagent, Thioiminium salt, Alcohols and alkyl iodides.*

1. Introduction

Dimethyl formamide (DMF) is not uncommon compound in the world of chemistry in general and organic chemistry in particular. It is often used as polar aprotic solvent for reactions involving polar intermediates and transition states [1]. Apart from this Jacques Muzart has explained the use and application of DMF as a reagent [2]. More interestingly there are certain reagents either organic or inorganic in which DMF acts as co-reagent or activator. Such compounds are often used as organocatalysts to accomplish numerous organic transformations. For example sodium periodate is an inorganic reagent which has been used as a $NaIO_4$-DMF complex to achieve direct conversion of alkyl halides into corresponding carbonyl compounds [3]. In this system DMF activates periodate molecule to enhance the nucleophilicity of its negatively charged oxygen. As a result of this enhanced nucleophilicity periodate attacks the alkyl halides efficiently which results in the direct conversion of primary and secondary alkyl halides into corresponding aldehydes and ketones respectively. Another very valuable organoreagent is N,N-dimethyliminium chloride commonly known as Vilsmier reagent. It is a versatile and powerful organic reagent which has been employed to achieve some key steps in synthetic schemes [4]. It is prepared from DMF by treating it with phosphoryl chloride or oxalyl chloride. Similarly trichlorotriazine (TCT) also known as cyanuric acid is well known organocatalyst for its application in organic reactions [5a]. The noteworthy point about TCT is that it is often used as a TCT-DMF complex. The literature is replete with data illustrating the synthetic potential of the TCT when used as TCT-DMF complex.[5b] DMF in this complex activates TCT to catalyse its reactions efficiently. For instance, it has been shown that TCT can promote efficiently the carboxylic acid activation, [6] Swern oxidation, [7] Friedel–Crafts acylation, [8] Beckman rearrangement [9] and glycosyl chlorination [10]. Giacomelli has used complex TCT/DMF to achieved number of chemical transformations like direct conversion alcohol into corresponding alkyl chlorides [11]. Beckmann rearrangement of different oximes [12] and selective protection of primary alcohols by a formyl residue [13]. These citation prove that TCT/DMF complex is very powerful organic reagent.

Keeping in view the synthetic potential of the TCT/DMF complex, Hullio et al [14] developed the ionic liquid version of DMF for this system to make this complex even more efficient and easy to handle and operate. The novel TCT/DMF-like ionic liquid complex (Fig.1) was used for all TCT/DMF dependent reactions with encouraging results.

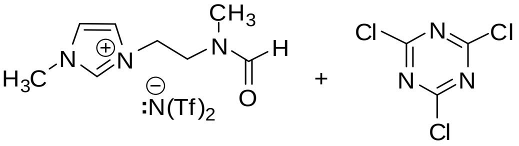
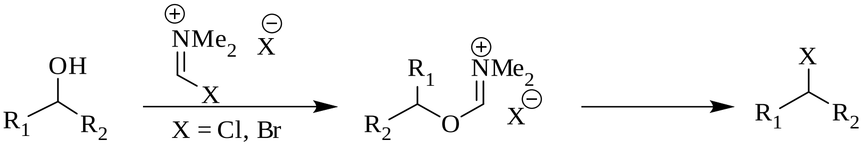


Fig.1. Novel TCT/DMF-like ionic liquid complex.

---

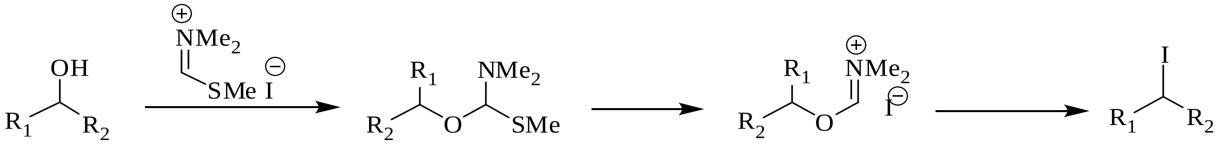
* Corresponding author: E-mail: ahmedalihullio @yahoo.com.
Te: +92-22-2771681-90-EXT: 2004.
Fax: +92-22-2771372.



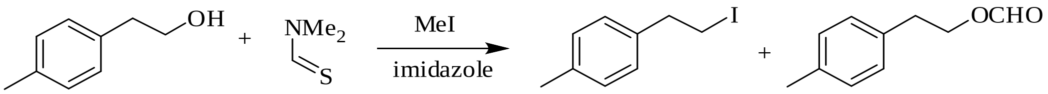
Scheme 1. Formation of haloalkanes with haloiminium salts.

