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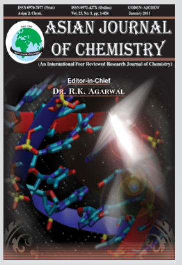

First Multipurpose Task Specific Ionic Liquid: Designing and Synthesis of Novel Dimethyl Formamide-Like Ionic Liquid and Its Applications as a Green Solvent Alternative to Dimethyl Formamide Dependent Reactions

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A novel imidazole based task specific ionic liquid with dimethyl formamide (DMF) functionality has been designed and synthesized. The proposed dimethyl formamide like task specific can be used as a green alternative solvent-cum-organocatalyst for wide range of organic reactions which essentially depend on DMF. Dimethyl formamide as a solvent, due to its inherited structural features is found to affect the outcome of many reactions. Some of DMF-dependent reactions are investigated in its ionic liquid version with encouraging results. DMF-like ionic liquid acts both as a green reaction media and recyclable organocatalyst. Main advantages include easy reaction procedure, short reaction duration, easy work up and moreover the wide scope applications.

Key Words: Dimethylformamide, Ionic liquid, Multipurpose applications, Nucleophilic substitution, Alkyl halides and azides, Sodium periodate, Oxidation of alkylhalides, Carbonyl compounds.

INTRODUCTION

Among the major problems confronted to synthetic chemists are tedious work up, long reaction time durations, lower yields and cumbersome purification processes and more over toxicity of the chemicals especially the solvents. Consequently search for convenient methodologies has been the part of active and vibrant research since the birth of synthetic organic chemistry. Only recently most of the convenience has been obtained by carrying out reactions in special type of solvents called ionic liquids. The ionic liquids have emerged as a green reaction media due to their unique plethora of the properties like non-inflammability, negligible vapour pressure, high thermal stability and reusability[1,2]. The most striking feature of ionic liquids the tunability of their properties *i.e.*, a solvent of desired properties can be synthesized. The use of ionic liquids as an alternative reaction medium has offered a panacea to both environmental problems and by avoiding the generation of chemical wastage[3-5]. Vast literature published in recent years bears the ample testimony to the scope and ever expanding vistas of opportunities of the ionic liquids to make reactions easy to perform by circumventing the tedious and laborious work up. Thus this methodology has enabled the synthetic chemists to save the time and energy with minimal loss of yields by reducing even in certain cases eliminating the lengthy work up and consequently reducing the stock of chemical wastage. Most noteworthy aspect of ionic liquids is the synthesis of the task specific ionic liquid *i.e.*, the ionic liquid in which a functional group has been anchored to serve the dual purpose of both as an organocatalyst as well as solvent. This has proved to be the landmark in the direction of the designing of organocatalyzed reaction in their ionic liquid versions. Many of the organocatalyzed reactions have been designed into what can be called as task specific ionic liquids[6]. These ionic liquids contain specific functionalities and are capable of carrying out specific tasks by acting as both reagent and solvent, such as the task-specific ionic liquid have been designed and applied with excellent results for Beckmann rearrangement[7], Brönsted acidic reactions[8], quinuclidine-catalyzed Morita-Baylis-Hillman reactions[9], asymmetric Michael addition reactions[10], Swern oxidation[11], Claisen-Schmidt reaction[12], Mannich reaction[13], ionic liquid-supported NHPI complex[14]. However, certain task-specific ionic liquids have shown limited success when used as solvents for reactions.

