

Ionic Liquids (ILs) in Direct Reductive Amination (DRA): A Review and Studies on the One Pot DRA of Aldehydes in 1-Butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄) IL

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Abstract: Preliminary study in the Direct Reductive Amination (DRA) reaction of carbonyl compounds using green solvents i.e. Ionic Liquids as opposed to traditional solvents has been performed. Limitations (toxicity, cost, selectivity and addition of catalyst) of the traditional solvents led to interest on alternative green solvents. Thus, studies in the use of Ionic Liquids in the DRA of carbonyl compounds is emerging. Presented here is a review of ILs use in the DRA of aldehydes and ketones. The successes recorded, selectivity and recyclability have been highlighted in the review. Further, one pot DRA of various amines with aromatic aldehydes including sterically hindered aldehydes in 1-Butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄) IL is illustrated. The reactions proceeded selectively with excellent yield without the use of catalyst/protecting group. Trend in the selectivity of conversion revealed that Basic > Acidic and less/non Sterically hindered > Sterically hindered aldehydes. Importantly, the synthesis of amines through the DRA of aldehydes and amines (aliphatic and aromatic) with and without steric hindrance was achieved.

Keywords: Direct Reductive Amination, Ionic Liquids, Aldehydes

1. Introduction

Amines are important precursors in the synthesis of pharmaceuticals, agrochemicals and other useful building blocks for nitrogen containing synthetic polymers. Amines can be synthesized by a variety of processes including the reduction of nitro, cyano, azide, carboxamide derivatives or alkylation of amines (using alkyl halides or sulfonates) [1]. However, direct reductive amination (DRA) of carbonyls (aldehydes/ketones) with amines using a suitable reducing agent in a single operation (e.g. one-pot), is one of the most suitable model reactions for the synthesis of amines [1]. In addition, the DRA process offers a number of advantages that include shorter reaction pathways, brevity, wide commercial availability of substrates, generally mild reaction conditions, and exceptionally high functional group tolerance [2]. Similar to other organic reactions, the reductive amination reaction is achieved using a suitable solvent. However, most of the solvents are associated with expensive and flammable characteristics, utilization of complex catalysts and low product yield. In general the reaction mechanism includes the initial formation of an intermediate carbinolamine, which dehydrates to form an imine, the latter is then reduced to yield the amine product [1]-[2]. These steps can be achieved either by first isolating the imine which is further reduced or in one pot (direct) without isolating the imine [1], [3]

Catalytic hydrogenation and the use of hydride reducing agents have been described as the two most common methods for achieving DRA [1], [4]. A critical issue in this reaction is the selectivity of reducing the carbonyl compounds to the desired product (amine). Various factors are adduced to be responsible for this; substrate structure, electronic effect, effect of reducing agent, effect of the reaction conditions and solvent effect. Ionic liquids have been identified as organic salts that exhibit low vapour pressure, recyclability, wide range of polarities, high thermal

stability and tunability [5]-[11] therefore seem useful as ideal alternative solvents.

In view of their green nature, ILs have been employed in a variety of reactions including DRA [4],[12]-[15],

Despite the number of studies on DRA of carbonyl compounds, there are a few studies that have focused on the use of ILs as suitable potential solvent on DRA reactions. Hence, this paper aims to present a brief review in the use of ionic liquids in DRA reaction, and also present the results of a preliminary investigation on the DRA of aldehydes with amine in [BMIM]BF₄ ionic liquid without using a protecting group.

1.1 Ionic Liquids

Ionic Liquids are salts that contain large organic cations with a variety of anions and have melting temperatures below 100°C. Interest in the field of ionic liquids (ILs) began to develop when they were found to have great potential in various applications including organic synthesis [4], [5],[8],[16], [17],[18].

Applications of the first generation ILs; ethylammonium nitrate and the chloroaluminate are limited due to their instability to moisture [19], [9]. Against this backdrop, and due to the potential of ILs to replace the traditional organic solvents, stable ILs (BMIMBF₄ and BMIMPF₆) have been developed. The increasing interest in ILs research has led to more studies in the area of ILs. Studies have focused on various cations and anions, design and synthesis of both biodegradable and non-biodegradable ILs as well as knowledge about their toxicity/green nature [10],[19]. Moreover, understanding of the physico-chemical properties such as good solvent effects, tunability, negligible vapour pressure, wide liquidus range and good electrochemical window, have led to wider applications of ILs [16],[20]-[25].