The idea consisted of replacing the ordinary DMF with DMF-like ionic liquid as a co-reagent for TCT. Apart from these reagents, there are numerous reactions mentioned in literature which reveal that some reactions only can proceed if executed in presence of DMF as a solvent [15]. The DMF-like ionic liquid is imidazolium based in which N-methyl formamide functionality has been anchored on imidazolium cation. Since ionic liquids are often reported with better results over conventional procedure, therefore proposed DMF-like task specific ionic liquid was expected and shown to have better results. The DMF-like ionic liquid was reported as world's first multipurpose ionic liquids due to its numerous and diversified applications in synthetic chemistry. To further prove the multifunctional nature of our DMF-like task specific ionic liquid, we are reporting its new application that involves the direct conversion of alcohols to corresponding alkyl iodides. It is a transformation that is widely utilized in organic synthesis and there are a number of reagents which are used for this purpose. [16-29]. It is well established fact that alcohols on reaction with haloiminium halides (Vilsmeier reagents) to give alkyl halides (Scheme 1). [30]. This reagent is found to be useful for the preparation of alkyl chlorides and bromides and this reaction is not amenable to the preparation of alkyl iodides. Alkyl halides are often used to achieve both functional group transformation reactions and carbon-carbon bond forming reactions. However among the halides, iodides are the most reactive as these are responsive to both weaker and stronger nucleophiles. This is why alkyl iodides can be found in most of synthetic schemes. Since alcohols are easily available type of compounds, thus they can be favorable choice for source to achieve alkyl iodide. Therefore large variety of reaction protocols has been introduced in literature some of which involve metal catalysts and other organocatalysts. Since Vilsmier reagent only converts alcohols into corresponding alkyl chlorides and bromides and fails to give alkyl iodides. To fill this gap Ellwood et al [31]. reported the procedure for direct iodination of alcohols with slight modification. They used *N*,*N*-Dimethyl-*N*-(methylsulfanylmethylene) ammonium iodide ($MeSCH{=}NMe_2^+\ I^-$). This reagent is slightly different from Vilsmier reagent and is basically prepared from *N*,*N*-dimethylthioformamide and iodomethane. The reagent was used to achieve the conversion of primary and secondary alcohols to corresponding alkyl iodides (Scheme 2).

On iodination of 2-(4-methylphenyl)ethanol with *N*,*N*-dimethylthioformamide (2 equiv) and iodomethane (4 equiv) in presence of imidazole in THF gave the expected iodide, together with formate ester as a side product. (Scheme 3) The formation of formate as a byproduct was explained by assuming the hydrolysis of the alkoxy iminium ion intermediate by ubiquitous water. Thus various drying agents were added (molecular sieves, $MgSO_4$, MgO) ensure the dry conditions but none was effective to prevent the formation of formate. Other draw back associated with this method includes the excessive use and generation of toxic chemicals (MeSH, DMF, imidazole) and cumbersome reaction procedure consisting of high temperature, prolong reaction times, costly, laborious, tedious product purification and limited substrate scope. The moisture sensitivity is chronic draw back associated with Vilsmier reagent and other similar reagents possessing carbon-nitrogen double bond. In fact such reagents are denatured by undergoing rapid hydrolysis under even slightly moist condition to regenerate DMF and other parts. Various groups have adopted different strategies to ensure dry conditions which make the operation even more laborious, tedious and cumbersome. We used DMF-Like MTSIL as a substitute for an ordinary DMF to get necessary iminium chloride under water resistant ionic liquid conditions. Our group designed and used Multipurpose DMF-like task specific ionic liquid for all DMF dependent reactions. This ionic liquid is hydrophobic and may form stable iminium chloride which can catalys all relevant reactions efficiently under ionic liquids conditions. The current procedure provides highly polar and dry conditions for safe formation and existence of water sensitive and polar iminium chloride.



Scheme 2. Proposed conversion of alcohols to iodides.



Scheme 3. Iodination of 2-(4-methylphenyl)ethanol**.**

2. Experimental

2.1. 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 CD_3OD and $CDCl_3$with Bruker AM 300 and 400 spectrometers (Rheinstetten-Forchheim, Germany) operating at 300 an 400 MHz, respectively. ^{1}H-NMR chemical shifts are reported in δ (ppm) and coupling constants in Hz. 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.

2.2. Synthesis scheme of DMF-Like ionic liquid

N-(2-Hydroxyethyl)-N-methyl formamide (4b)

To a solution of *N*-methylaminoethanol (4a) (7.28 g, 0.097 mole) in dry acetonitrile (100 ml) was added anhydrous ammonium formate (5.23 g, 0.145 mol) and the resulting mixture was heated at 95°C (bath temperature) for 15 hrs. After cooling the reaction mixture, the acetonitrile was removed under reduced pressure. The residue was diluted with ethyl acetate (50 ml) and washed with distilled water (3×25 ml). The organic layer was concentrated and dried over anhydrous Na_2SO_4 and then further purified by flash chromatography to yield (8.7 g 87 %) colorless liquid formamide (4b).