Extensive literature survey about the role of solvent to affect the outcome of reactions, reveals that there are certain reactions which produce different results when carried out in the different solvents especially in DMF[15]. The variation can be seen in terms of enhanced reaction rate, softened reaction conditions, even more striking being the formation of quite different products. Most of nucleophilic substitution reactions which appear in sequence of total synthesis are carried out in DMF principally due to two reasons. First it promotes the reactions involving the polar intermediates or transition states, second it facilitates the removal of leaving group by its formamide functionality. Many reactions which been reported to be highly influenced by dimethyl formamide. Das *et al.*[16] reported $NaIO_4$-DMF as a novel reagent for direct oxidation of organic halides to corresponding carbonyl compounds. Abad[17] reported the conversion of alkyl halides into alcohols *via* DMF-catalyzed formyloxylation reaction by silver salt. Cao *et al.*[18] reported the new microwave-assisted chemoselective reaction controlled by nature of solvent for the synthesis of pyrido[2,3-d]pyrimidine derivatives. Chlorination of 2-hydroxyethylamides containing electron-donor substituents at 23 °C with $SOCl_2$ proceeds *via* 2-substituted-2-oxazolinium hydrochlorides that undergo DMF-catalyzed reaction *in situ* to be transformed into 2-substituted-2-oxazolines[19]. Vinyl arenes have been shown to undergo highly efficient cycloaddition with electron-deficient alkynes affording 1,2-disubstituted-3,4-dihydronaphthalenes catalyzed by N,N-dimethyl formamide dimethyl acetal[20]. Process for the preparation of 1,1-dioxo-7-substituted cephems involves the acid chloride which is prepared from the corresponding acid by DMF-catalyzed reaction with oxalyl chloride in methylene chloride[21]. The diethyl 3,4-dihydroxy-2,5-thiophene dicarboxylate undergo facile dialkylation with sterically hindered alkyl-dibromides, using DMF-trialkylamine as a reaction system[22]. The ethylene glycols and carboxylic acid undergo facile DMF-facilitated O-alkylation to furnish diethers and esters respectively[23]. There are certain organic reagents which work efficiently when used in DMF, *i.e.*, TCT. DMF complex is powerful mutipurpose reageant (*e.g.*, 2,4,6-trichloro[1,3,5]-triazine and *N,N*-dimethylformamide).

Keeping in view the significant role of DMF in affecting the outcome of certain reactions, it was envisioned to synthesize its ionic liquid version in order to take full and efficient advantage of properties of DMF together with ionic liquid properties. The idea of DMF structure and ionic liquids appears to be promising to the curious mind. To that end, we designed the structure of ionic liquid containing N-methyl and N-formyl functionality which could not only closely manifest its properties like DMF but also behave as reasonable ionic liquids without any inherited drawbacks like viscosity. Keeping all these factors in focus, we carved out the simplest possible version of DMF-like ionic liquid is shown as Fig. 1.

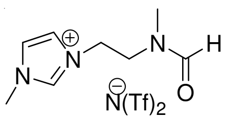


Fig. 1. Conceived structure of proposed DMF-like task specific ionic liquid

In order to check the efficacy of proposed task specific ionic liquids, we have decided to report only two types of synthetically useful reactions. The first example include direct conversion of alkyl halide to corresponding alkyl azide which is essentially nucleophilic substitution reaction. The versatile reactivity and the synthetic usefulness of the azido group is well documented and there are several methods available for the synthesis of azido compounds. The most common method utilizes nucleophilic substitution of alkyl halides with sodium azide or lithium azide in various solvents especially in dimethyl formamide. However, these methodologies often suffer from complex procedures, long reaction times and low yields. In addition, there is usual purification problems associated with these concentional methods *i.e.*, distillations of products from the incomplete reactions since some alkyl azides decomposes rapidly with danger of explosion. Consequently, it is decided to include this reaction for checking in task specific ionic liquids.

The second example of reaction includes direct oxidation of organic halides to the corresponding carbonyl compound. This is synthetically useful and well known transformation since 1949 when the Hass-Bender reaction was reported which involves oxidation of alkyl halides[24,25]. Since then several methods have been developed to achieve various selectivities and compatibilities[26,27] such as Sommelet reaction[28] specific for benzylic halides, the Krohnke reaction (pyridine followed by *p*-nitroso dimethylaniline)[29] and Kornblum reaction (DMSO/$NaHCO_3$) which is limited to active halides and requires very high temperature. Some amine N-oxides[30] are also used for this oxidation. Masaki *et al.*[31] have reported the photooxidation of aryl bromides with mesoporous silica FSM-16. More recently, 2-dimethyl amino-*N,N*-dimethyl aniline-N-oxide[32] was used for this conversion in high yield. The direct oxidation of alkyl halide into their corresponding carbonyl comounds $NaIO_4$-DMF is the powerful technique. In this case DMF acts both as a solvents as well as an activator of the sodium periodate.

The dependency of the reaction is manifested from the mechanism of the reaction as shown in Fig. 2.

Since in latter example the oxidation of alkyl halide with sodium periodate is DMF dependent, it is decided to perform this reaction in proposed novel DMF-like ionic liquid. More DMF-depended reactions will remain under investigation.