Polarity is the commonly used concept to classify solvents. The IUPAC defines solvent polarity as "the sum of all possible, non-specific and specific, intermolecular interactions between the solute ions or molecules and solvent molecules, excluding such interactions leading to definite chemical alterations of ions or molecules of the solute" [5],[6],[26],[27]. Thus, Reichardt's betaine dye (ET(30) and ENT), Kamlet-Taft solvatochromic parameters and Nile red are used as empirical scales for solvent polarity. Accordingly, Poole C. F in 2004, concluded that all evidence points to the ILs as a unique class of polar solvents. For example, he observed a polarity value for alkylammonium nitrate equivalent to the polarity of water. Also, the tetraalkylammonium sulfonate salts have smaller values, between 0.4 and 0.65, similar to the 1, 3 dialkylimidazolium salts, which are more representative of polar solvents such as dimethyl sulfoxide and dimethylacetamide at the lower end of the range and formamide and aliphatic alcohols at the higher end [5].

Elsewhere, the polarity of ILs has been reported to be an anionic contribution [22]. For example, it has been showed that 1-alkyl-3-imidazolium ILs with anion [PF₆]-, [BF₄]-, [(CF₃SO₂)₂N]- and [NO₃]- are in the same polarity region than alcohols such as methanol, ethanol and butanol. Also, it has been showed that ILs BMIMPF₆, C8MIMPF₆, BMIMNO₃ and N-BPyBF₄ are more polar than acetonitrile and less polar than methanol [22]. Thus, implying a direct proportionality of ionic liquids polarity to its anionic polarity.

Lungwitz et al. 2010 concluded that dipolarity/polarisability of ILs, is a function of cation-anion interaction rather than only a function of individual anion or cation properties. The result of their study shows that, for [RMIM] ILs with strongly coordinating anions such as chloride or nitrate, a strong cation-anion interaction has an increasing effect on the dipolarity/polarisability and decreases with increasing chain length R [15].

While taken into account the reason of Flory-Huggins theory that the short-range interactions between anions, cations, and molecules of the solute has been suggested that ILs can possess additional solvent power if non-coulomb interactions between anions and cations are repulsive [28].

In his review, Welton T., 2004 reported the use of Abraham solvation model for solvent-solute interaction which has been used to determine the solvent properties of ILs [20]. This led to the conclusion that ILs interacts with solute via high dipolar and dispersion forces and also acting as strong hydrogen bond bases. Moreover, the hydrogen bond basicity was dominated by the choice of anion and the hydrogen bond acidity was observed to arise from the cation of the ILs. It was also found that ILs with aromatic ions will be more capable of π - π and n - π type interactions with solutes [20].

Thus the ability to synthesis ionic liquids to the desired (polar or less polar) characteristics led to their being termed designer (tunable) solvents and consequently used in various applications. One of the many applications by which ILs have shown positive impacts is their use as solvents for synthesis and catalysis in a variety of reactions [5],[6],[25]-

[30]. They are being used either as solvents or catalyst in organic reactions that include among others Friedel Craft alkylation, purification of gases, Heck reaction, oxidation and hydrogenation reactions, Suzuki cross-coupling, esterification, Peptide synthesis, Baylis-Hillman reaction, Beckmann rearrangement, Diels-Alder reaction, Halogentaion of organic compounds and Reduction of aldehydes and ketones otherwise known as the direct reductive amination reaction (DRA) [4], [8], [9], [18], [19], [23], [26], [31], [32], [33].

1.2 DRA in ILs

Studies on the reductive amination reaction of aldehydes and ketones using ionic liquids are limited, although, some of the few studies have shown some potential of using ionic liquids in the synthesis of both aldehydes and ketones. Different types of ionic liquids, mainly based on the imidazolium and pyridinium cation where studied by several authors. Also, anions such as NTf₂ and BF₄ have all been used and various levels of success were recorded.

Ohta et al achieved the DRA of carbonyl compounds with amines using three different ionic liquids which includes: [BMIM][BF₄], [BMIM][Cl] and [EMIM][Cl]. Besides, the effect of catalyst addition to the selectivity of the reaction was also studied; therein the DRA of ketones in ionic liquids other molecular solvents were investigated. For the DRA of ketone substrates, the ionic liquid BMIMBF₄ was found to be superior to other organic solvents used including EMIMCl and BMIMCl [12]. Furthermore, the counter anion of the ionic liquid has a significant influence on the selectivity, and at the same time, a high reaction temperature was found to be crucial for the excellent selectivity [12]. Also, the combination of BMIMBF₄ and the irridium catalyst gave the best selectivity for the DRA of ketone, thus raising the significance in the use of catalyst. Overall excellent yields in the range of 95%-97% were achieved [12].