Spectral data:

^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.63 (s,1H), 5.50 (broad, 1H), 3.69 (t, *J*= 6.85Hz, 2H), 3.51 (t, *J*=6.85Hz, 2H), 3.20 (s, 3H); MSEI m/z (%), 103 (12), 102 (46), 88 (45), 72 (100), 74 (55); HRMS (ESI): calcd for $C_4H_9NO_2$ (M^+), 103.120 found: 103.118.

N-(2-Iodoethyl)-N-methyl formamide (4c)

To a solution of compound (4b) (8.7 g, 0.084 mol) and NaI (18.89 g, 0.126 mol) in dry CH_3CN (150 ml) was added pure and clear $ZrCl_4$ (9.79 g, 0.042 mol) in several portions. The mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. After 40 min, the reaction mixture was cooled and diluted with ether (100 ml) and water (100 ml). The organic layer was separated and washed with an aqueous solution of NaS_2O_3 (10%, 100 ml), then H_2O (100 ml). The organic layer was separated, concentrated and dried over anhydrous Na_2 SO_4. Complete evaporation of the solvent under reduced pressure gave desired iodide (4c) (16.0 g, 89%) of a very high purity.

Spectral data:

^{1}H-NMR (300 MHz-$DCCl_3$, ppm) δ: 7.78 (s,1H), 4.00 (t, *J*=6.85Hz, 2H), 3.59 (t, *J*= 6.85Hz, 2H), 3.24 (s, 3H); MSEI m/z (%), 213 (15), 87 (100), 72 (88), 199 (13), 185 (10); HRMS (ESI): calcd. for $[C_4H_8INO]M+$ 213.017, found: 213.016

1-[2-(Formylamino)ethyl]-3-methyl-1H-imidazol-3-ium iodide (4d)

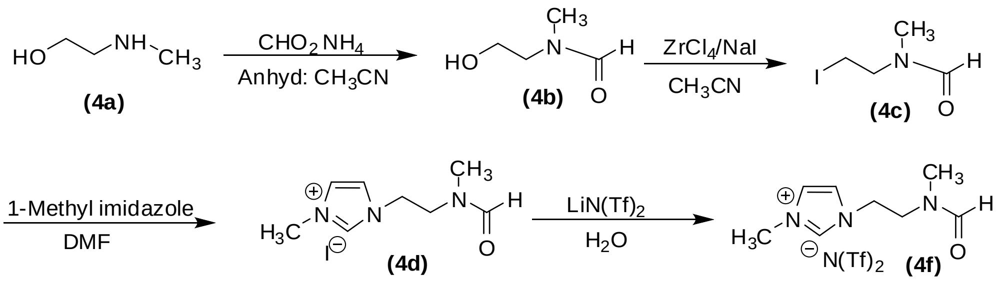
Freshly distilled N-methyl imidazole (6.40 g, 0.078 mol) and (16.0 g, 0.075 mol) of *N*-(2-iodoethyl)-*N*-methyl formamide (4c) were added to 100 ml of acetonitrile (CH_3CN) and brought to reflux with stirring under nitrogen at 80°C for 24 hr. After completion of reaction, as evident from TLC analysis, the reaction mixture was cooled to room temperature a solid compound is collected during cooling process. The acetonitrile was removed by rotary evaporator under vacuo. The resulting white solid is washed with ethyl acetate dried under reduced pressure at 30°C for 6 hr to afford imidazolium iodide (4d) yield 10.86 g, 86%.

Spectral data:

^{1}H NMR (300 MHz, CD_3OD, ppm) δ: 9.46 (s, 1H), 8.59 (s, 1H), 8.46 (s, 1H), 7.79 (s,1H), 4.62 (t, *J*= 6.85Hz, 2H), 4.01 (t, *J*= 6.85 Hz, 2H), 3.38 (s, 3H), 3.71 (s, 3H); ^{13}C NMR ($CDCl_3$, 300 MHz, ppm) δ: (161.49, CHO) (140.28, CH) (123.30, CH) (116.41, CH) (51.27, CH_2) (46.97, CH_2) (37.20) (32.26, CH_3); HRMS (ESI^+) m/z(%): calcd for $[C_8H_{14}N_3O]^+$: 168.216 found 168.214; HRMS (ESI-) m/z(%): calcd. For $[I]^-$: 126.90, found: 126.90.