EXPERIMENTAL

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

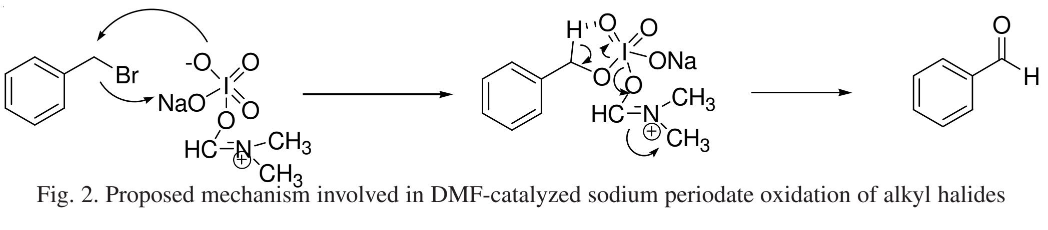


Fig. 2. Proposed mechanism involved in DMF-catalyzed sodium periodate oxidation of alkyl halides

(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.

Synthesis scheme of DMF-like ionic liquid

N-Methyl 2-aminoethanol (i): 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, 2N), stirred for 10 min and the organic layer was separated. The aqueous part was extracted with 25 mL of dichloromethane. 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 colourless liquid product; b.p. 150-155 ºC. ^{1}H NMR (400 MHz-$CDCl_3$): δ 2.35 (d, 3H, $^{4}J_{3,5}$ = 0.63 Hz, H-5), 2.60 (m, 2H, $^{3}J_{2,3}$ = 5.5 Hz, $^{4}J_{3,5}$ = 0.63 Hz, H-3), 3.54 (t, 2H, $^{3}J_{2,3}$ = 5.5 Hz, H-2), 3.64 (s-broad, 1H, H-1); ^{13}C NMR ($CDCl_3$), (300 MHz) δ (36.05, CH_3), (54.30, CH_2), (60.30, CH_2); MSEI m/z (% rel. abound.): 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 (ii): Triphenyl phosphine (267.5 g, 1.02 mol) was dissolved in 200 mL anhydrous acetonitrile in a 300 mL round bottom flask. Then (83.7 g, 0.36 mol) of trichloroisocynuric acid was added slowly over *ca.* 0.5 h. The reaction mixture was stirred and heated at 60 ºC. 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. The most of the acetonitrile was removed by rotary evaporator and residue was extracted with 100 mL (4 × 25 mL) diethyl ether. The organic layers were combined, concentrated and dried over Na_2SO_4. The product was further purified with flash chromatography to give 44.51 g (70 %) 2-chloro, N-methyl ethylamine as colourless liquid with b.p. 109-111 ºC. ^{1}H NMR (400 MHz-$CDCl_3$): δ 2.54 (d, 3H, $^{4}J_{3,2}$ = 0.63 Hz, H-2), 2.72 (m, 2H, $^{3}J_{4,3}$ = 6 Hz, H-3), 2.96 (s-broad, 1H, H-1), 3.50 (t, 2H, $^{3}J_{4,3}$ = 6 Hz, H-4); ^{13}C NMR ($CDCl_3$), (300 MHz) δ (34.93. CH_3) (42.34, CH_2) (57.55, CH_2); HRMS (ESI): calcd. for C_3H_8NCl (M^+) 93.555, found: 93.550.

N-(2-Chloroethyl)-N-methyl formamide (iii): To a solution of N-methyl-2-chloro ethyl 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 °C (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 (4 × 50 mL). 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 %) colourless liquid formamide. ^{1}H NMR (400 MHz-$CDCl_3$): δ 3.22 (s, 3H, $^{4}J_{4,2a}$ = 0.5 Hz, $^{4}J_{5,4}$ = 0.63 Hz H-4), 3.58 (t, 2H, $^{3}J_{6,5}$ = 6.68 Hz, H-6), 3.92 (t, 2H, $^{3}J_{6,5}$ = 6.68 Hz, $^{4}J_{5,2a}$ = 0.63 Hz, $^{4}J_{5,4}$ = 0.63 Hz H-5), 8.02 (s, 1H, $^{4}J_{4,2a}$ = 0.5 Hz, $^{4}J_{5,2a}$ = 0.63 Hz, 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_8NOCl (M^+) 121.565, found: 121.568.