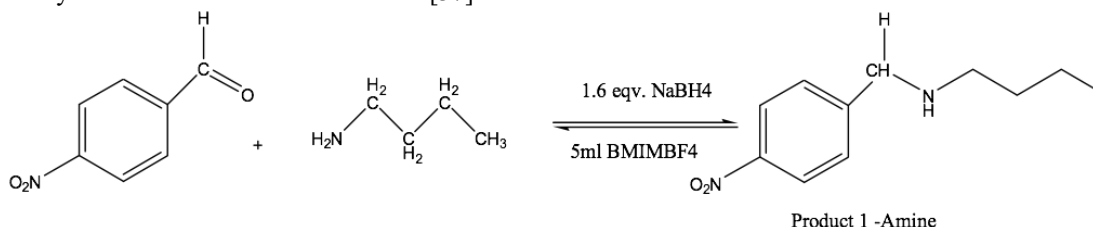
Similarly, anionic contribution was found to play a major role in the selectivity and reaction rate when Nagaiah et al described the combination of water as a co-solvent in ILs for the DRA of carbonyl compounds. therein, the reaction was investigated using NaBH₄ as a reducing agent in two different ionic liquids; BMIMBF₄ and BMIMPF₆ and the former was found to be more effective in terms of conversion (selectivity) and reaction rates [34]. Their work involved reacting of alicyclic/aromatic aldehydes and amines or imines containing up to two different substituent groups. Excellent yields of not less than 81% irrespective of the type of aldehydes or amines were recorded [34].

Among the most interesting studies carried on the use of ionic liquids in DRA reaction is the one carried by Hardacre et al in which fenpropimorph was produced [35]. Although the imidazolium based ionic liquid BMIMBF₄ was used, so far, the DRA studies in ionic liquids by this research group appeared to be the only one in which the ionic liquid based on pyridinium cation was used. The one-pot synthesis of the fungicide fenpropimorph has been achieved through two different synthetic strategies. Heck coupling followed by reductive amination and aldol condensation followed by

hydrogenation/reductive amination [35]. Homogenous and heterogenous palladium catalysts were also utilised in the reaction to provide catalyst/solvent system suitable for recycling [35].

In addition, Prasad et al reported the DRA of aromatic aldehydes/ketones with various (aromatic and aliphatic) amines using NaBH₄ in the bronsted ionic liquid BMIMBF₄ [36]. The group was the first to report the generation of an imine in the ionic liquid, thus corroborating other reports on the formation of imine or iminium ion in DRA reaction [36]. Yields of between 68 – 97% were recorded [36].

The chemistry of organotin has drawn special attention in their use as catalyst/reagents in organic synthesis [37]. Thus, Legoupy and co-workers were able to obtain DRA of carbonyl compounds in an organotin reagent supported on an ionic liquid catalyst using phenyl silane as a reducing agent [37]. Interestingly, the one-pot solvent free reduction of aldehydes and ketones with different primary and secondary cyclic and acyclic amines developed produced products with high efficiency and excellent yields [37]. Further the method facilitates purification of the products, thus minimising the contamination by tin as obtained in other reactions [37].



Scheme 1: Reductive amination of nitrobenzaldehyde in IL

Products were assayed by thin-layer chromatography (TLC) on alumina coated plates. Chromatograms were developed with chloroform/hexane, ethylacetate/hexane or methanol/chloroform. The preparation of purified products was carried out in the following steps: (a) solvent extraction, (b) flash chromatography, (c) column chromatography and (d) crystallisation. The purified products were consequently characterised by NMR. NMR was recorded in CDCl₃ on a Bruker Advance 400 NMR spectrometer, operating at 300 MHz.

3. Results

The choice of the different compounds as provided in Table 1 is to establish the reactivity and/or selectivity of the DRA reaction in the ionic liquid BMIMBF₄ with respect to hydrocarbon groups. One common challenge associated with