1-[2-(Formylamino)ethyl]-3-methyl-1H-imidazol-3-ium triflimide (4e)

To a solution of 1-[2-(formylamino)ethyl]-3-methyl-1*H*-imidazol-3-ium iodide (4d) (10.86 g , 0.036 mol) in deionized water (40 mL) was added lithium triflimide (10.33g, 0.036 mol). The mixture was stirred at 40 °C for 24 h. Upon completion of the reaction, the reaction mixture was



Scheme 4. Synthetic scheme of the proposed DMF-like task specific ionic liquid. Reaction conditions: (i) 1.0 equiv N-methylaminoethanol (4a) 1.5 equiv anhydrous ammonium formate, acetonitrile, 95°C 87 %; (ii) 1.0 equiv (4b), 1.5 equiv NaI, 0.5 equiv $ZrCl_4$, CH_3CN (150 ml), r-t, (4c) 89%; (iii) 1.0 equiv N-methyl imidazole 1.1 equiv N-(2-iodoethyl)-N-methyl formamide (4c), CH_3CN, at 80°C for 24 hr, (4d)86%; (iv) 1.0 equiv (4d), 1.0 equiv lithium triflimide, water, 40 °C for 24 h. (4e) 90%.

cooled to room temperature and extracted with CH_2Cl_2.The combined organic extracts were concentrated and washed with deionized water, dried over anhydrous $MgSO_4$. After complete removal of solvent, the residue was further dried in vacuo (0.3 mmHg) to afford analytically pure ionic liquid (4e) (14.85g, 90%) as a clear yellowish liquid.

Spectral data

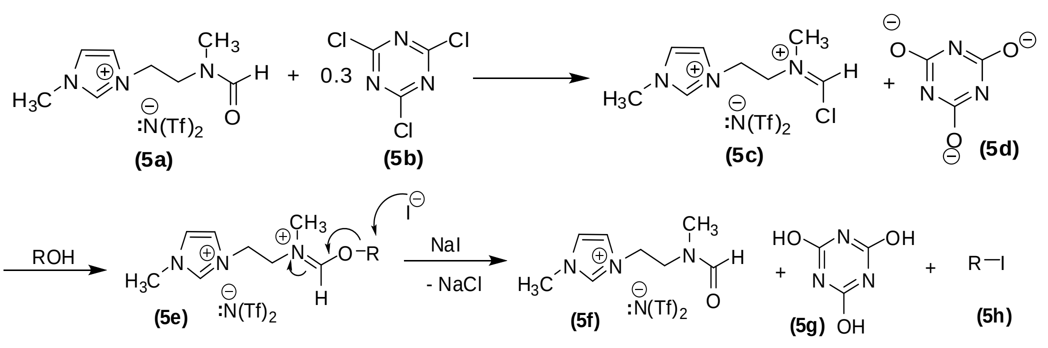
^1H NMR (300 MHz, CD_3OD, ppm) δ: 9.46 (s, 1H), 8.59 (s, 1H), 8.46 (s, 1H), 7.79 (s,1H), 4.62(t, *J*= 6.85Hz, 2H), 4.01 (t, *J*= 6.85 Hz, 2H), 3.38 (s, 3H), 3.71 (s, 3H); ^{13}C NMR ($CDCl_3$, 300 MHz, ppm) δ: (161.49, CHO) (140.28, CH) (123.30, CH) (116.41, CH) (51.27, CH_2) (46.97, CH_2) (37.20) (32.26, CH_3); HRMS (ESI^+) m/z(%): calcd. for $[C_8H_{14}N_3O]^+$: 168.2161, found: 168.2160; HRMS (ESI^-) m/z(%): calcd. for $[N(SO_2CF_3)_2]^-$: 279.9173, found: 279.9179.

2.3. General procedure for iodination of alcohol in multi-purpose DMF-like TSIL

2,4,6-Trichloro-[1,3,5] triazine (183 mg, 1.00 mmol) was added to ionic liquid (106 mg, 0.25 mmol), maintained at 25 °C. After the formation of a white solid, the reaction was monitored (TLC) until complete disappearance of TCT, Then isoamyl alcohol (88 mg, 1.00 mmol) and sodium iodide (150 mg, 1.00 mmol) were added in (1.5 ml) DMF-like ionic liquid. Two drops of CH_3CN were added to allow mixing. After the addition, the mixture was stirred at room temperature, during stirring the reaction progress was monitored by (TLC) until completion (3 h). After the completion of reaction the alkyl iodide product was extracted with diethyl ether. Removal of ether under *vaccu* yielded pure alkyl iodide. The ionic liquid was recovered by washing with Water (6.0 ml) which removed water soluble by products leaving the pure ionic liquid ready for reuse