N-(2-Iodoethyl)-N-methyl formamide (iv): To a solution of N-(2-chloroethyl)-N-methyl formamide (**iii**) (51.84 g, 0.24 mol) in 25 mL of anhydrous acetone is 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 stirring is continued for 20 h. The precipitate formed is collected by filtration and washed with 100 mL of acetone. The combined filtrate is evaporated and residue is distilled to give colourless oil. It was further purified by flash chromatography to give 66.34 g, 73 % yield. ^{1}H NMR (400 MHz-$CDCl_3$): δ 3.24 (s, 3H, $^{4}J_{4,2a}$ = 0.5 Hz, $^{4}J_{5,4}$ = 0.63 Hz, H-4), 3.60 (t, 2H, $^{3}J_{6,5}$ = 7.77 Hz, H-6), 4.00 (t, 2H, $^{3}J_{6,5}$ = 7.77 Hz, $^{4}J_{5,4}$ = 0.63 Hz, $^{4}J_{5,2a}$ = 0.63 Hz H-5), 7.79 (s, 1H, $^{4}J_{4,2a}$ = 0.5 Hz, $^{4}J_{5,2a}$ = 0.63 Hz, 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_8NOI (M^+) 213.017, found: 213.016.

1-[2-(Formylamino)ethyl]-3-methyl-1*H*-imidazol-3-ium iodide (v): 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 (**iv**), were added to 100 mL of acetonitrile (CH_3CN) and subjected to reflux with stirring under nitrogen at 80 °C for 24 h. 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 h to afford imidazolium iodide (**v**) yield 46.56 g, 89 %. ^{1}H NMR (400 MHz-CD_3OD): δ 3.16 (s, 3H, $^{4}J_{11,9a}$ = 0.5 Hz, $^{4}J_{7,11}$ = 0.63 Hz, H-11), 3.92 (t, 2H, $^{3}J_{6,7}$ = 6.63 Hz, $^{4}J_{2,6}$ = 0.6 Hz, $^{5}J_{4,6}$ = 0.3 Hz, $^{4}J_{5,6}$ = 0.4 Hz H-6), 4.19 (t, 2H, $^{3}J_{6,7}$ = 6.63 Hz, $^{4}J_{7,9a}$ = 0.63 Hz, $^{4}J_{7,11}$ = 0.63 Hz, H-7), 7.40-7.98 7.40 (s, 1H, $^{3}J_{4,5}$ = 1.4 Hz, $^{4}J_{5,2}$ = 1.3 Hz, $^{4}J_{5,6}$ = 0.4 Hz, H-5) 7.70 (s, 1H, $^{4}J_{4,2}$ = 0.8 Hz, $^{3}J_{4,5}$ = 1.4 Hz, $^{5}J_{4,6}$ = 0.3 Hz, H-4) 7.98 (s, 1H, $^{4}J_{2,6}$ = 0.6 Hz, $^{4}J_{4,2}$ = 0.8 Hz, $^{4}J_{5,2}$ = 1.3 Hz H-2), 7.75 (s, 1H, $^{4}J_{7,9a}$ = 0.63 Hz, $^{4}J_{11,9a}$ = 0.5 Hz, H-9a); ^{13}C NMR ($CDCl_3$), (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 triflate (vi): To a solution of 1-[2-(formylamino)ethyl]-3-methyl-1*H*-imidazol-3-ium iodide (**iii**) (46.56 g, 0.16 mol) in dry acetonitrile (20 mL) was added silver triflate (41.12 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 **4b** as a clear liquid with a very light brown colour with yield 67 g, 100 % yield. ^{1}H NMR (400 MHz-CD_3OD): δ 3.16 (s, 3H, $^4J_{7,12}$ = 0.63 Hz, $^4J_{9a,12}$ = 0.5 Hz H-12), 3.75 (s, 3H, H-11), 3.82 (t, 2H, $^4J_{2,6}$ = 0.6 Hz, $^5J_{4,6}$ = 0.3 Hz, $^4J_{5,6}$ = 0.4 Hz, $^3J_{6,7}$ = 6.63 Hz, H-6), 4.08 (t, 2H, $^3J_{6,7}$ = 6.63 Hz, $^4J_{7,9a}$ = 0.63 Hz, $^4J_{7,12}$ = 0.63 Hz H-7), 7.75 (s, 1H, $^4J_{7,9a}$ = 0.63 Hz, $^4J_{9a,12}$ = 0.5 Hz H-9a) 8.40-9.47 8.40 (s, 1H, $^3J_{4,5}$ = 2.1 Hz, $^4J_{5,2}$ = 1.19 Hz, $^4J_{5,6}$ = 0.4 Hz, H-5) 8.65 (s, 1H, $^3J_{4,5}$ = 2.1 Hz, $^5J_{4,6}$ = 0.3 Hz, H-4) 8.47 (s, 1H, $^4J_{2,6}$ = 0.6 Hz, $^4J_{5,2}$ = 1.19 Hz, H-2); ^{13}C NMR ($CDCl_3$), (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) (CF_3 108.84, 116.71, 124.59, 132.46); HRMS (ESI): calcd. for $C_8H_{14}N_3O(M^+)$ 168.216, found: 168.218.