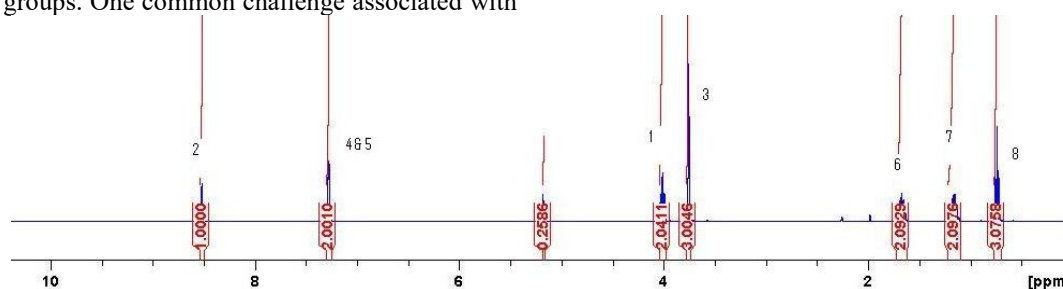
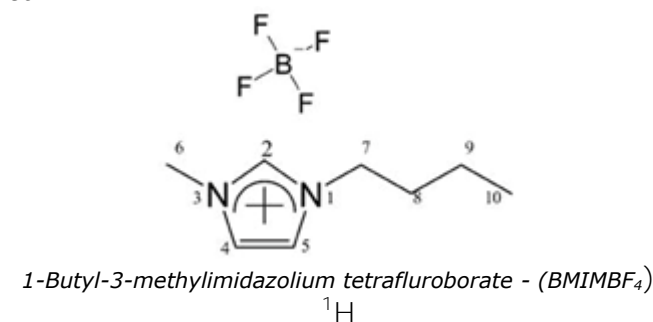
Asymmetric reductive amination of carbonyl compounds using N,N,N - Tributylpropanaminium based novel chiral IL has been achieved [14]. The chiral IL was found to play a dual role; as a medium and reducing agent for proficient conversion of ketones to amines. The chiral ILs were found to be efficient in promoting the reductive amination of carbonyl compounds with aromatic amines to afford chiral secondary amines. The study did not only prove the stereoselectivity of the reaction, but it also proved the recyclability and up to three times reusability of the ILs. yield of over 70% has been recorded in one of the reaction [14].