3. Results and Discussion

The required multipurpose DMF-like task specific ionic liquid was prepared with a modified synthetic scheme which is even more efficient than reported one. The scheme started with *N*-formylation of *N*-methylaminoethanol (4a) to give formamide (4b). The direct iodination of latter with zirconium chloride and sodium iodide ($ZrCl_4$/NaI) [32] leads to its iodo derivative (4c) which reacts with 1-methyl imidazole to form imidazolium iodide salt (4d). Anionic metathesis of iodide with lithium triflimide and further purification with silica gel chromatography gives required ionic liquid (4f) in quantitative yields (Scheme 4). This ionic liquid demonstrates insolubility in nonpolar organic solvents like n-hexane and low polar solvents like ether but is soluble in polar organic solvents like CH_2Cl_2 and CH_3OH. These



Scheme 5. Preparation of iminium chloride from DMF-like MTSIL and iodination of alcohols. Reaction conditions: (i) 1.0 equiv Trichlorotriazine, 0.25 equiv ionic liquid, 25 °C, (ii) 1.0 equiv isoamyl alcohol, 1.0 equiv sodium iodide, (1.5 ml) DMF-like ionic liquid, r,t 3hrs, alkyl iodide.

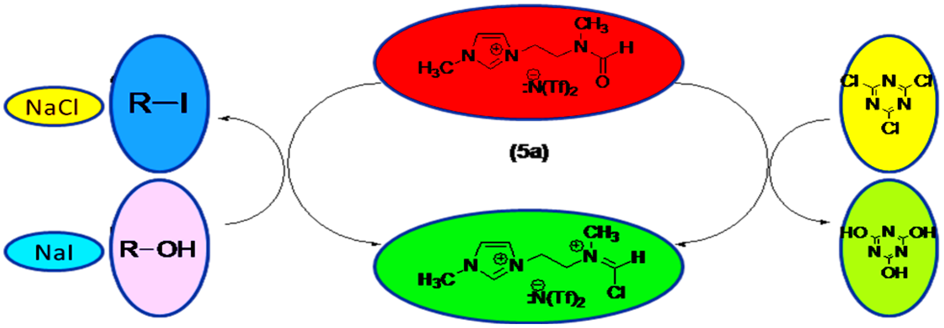


Fig.2. Catalytic cycle.

conditions are responsible for operational convenience offered by ionic liquids. Reaction conditions: (i) 1.0 equiv *N*-methylaminoethanol (4a) 1.5 equiv anhydrous ammonium formate, acetonitrile, 95°C 87 %; (ii) 1.0 equiv (4b), 1.5 equiv NaI, 0.5 equiv $ZrCl_4$, CH_3CN (150 ml), r-t, (4c) 89%; (iii) 1.0 equiv N-methyl imidazole 1.1 equiv *N*-(2-iodoethyl)-N-methyl formamide (4c), CH_3CN, at 80°C for 24 hr, (4d) 86%; (iv) 1.0 equiv (4d), 1.0 equiv lithium triflimide, water, 40 °C for 24 h. (4e) 90%. Since we are focusing on iminium chloride catalysed reaction, the ionic liquid version of iminium chloride (5c) was prepared by treating the ionic liquid (5a) with trichlorotriazine (TCT) (5b) according to reported procedure [33] (Scheme 5). The ionic liquid based iminium chloride intermediate (5c) was then examined for direct conversion of alcohols into alkyl iodides by slight modification in reported methods used for preparation of alkyl chlorides and bromides. The current methods consists of treating an alcohol with intermediate **(5c)** that would try to form alkyl chloride but we will add a competent nucleophile i.e., iodide in situ in form of sodium iodides to get required alkyl iodide. The iodination potential of proposed ionic liquid was tested initially with isoamyl alcohol. In first step ionic liquid version of iminium ion (5c) was prepared by treating DMF-like MTSIL with (0.3 eqvt) trichloro triazine. Then 1 eqvt of amyl alcohol was added to slightly excess (1.2 eqvt) of (5c). After stirring the mixture at room temperature for 1.2 hrs 1.2 eqvt of sodium iodide was added and stirring was continued till completion of reaction under same conditions. As revealed by TLC analysis, the reaction was completed within 3.5 Hrs. The product was simply extracted with diethyl ether and removal of solvent under *vacco* yielded pure amyl iodide in quantitative yield 87 %. The ionic liquid was washed with water to remove salts i.e., NaCl and trihydroxy triazine and dried under high vacuum and could be used for next run. The reaction system worked quite well as per expectations. The key features of the present methodology included the production of quantitative yields, reaction with almost equimolar ratio of reactants whereas other reported systems required higher loading for better yields of the product. No extra weak base was needed to neutralize the proton produced by alcohol as trihydroxy triazine was sufficient to neutralize it. Formation of little amount of amyl chloride can be circumvent either by slightly prolonging the reaction time or by using more amount of sodium iodide. After recovering the product by extracting the product with ether, the ionic liquid was washed with water for removing inorganic ions like sodium chloride, and trihydroxy triazine. These evidences prove the present methodology an operationally simple procedure offering best alternative over rest of other options. Using these optimized reaction conditions, the proposed methodology was investigated for the substrate scope and functional group compatibility. The results obtained are illustrated in Table 1. Variety of alcohols tested under these conditions bear the testimony to the comprehensive effectiveness of the current study. Primary alcohols were converted in excellent yield to the corresponding iodides (Table 1, entries 1−5). Some of the compounds gave little amounts of chloro derivatives (Table 1, entries, 1,4,7) which were converted into iodo derivatives with further stirring and that time duration is mentioned in Table 1. Unlike *N*,*N*-Dimethyl-*N*-(methylsulfanylmethylene) ammonium iodide ($MeSCH{=}NMe_2^+I^-$) catalysed iodination of alcohol, no the formate ester of the original alcohol was formed as the byproduct. With a neopentylic primary alcohol (Table 1, entry 4), the yield of iodide was dismal yet something positive because in previous case zero conversions are reported. Besides the neopentyl iodide some amount of 2-methyl butyl iodide was also detected which is formed due to rearrangement of primary neopentyl cation into 2-methyl butyl which bears secondary carbocation. This happens due to highly polar conditions. Conversion of variety of secondary alcohols to the corresponding iodides was also achieved under same conditions, but with extended reaction times. Nevertheless, secondary iodides could be obtained in good yields (Table 1, entries 6−7). Almost every method of iodination has been reported to have failed to cause iodination of tertiary alcohol. Tertiary alcohols responded to present system and formed good yields of tertiary iodides (Table 1, entry 12). This outstanding observation can be rationalized by fact that tertiary carbocations are easily formed in highly polar environment and can be trapped by suitable nucleophiles like iodide ion. Given the observed difference in reaction rate between primary and secondary alcohols, two primary−secondary