Conversion of alkyl halides to alkyl azides

Standard procedure for DMF as a solvent: The alkyl halide (10 mmol, 1 equivalent) and sodium azide (13 mmol, 1.3 equivalent) were mixed in 20 mL of DMF and 10 mL of water to form homogenous solution. The resulting solution was refluxed with magnetic stirring until TLC and gas chromatography indicated the completion of the reaction. On completion of reaction, the reaction mixture was cooled to room temperature and poured into 30 mL of distilled water in 100 mL conical flask. The organic phase was extracted with 3 × 20 mL ether. The combined ether extracts were concentrated and dried over anhydrous sodium sulphate. The removal of solvent under *vacuo* furnished the required product. The product was characterized by spectroscopic techniques.

Standard procedure for DMF-like ionic liquid asa solvent: The 1.3 equivalents of sodium azide and 1 mol equivalent of alkyl halide were added to 10 mL of DMF-like ionic liquid to give thick slurry. To reduce the thickness the 10 mL of dichloromethane was added. The reaction mixture heated and stirred magnetically at 40 ºC under nitrogen for appropriate time. The progress of reaction was monitored by TLC analysis. After completion of reaction as indicated by TLC, dichloromethane was removed under *vacuo* and product was extracted with diethyl ether (3 × 5 mL). All the ether extracts were combined and concentrated, dried and purified by flash chromatography with ethyl acetate and *n*-hexane (1:1) as eluent to afford the pure product.

Oxidation of alkyl halides to carbonyl

General procedure for plain DMF as a solvent: Alkyl bromide (2 mmol) was taken in round bottom flask along with sodium metaperiodate ($NaIO_4$) (2 mmol). The above mixture was dissolved in 30 mL of N,N-dimethyl formamide (DMF). The reaction mixture was heated at reflux. The progressed of reaction was monitored by TLC by comparison with the starting material (10 % ethyl acetate in hexane). The reaction was completed in 40 min. The reaction was cooled and treated with 20 mL of water then extracted with ether (2 × 30 mL). The combined ether layers were dried over anhydrous magnesium sulphate ($MgSO_4$) then filtered off and concentrated. GLC analysis of the reaction mixture showed the presence of corresponding carbonyl compounds. Purification by column chromatography on 60-100 mesh silica gel gave carbonyls. Formation of carbonyls were further confirmed by melting points of its 2,4-nitrophenylhydrazone derivative.

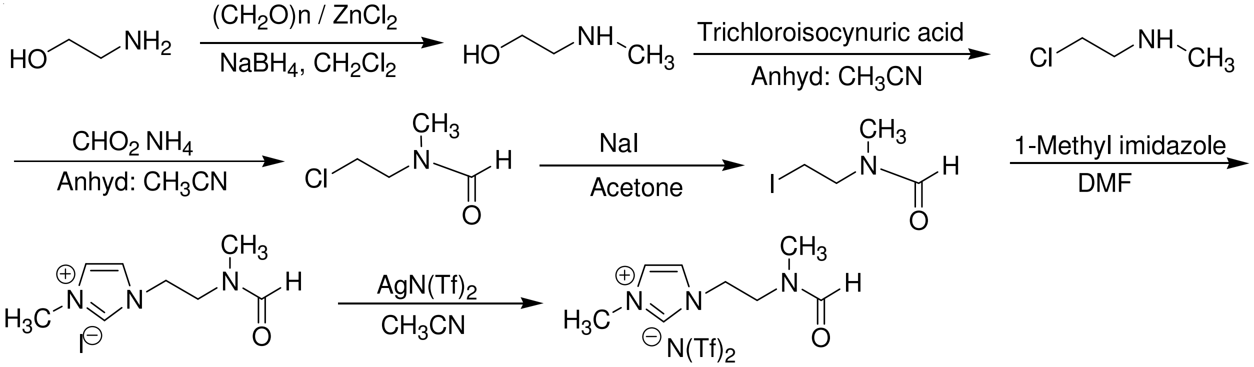
General procedure for DMF-like ionic liquid as a solvent: Equimolar amount of alkyl bromide (2 mmol) and sodium metaperiodate ($NaIO_4$) (2 mmol) were added to 5 mL DMF-like ionic liquid to give thick slurry. To reduce the thickness the 5 mL of dichloromethane was added. The resulting solution was stirred magnetically at 40 to 50 ºC for appropriate time. The progress of reaction was monitored by TLC analysis.