2. Experimental Section

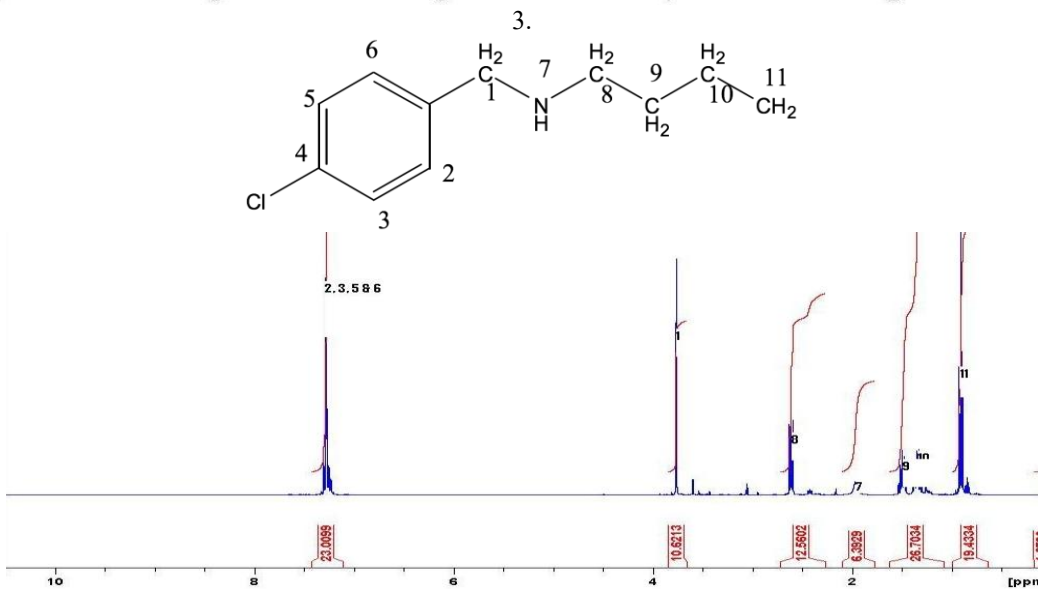
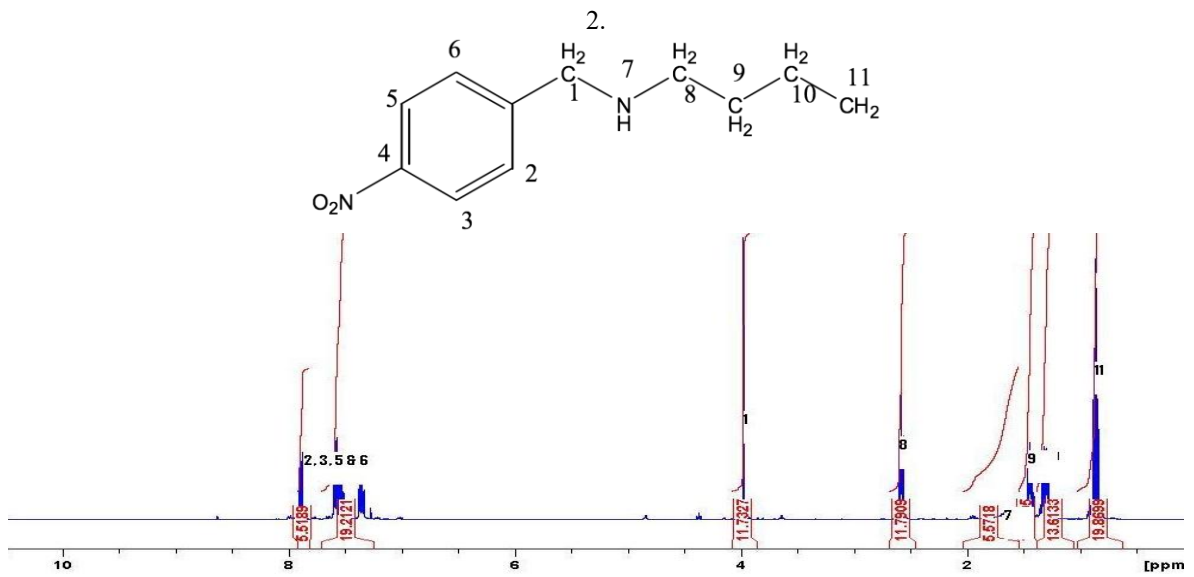
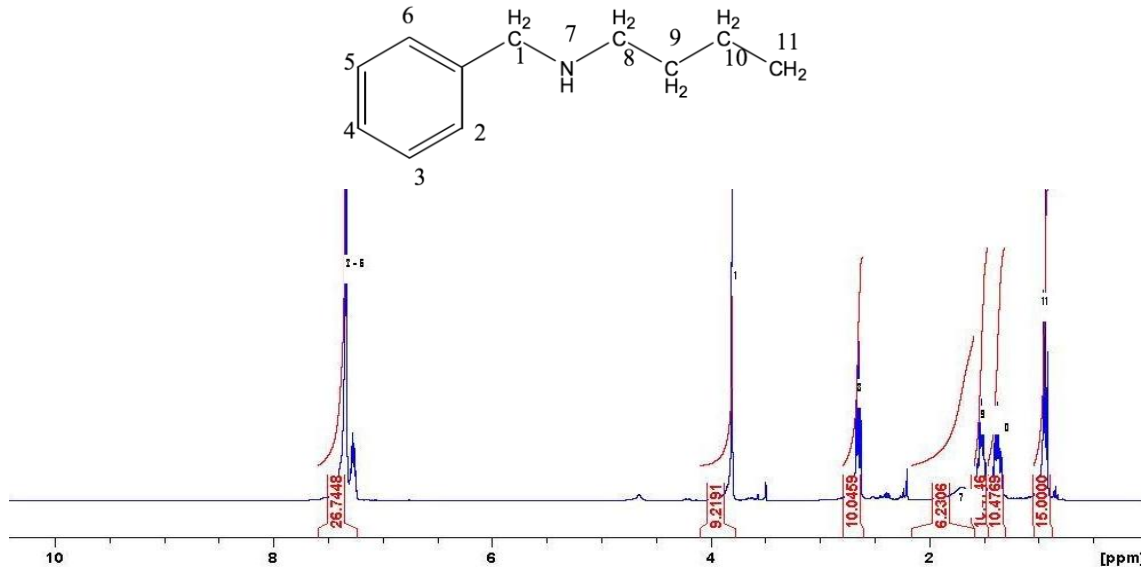
2.1 General Consideration

Chemicals used in the experiment were commercially available. IL synthesis and DRA in IL (Scheme 1) were carried based on the literature provided procedures [1],[1],[38].