Table 1. Ionic liquid catalysed direct conversion of alcohols into corresponding alkyl iodides.[a]

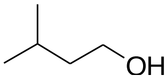
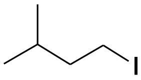
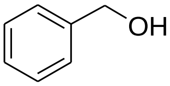
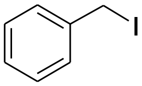
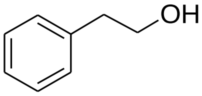
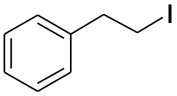
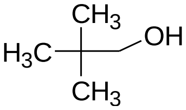
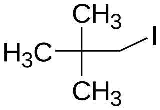
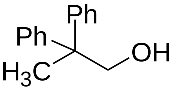
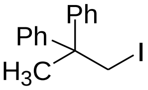
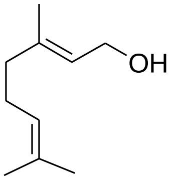
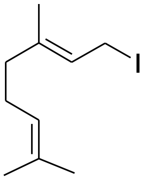
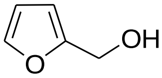
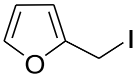
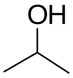
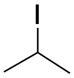
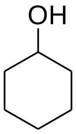
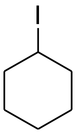
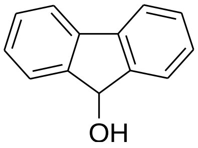
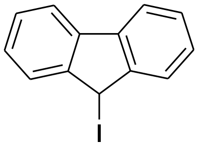
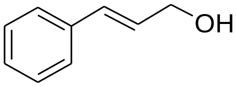
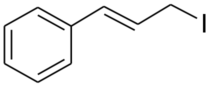
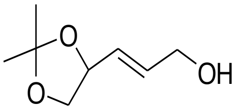
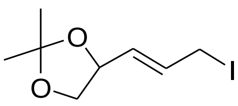
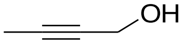
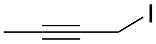
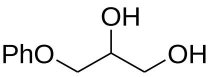
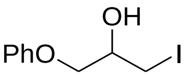
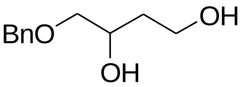
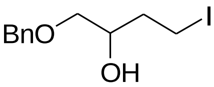
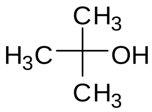
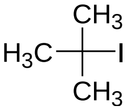
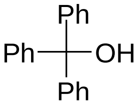
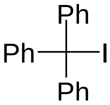
Entry	Alcohol	Alkyl iodide Reaction	Time (h)	Yield (%)
1			3.00	92
2			1.20	96
3			1.50	87
4			3.30	38
5			4.00	30
6			1.40	89
7			1.00	92
8			94	94
9			2.50	91
10			0.40	86
11			1.00	1.00
12			1.20	87
13			1.00	86
14			1.00	82
15			1.00	85