After completion of reaction as indicated by TLC, the dichloromethane was removed under *vacuo* and product was extracted with diethyl ether (3 × 5 mL). All ether extracts were combined, concentrated and dried. The products were further purified by flash chromatography with ethyl acetate and *n*-hexane (1:1) as an eluent. The rest of viscous ionic liquid was further washed with ether and dried for 1h under vacuum at 80 ºC and recycled for reuse.

RESULTS AND DISCUSSION

Synthesis of DMF-like task specific ionic liquid: After the selection of structure, a reterosynthesis was carried out to find and fix the pertinent and facile synthetic scheme. As many synthetic routes can be foreseen, the choice of reaction scheme was dictated by the availability of chemicals in our laboratory and thus finalized synthetic scheme was arrived at as shown in **Scheme-I**.

The N-methylation of aminoethanol was achieved by reductive amination with paraformaldehyde to give N-methyl aminoethanol (i) through protocol reported by Battacharyya *et al.*[33]. The N-methyl amino alcohol (i) was converted to corresponding chloro derivative (ii) by triphenyl phosphine and trichloroiso-cynuric acid[34]. At this stage, N-formylation was



Scheme-I: Synthetic scheme of the proposed DMF-like task specific ionic liquid prefered over conversion of chloride into iodide because in this reaction, formamide would also facilitate the halide substitution. The N-formylation was achieved by heating the secondary amine with ammonium formate to get the quantitative yields of N-choloroethyl-N-methyl formamide (**iii**) as reported by Reddy *et al.*[35]. The substitution of chloro group was achieved through ordinary method of heating the N-(2-chloroethyl)-N-methyl formamide (**iii**) with sodium iodide in dry acetone to get iodo derivative N-(2-iodoethyl)-N-methyl formamide (**iv**).The N-alkylation of imidazole was achieved by using the methodology developed by Jairton *et al.*[36]. Finally, the anionic metathesis of iodide salt with triflate was better achieved through the procedure used by He and Chan[10].

Thus the successful synthesis specific DMF-like ionic liquid 1-[2-(formylamino) ethyl]-3-methyl-1*H*-imidazol-3-ium triflate (**vi**) was achieved.

Evaluation of efficiency as solvent: After this, next task was its evaluation as a competent substitute of common DMF as a solvent. There is large number of reactions which depend on the DMF as a solvent, as mentioned before, which can be investigated in this novel DMF-like ionic liquid. However presently we are just describing only two reactions which include nucleophilic substitution reactions specifically conversion of alkyl halides to alkyl azides and direct oxidation of alkyl halide to their corresponding carbonyl compounds by DMF-NaIO$_4$.

Nucleophilic substitution reactions are one of the synthetically useful reactions, used for functional group transformation. These reactions are mostly carried out efficiently in DMF solvent, which activates the process. This simple DMF-dependent reaction was investigated in ionic liquid version of DMF with promising results. The second synthetically reaction to be tested is direct oxidation of alkyl halides to corresponding carbonyl compounds with sodium periodate in DMF. This reaction has also been studied in DMF-like ionic liquid with many advantages over ordinary DMF.

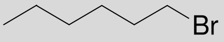
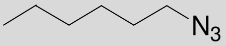
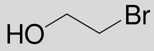
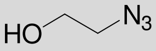
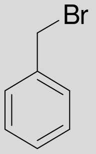
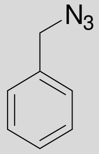
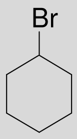
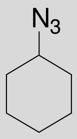
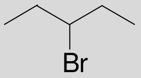
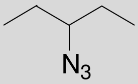
Comparative studies of nucleophilic substitution of alkyl halides in DMF and DMF-like task specific ionic liquid: In each reaction, 1 mol equivalent alkyl bromide was treated with 1.3 mol equivalents of sodium azide in ordinary solvent and was allowed to reflux for required time traced by TLC analysis. The same reaction with similar moles ratio of reactants was also used in DMF-like ionic liquid. In this case, 1 M of dichloromethane was added as a co-solvent to reduce the viscosity of the reaction mixture. The reaction mixtures were stirred magnetically with heating at 40 to 50 ºC. After completion of reactions in both solvents the overall yields turned out to be relatively better in case of ionic liquid as compared to ordinary ionic liquid. Apart from this, DMF-like ionic liquid exhibited few other advantages over the ordinary DMF solvent, such as higher rate of reactions, quick completion of reaction, easy work up and recovery of the product and recycling of the solvent. The higher yields and rate enhancement can be attributed to highly polar nature of ionic liquid because reactions with polar species are favoured in polar solvents. The benzyl bromides gave best yields in both cases gave best results. The results obtained from the study of reaction between sodium azide NaN$_3$ and different alkyl bromides are summarized in Table-1.