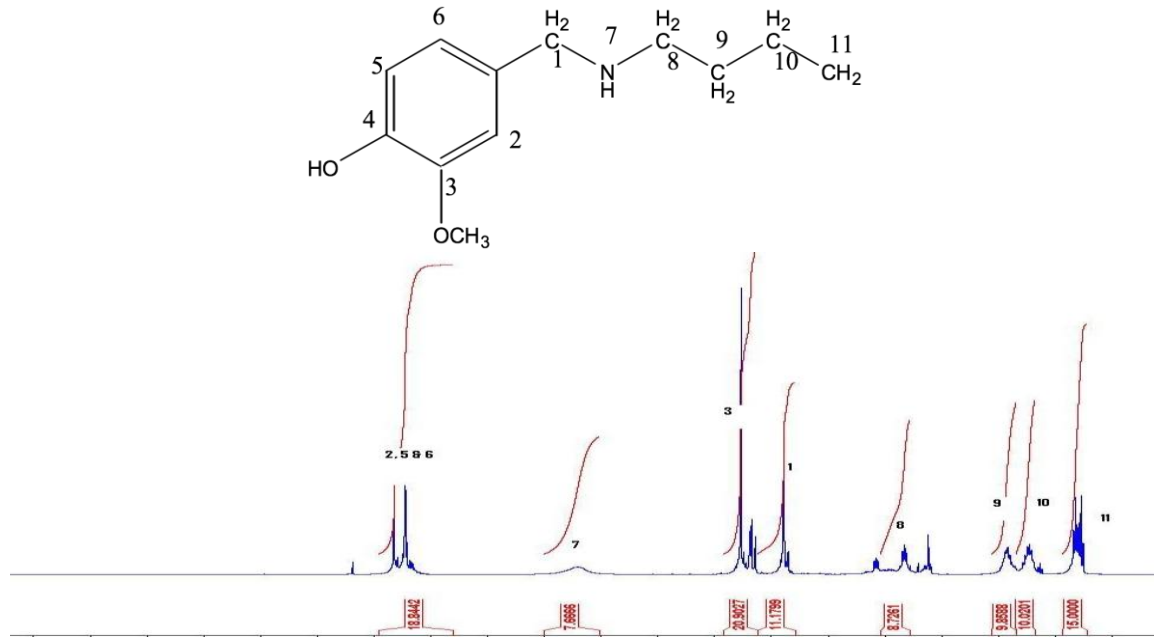
all the reactions is the formation of unidentified by products. While in all the reactions, the desired products were obtained on different yields (Table 1), the reaction between aldehydes and aliphatic amines appeared to be more favourable. Although favourable, the reaction times were between 15-24 hrs compared to the aromatic reaction time of 30 mins all at 35 °C.



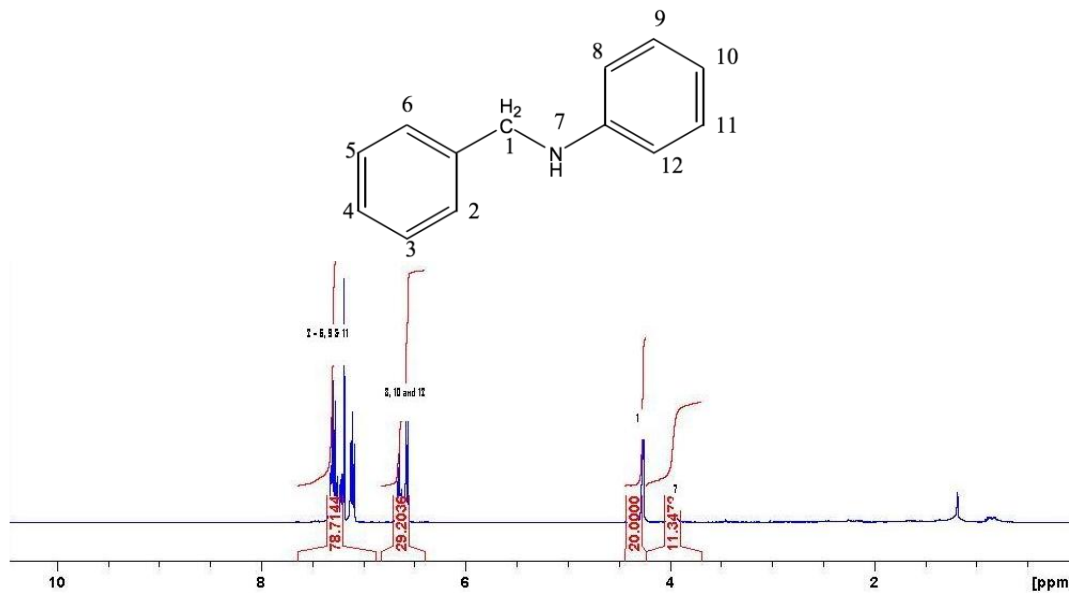
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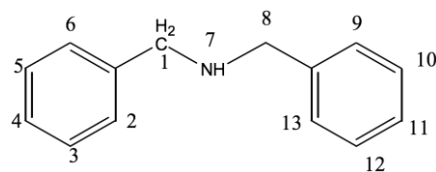
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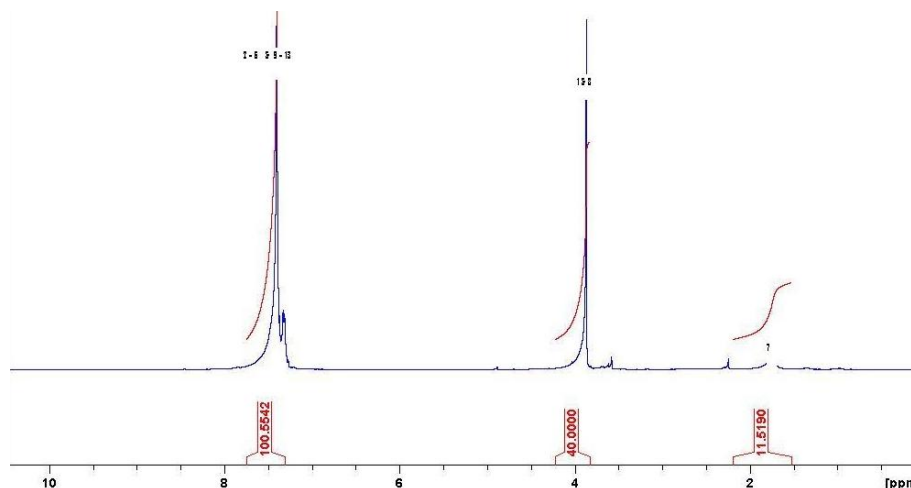