Table 1. *(Continued)*

Entry	Alcohol	Alkyl iodide Reaction	Time (h)	Yield (%)
16	 $H_3C-C(CH_3)_2-OH$	 $H_3C-C(CH_3)_2-I$	2.00	47
17	 $Ph-C(Ph)_2-OH$	 $Ph-C(Ph)_2-I$	2.30	41

[a] Reaction condition: Trichlorotriazine: DMF-like ionic liquid:alcohol:sodium iodide, 1:1:1:1(mole ratio); temperature 25°C, two drops of CH_3CN were added to allow mixing. Mixture was stirred until completion of reaction.

diols were subjected to the iodination conditions to find out whether selective reaction was possible. A 1,2-diol (Table 1, entry 13) and 1,3-diol (Table 1, entry 14) gave a moderate yield of the iodo alcohol resulting from preferential reaction of the primary alcohol with the secondary alcohol remaining unreacted. Two allylic alcohols were investigated (Table 1, entries 10, 11) and gave clean and quantitative amount of allylic iodides. Unlike reported procedures, the better yields in reduced time in present system arise from enhanced stability of iminium chloride under hydrophobic and highly polar ionic liquid conditions.

3.1. Cycle of catalysis

The concept of recoverable and recyclable catalysts has become extremely important from both environmental and economic points of view. Water soluble sodium chloride and trihydroxy triazine were removed by simply washing the used ionic liquids with water. After washing the ionic liquid was dried under *vacco* and desiccator and reused.

3.2. Recycling studies

The recycling potential of our ionic liquid for iodination of alcohols was tested using iodination of isoamyl alcohol as test reaction. Data obtained is shown as graph in (Figure 3). Slight reduction in yields of both recovery of ionic liquid and iodo compound can be seen. This is partly due to the entering of ionic liquid in reaction by its reaction with reagents like TCT.

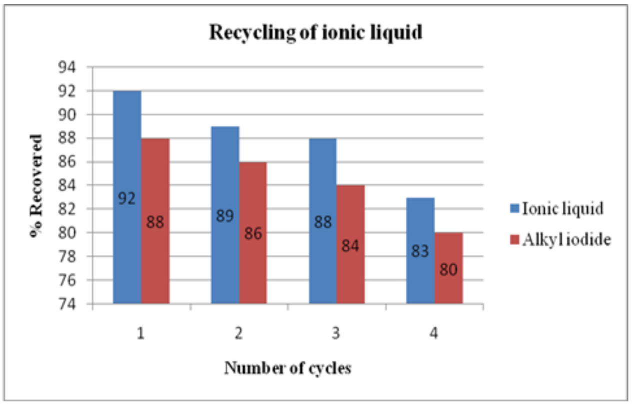


Fig.3. Recycling study of the multipurpose DMF-like task specific ionic liquid

4. Conclusion

An operationally simple and a viable methodology for direct and efficient conversion of alcohol into alkyl iodide has been introduced. The ionic liquid conditions allow the conversion of a wide range of primary and secondary alcohols to the corresponding alkyl iodides in good yield. Different types of alcohols like primary, secondary even tertiary alcohols responded to these iodination conditions. Allylic and propagylic alcohols were also underwent successful iodination.

Reference

[1] http://en.wikipedia.org/wiki/Dimethylformamide.

[2] J. Muzart, Tetrahedron, 65 (2009) 8313-8323.

[3] D. Samita, A.K. Panigrahi, G. C. Maikap, Tetrahedron Lett., 44 (2003) 1375-1377.

[4] S. Weike, W. Yiyi, J. Ling, Y. Yanyan, Z. Linyao, C. Zhiwei, L. Zhenhua, L. Jianjun, 42 (2010) 503–555.

[5] (5a) K. Venkataraman, D. R. Wagle, Tetrahedron Lett., 20 (1979) 3037–3040. (5b) G, Blotny, Tetrahedron, 62 (2006) 9507-9522.

[6] (a) D.C. Forbes, E.J. Barrett, D.L. Lewis, M.C. Smith, Tetrahedron Lett., 41 (2000) 9943-9947. (b) B.P. Bandgar, S.S. Pandit, Tetrahedron Lett., 43 (2002) 3413-3414. (c) D. Luca, L. Giacomelli, G. Taddei, M. J. Org. Chem., 66 (2001) 7907-7909. (d) G. Giacomelli, A. Porcheddu, M. Salaries, Org. Lett., 5 (2003) 2715-2517.