NaIO$_4$-Catalyzed oxidation of the alkyl halides to carbonyl compounds in DMF-like ionic liquid: The oxidation of alkyl halides with sodium periodate in ordinary DMF solvent was performed as reported earlier[16]. It involved the refluxing of the equimolar amount of alkyl halide and sodium periodate. The reaction procedure and work up were quite tedious. The similar reactions were run in DMF-like ionic liquids. The reaction required just stirring and heating the mixture at 40 to 50 ºC.

As per expectation promising results were achieved with added advantages over the simple DMF. These include relatively improved yields, shorter reaction times, less use of energy, easy recovery of products and recycling of solvent.

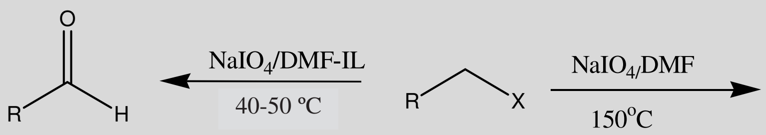
TABLE-1
COMPARISON OF NUCLEOPHILIC SUBSTITUTION IN DMF AND DMF-LIKE IONIC LIQUIDS

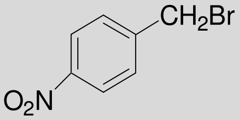
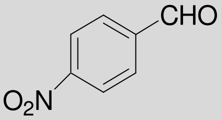
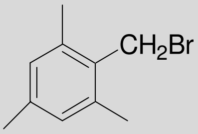
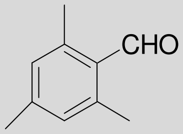
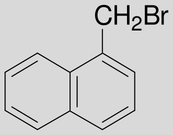
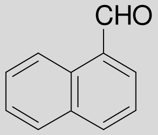
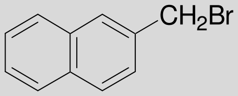
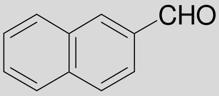
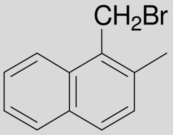
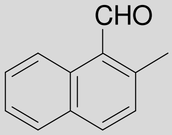
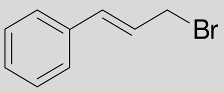
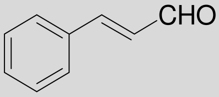
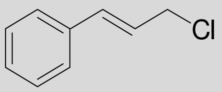
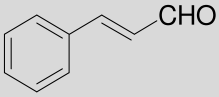
(Slow Rate) $R{-}N_3 \xleftarrow[\text{DMF}]{NaN_3} R{-}X \xrightarrow[\text{DMF-Like IL}]{NaN_3} R{-}N_3$ (Fast Rate) (Improved Yield)

Entry	Reactant	Product	Yield (%)[a]	Yield (%)[b]
1			77	78
2			67	69
3			79	79
4			45	47
5			56	60

[a]Indicates product obtained with ordinary DMF; [b]Indicates product obtained with DMF-like ionic liquid.

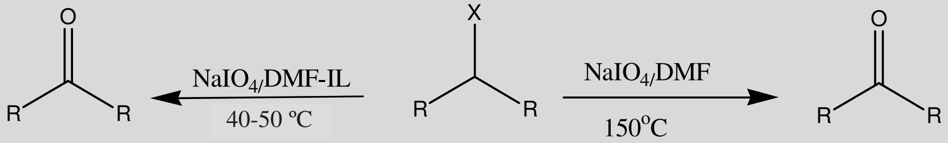
TABLE-2
COMPARISON OF OXIDATION OF PRIMARY ALKYL BROMIDES WITH SODIUM PERIODATE IN DMF AND DMF-LIKE IONIC LIQUIDS