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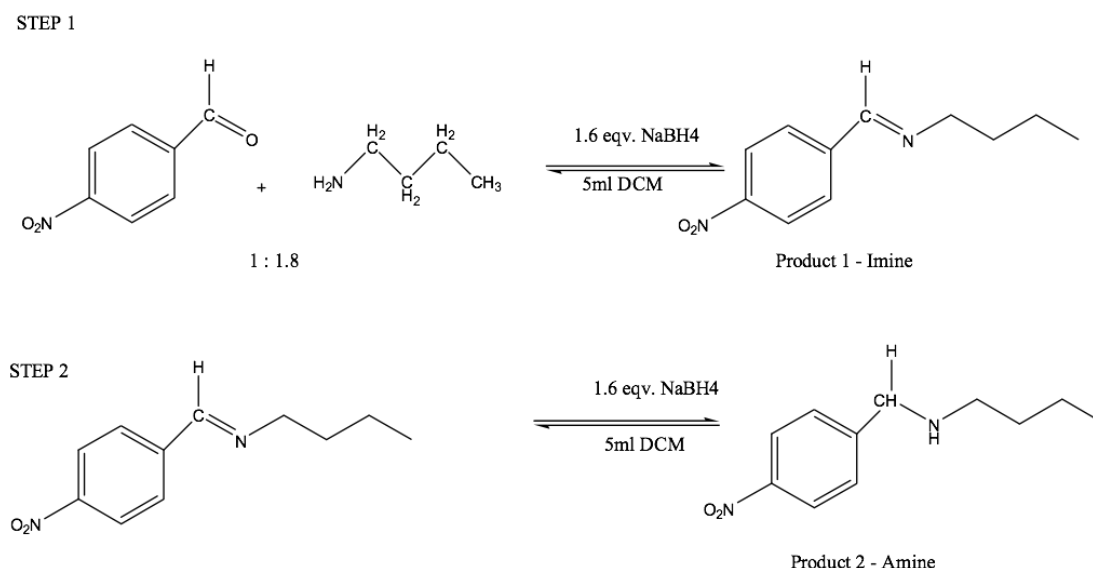
Result Summary

4. Discussions

This study set out with the aim of investigating the DRA of aldehydes with amine in the BMIMBF₄ IL, in the absence of a protecting group, catalyst or co-solvent. As previously stated, studies on the use of ionic liquids in DRA reaction are sparse. In the few instances, where the various ILs were used, good to excellent yields of the desired products were obtained in the presence of either catalyst or co-solvent [12],[14],[34]-[37]. As a result, this preliminary study focused on the use of BMIMBF₄ ionic liquid for the DRA of

the carbonyl groups. Another area of focus in this study is to investigate further the DRA in BMIMBF₄ of the carbonyl groups that have more than one functional group attached to them and therefore bridge the existing gap in this field of study.

Furthermore, the present study is aimed at one pot synthesis of amines by DRA in BMIMBF₄ unlike the stepwise method (Scheme 2). In this instance, the intermediate product (imine) is first formed, while the final product (amine) is formed only after further reduction of imine (Scheme 2).