[7] L. De Luca, G. Giacomelli, A. Porcheddu, J. Org. Chem., 66 (2001) 7907-7909.

[8] C.O. Kangani, B.W. Day, Org. Lett., 10 (2008) 2645-2548.

[9] (a) L. De Luca, G. Giacomelli, A. Porcheddu, J. Org. Chem., 67 (2002) 6272-6274. (b) Y. Furuya, K. Ishihara, H. Yamamoto, J. Am. Chem. Soc., 127 (2005) 11240-11241. (c) C. Betti, D. Landini, M. AMaia, M. Pasi, SynLet., (2008) 908-910.

[10] L. De Luca, G. Giacomelli, A. Porcheddu, Org. Lett., 4 (2002) 553-555.

[11] L. De Luca, G. Giacomelli, A. Porcheddu, J. Org. Chem., 67 (2002) 6272-6274.[12] L. De Luca, G. Giacomelli, A. Porcheddu, J. Org. Chem., 67 (2002) 5152-5155.

[13] C.W. Chang, S.S Chang, C.S. Chao, K.T. Mong, Tetrahedron Lett., 50 (2009) 4536-45-42.

[14] A. A. Hullio, G.M Mastoi, K. M. Khan, Asian J. Chem, 23 (2011) 5411-5418.

[15] (a) D. Abhishek, A.K. Upadhyay, K. Pradeep, Tetrahedron lett., 51 (2010) 744. (b) K. Savita, K. Ajay, A. K. Gupta, Synth. Commun. 32 (2002) 2885-2891.

[16] S. Hartinger, In Science of Synthesis, Georg Thieme Verlag: New York, 35 (2007) 589− 672.

[17] B. R Castro, Org. React., 29 (1983) 1– 162.

[18] P J. Garegg, B. Samuelsson, J. Chem. Soc., Chem. Commun., 12, (1979) 978– 980.

[19] S.Hanessian, M.M. Ponpipom, P. Lavallee, Carbohydr. Res., 24 (1972) 45– 56.

[20] H. Loibner, E. Zbiral, Helv. Chim. Acta, 59 (1976) 2100–2113.

[21] (a) S.R. Landauer, H.N. Rydon, J. Chem. Soc. 1953, 2224–2234. (b) H. N. Rydon, Org. Synth. Coll., 6. 1988, 830– 832.

[22] M.E. Jung, P.L. Ornstein, Tetrahedron Lett., 18 (1977) 2659–2662.

[23] (a) G.A. Olah, S. Narang, B.G.B. Gupta, R. Malhotra, J. Org. Chem. 44 (1979) 1247– 1251 (b) T. Morita, S. Yoshida, Y.Okamoto, H. Sakurai, Synthesis, 6 (1979) 379-384.

[24] J.F. Norris, Am. Chem. J. 38 (1907) 627– 642.

[25] W.W. Hartman, J.R. Byers, J.B. Dickey, Org. Synth. Coll. 2 (1943) 322-323.

[26] M. Lauwers, B. Regnier, V. Van Eenoo, J. N. Denis, A. Krief, Tetrahedron Lett., 20 (1979) 1801– 1804.

[27] M. Di Deo, E. Marcantoni, E. Torregiani, G. Bartoli, M. C. Bellucci, M. Bosco, L. Sambri, J. Org. Chem., 65 (2000) 2830–2833.

[28] A. Kamal, G. Ramesh, N. Laxman, Synth. Commun., 31 (2001) 827– 833.

[29] H. Tajik, F. Shirini, M. A. Zolfigol, F. Samimi, Synth. Commun. 36 (2006) 91– 95.

[30] (a) H. Eilingsfeld, M. Seefelder, H. Weidinger, Angew. Chem. 72 (1960) 836– 845. (b) S. Hanessian, N. R. Plessas, Chem. Commun., (1967) 1152– 1155. (c) R. F. Dods, J. S. Roth, Tetrahedron Lett., 3 (1969) 165– 168. (d) D. R. Hepburn, H. R. Hudson, J. Chem. Soc., Perkin Trans. 1 (1976) 754– 757.

[31] R. Adam Ellwood, J. Porter Michael, J. Org. Chem., 74 (2009) 7982–7985.

[32] H. Firouzabadi, N. Iranpoor, M. Jafarpour, Tetrahedron Lett., 45 (2004) 7451–7454.

[33] A.A. Hullio, G.M. Mastoi, Chin. J. Chem., 1 (2012) (accepted).