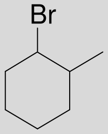
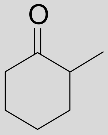
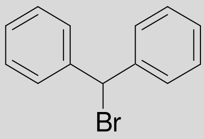
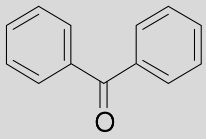
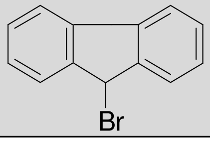
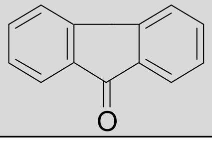


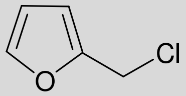
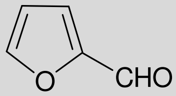
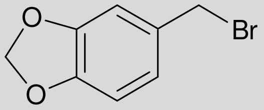
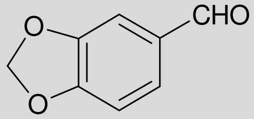
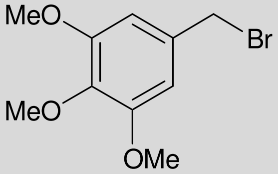
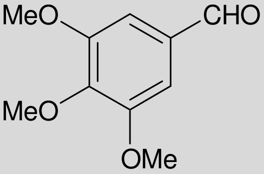
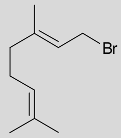
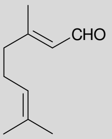
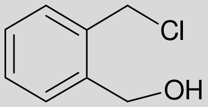
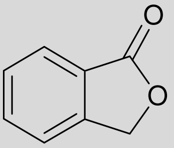
Entry	Substrate	Product	Time[a]	Yield (%)[a]	Time[b]	Yield (%)[b]
1	$C_8H_{17}Br$	$C_8H_{16}O$	45	85	40	86
2			40	80	35	80
3			50	87	46	48
4			35	80	32	82
5			35	82	35	85
6			45	85	40	82
7			50	90	46	91
8			55	84	55	85

[a] Time and yield in case of ordinary DMF; [b] Time and yield in case of DMF-like ionic liquid

TABLE-3
COMPARISON OF OXIDATION OF SECONDARY ALKYL BROMIDES WITH SODIUM PERIODATE IN DMF AND DMF-LIKE IONIC LIQUIDS



Entry	Substrate	Products	Time[a]	Yield (%)[a]	Time[b]	Yield (%)[b]
1			40	84	40	86
2			45	90	45	92
4			45	78	50	80

5			50	62	50	66
6			40	76	40	80
7			55	71	50	83
8			40	78	40	84
9			50	61	50	69

[a]Time and yield in case of ordinary DMF; [b]Time and yield in case of DMF-like ionic liquid.

The wide structural diversity was employed for assessing the potential of the proposed novel ionic liquid. The results obtained are shown in Tables 2 and 3.

The major reason for softer conditions like reduced time duration, lower temperature lies in the highly polar nature of ionic liquid. Polar nature of ionic liquid facilitates the removal of halogen as a leaving group on the one hand and it stabilizes the polarized transition state on the other hand. These attributes of our designed DMF-like ionic liquid render it the best alternative to ordinary DMF for reactions whose outcomes are influenced by it.

Recycling efficiency: For each new experiment fresh DMF-like ionic liquid was used in order to check the extent of efficacy of this ionic liquid in all chemical reaction under uniform conditions. Recycle efficiency was also checked for the reaction that produced best yields *i.e.*, oxidation of benzyl bromide (Table-3), compound **2** and also its conversion to azide (Table-1), compound **3**. The results found are shown in Table-4.

TABLE-4
RECYCLING EFFICIENCY OF THE DMF-LIKE IONIC LIQUID FOR PERIODATE OXIDATION OF BENZYL BROMIDE AND BENZYL BROMIDE TO AZIDE

Number of recycles	1	2	3	4
Recovered ionic liquid	88	82	82	80
Product yield (%)[a]	89	86	85	80
Product yield (%)[b]	85	84	81	78

Yield[a] of aldehyde and yield[b] of azide.

Conclusion

A novel DMF-like task specific ionic liquid has been designed and synthesized efficiently through a viable synthetic scheme. This has been demonstrated to be acting both as green solvent and recyclable organocatalyst for reported reactions. This ionic liquid version of ordinary DMF can be used as a green alternate for not only all DMF-dependent reaction but many other applications can also be envisaged and performed. Due to such a wide number of applications it is, to best of our knowledge, only first ionic liquid of its nature with multipurpose applications. Couple of its application has been shown and rest of the application and other aspects of the given ionic are under study.

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