Scheme 2: Reductive amination of nitrobenzaldehyde in DCM

Scheme 1 was found to be reproducible, as such employed all through the DRA in the ionic liquids BMIMBF₄. The outcome of the reaction in the ionic liquids was promising. Thus, the products; imine and amine were seen on TLC to be more pronounced at RF values of 4.5 and 2 respectively. Neat and reproducible resolutions were found when the mobile phase is either chloroform or ethylacetate/hexane than in methanol/chloroform which gives very low resolution. Generally, the order of separation of the products was observed to be due to increase the molecular weight. Also, the observed separation scenario is the appearance of

unexpected spots that have the same RF values with the desired products, hence the use of ethylacetate/hexane. Studies have shown the possibility of obtaining side products in many DRA reactions; alcohol and other amine substances are so far among the identified side products[1],[3],[12]. This may undoubtedly be another reason behind the non-separation of some side products from the desired products in our experiments.

Assigning of protons in the above products spectra, is based on the following:

- The signal integration ratio as provided in the spectra e.g. 5 and/or 10 to represent a proton, the deciding factor in the total number of proton atoms in a structure. Though the signal integration in some instances are not exact, they are however approximately 1:1.
- The chemical shift is due to electron density, hybridisation state and the nature of any pi bonding electron density; for instance protons attached to aromatic rings are influenced the most due to the induced ring current of the aromatic pi electrons, thus appear in the down shift range of between 6.5ppm-8.5ppm and those attached to the alkenes appear between 4.6ppm-5.7ppm. Those appearing at the up shift are the methyne (=ch-). Hence the appearance of the nh group throughout the spectra.
- Peak splitting as in the case of the central ch2 and ch3, thus following the n+1 rule. The proton around an electronegative group, though appear at the downfield also obey the rule.
- In general, we were guided by the summary of the coupling constants of protons (*para* or *ortho*) substituted.

Table 1: Summary of Results

Reactants	Entry	Yield (%)
Benzaldehyde + Butylamine	No. 1	83
Nitro-benzaldehyde + Butylamine	No. 2	72
Chloro-benzaldehyde + Butylamine	No. 3	64
Vanillin + Butylamine	No. 4	71
Benzaldehyde + Aniline	No. 5	55
Benzaldehyde + Benzylamine	No. 6	81

The reason behind the yield/conversion disparity might be due to the functional groups attached to the aromatic aldehydes. Steric hindrance in amines has been attributed to be a limitation for DRA reaction with aldehydes [1],[4]. This could also be the case for either sterically hindered aldehydes or aldehydes containing electron withdrawing groups as in the case of nitro benzaldehyde and vanillin reported herein. Hence, the reaction with aniline, did not give good yield as compared to that with benzylamine; thus, two proposals can be made; the nitrogen (an electron withdrawing group) which is directly attached to the benzyl ring and/or the solvent polarity might be responsible. The reaction with benzylamine however, was possible due to perhaps the introduction of the methyn group which relatively increases the basicity.

Furthermore, the selectivity of the IL towards aliphatic aldehydes and aliphatic amines infer that basicity and the absence of other functional group are a driving factor in DRA reaction using BMIMBF₄ ionic liquid.

The reactivity of aldehydes [1] can be a good reason behind the DRA of nitro benzaldehyde and vanillin with benzylamine (Entry 4, 5, & 6). Considering the yield with vanillin compared to nitro benzaldehyde, it is obvious that there is likely a better protection of the OH and the OCH₃ in vanillin by the ionic liquid than the nitro group in nitro benzaldehyde.

5. Conclusion

Conventional solvents currently account for most of the successes recorded in amine production through the direct reductive amination reaction. However, their limitations (toxic, need for protecting groups and longer reaction chain) brought about the need in the use of ionic liquids as alternative solvents. Scientific studies have confirmed that ionic liquids are non-combustible, recyclable and tunable among others, thus, termed green solvents. Consequent upon their green nature, ionic liquids are being used for various organic and in-organic applications.

In this study, the one pot synthesis of amines through the DRA of aldehydes and amines (aliphatic and aromatic) with and without steric hindrance in IL BMIMBF₄ has been achieved. However, more basic studies are needed in reducing the unidentified side products that accompany the reaction and establishing the minimum percentage purity of the IL that will make it feasible for the reaction.

Overall, the first review on the use of ionic liquids in DRA is presented. Further more, conversion trend is established to be in the order *Basicity > Acidity and less/non Sterically hindered > Sterically hindered aldehydes*.

6. Acknowledgement

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http://smos.sogang.ac.kr/wiki/images/8/85/Bmim_bf4_2.jpg

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