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## A SOLVENTLESS PROCESS FOR THE SYNTHESIS OF IMIDAZOLIUM-BASED IONIC LIQUIDS

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### ABSTRACT

**Benzyl imidazole (1a) was successfully synthesized from the N-alkylation of imidazole with benzyl bromide. The product (1-benzylimidazole) was further alkylated using neat butyl bromide to yield an imidazolium ionic liquid, (1-Benzyl-3-butylimidazoliumbromide (2a)). Similarly, 1-methylimidazole (1b) was reacted with benzyl bromide to yield 1-Methyl-3-butylimidazolium bromide (2b). The synthesized compounds were characterized by spectroscopic techniques and elemental compositions were established on the basis of C, H, N elemental analyses. Proton NMR of both ionic liquids 2a and 2b reveals the presence of downfield signals at 10.08 and 11.681 ppm respectively, which were assigned to the C-2 proton of the imidazole rings in the respective 2a and 2b confirming the successful synthesis of the two ionic liquids.**

**Key words: Ionic liquid; imidazole; alkylation; solventless-synthesis**

### INTRODUCTION

To date, most manufacturing processes in the fine chemical, agricultural, and pharmaceutical industries are carried out mainly in organic solvents. This results in the discharge of a significant amount of solvents into the environment. However, the majority of common organic solvents are toxic, for example; chlorinated organic solvents are suspected carcinogens, and are harmful to aquatic life (McDermott and Heffron, 2013). The increasing concern about environmental safety and protection leads to increased interest in developing a greener alternative to the use of organic solvents. Studies in this area have uncovered cleaner and relatively benign chemical processes that avoid or minimize the use of traditional organic solvents. Among the remarkable discoveries are the solvent-less (neat) reactions (Tanaka, 2004), reactions in supercritical carbon dioxide (Gladysz and Curran, 2002), and reactions in aqueous media (Li, 2005; Jessop and Leitner, 2007). In a similar development, inorganic solvents such as ionic liquids and per-fluorinated liquids are being explored as alternatives to most organic solvents (Jessop and Leitner, 2007). Ionic liquids (ILs) are organic salts with melting points below 100°C. They are distinctly different from common solvents, in that they are composed entirely of ions. Furthermore, while common salts contain small anions (Cl<sup>-</sup>, ) and cations (K<sup>+</sup> and Na<sup>+</sup>) closely packed in an ionic lattice, forming high melting point crystals, that limit

their application as a reaction media, ionic liquids contain organic or inorganic anions and bulky organic cations. The ions are weakly held resulting in liquids or solids of much lower melting points (Deetlefs *et al.*, 2006; Blesic *et al.*, 2007). They are generally nontoxic, inflammable, thermally and chemically stable, low viscous and can dissolve both organic and inorganic compounds (Seddon, 1997; Noda *et al.*, 2001; Earle *et al.*, 2006; He, 2015). The cationic components are commonly ammonium, phosphonium and N-substituted heterocyclic compounds of pyridines, pyrrolidines and imidazoles with varying N-alkyl substitutions (Freire *et al.*, 2009; Gao *et al.*, 2008; Kogelnig; Padaszyński and Domanska, 2013; Breitbach, 2008; Tshemese *et al.*, 2018).

The imidazolium-based ILs usually composed of an imidazole ring with substitution on position 1 and 3 (i. e the N atoms). This class of ILs offers unique and interesting properties as they contain both hydrophilic and hydrophobic regions. They have found applications as ligands in organometallic complexes and catalysts in organic synthesis (Ibrahim *et al.*, 2018a; Nguyen *et al.*, 2017; Gok, 2014; Aktas, 2013) and electrostatic stabilization of nanomaterials (Tshemese *et al.*, 2018). In the current study, we report a straightforward and solventless protocol for the synthesis of imidazolium-based ionic liquids (IILs) with methyl, butyl, and benzyl side chains. The IILs were characterized by <sup>1</sup>H NMR, FTIR, and elemental analyses.

## MATERIALS AND METHODS

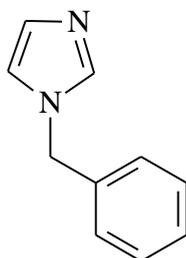
### Materials and Instrumentation

Imidazole and alkyl bromides were purchased from Sigma Aldrich and were used as received. All solvents used were of analytical grade and were used without further purification. The products were purified either using microcolumn chromatography or by washing with an appropriate solvent.  $^1\text{H}$  NMR spectral data were obtained using Joel 400 MHz NMR machine (Joel 1500 model). Chemical shifts were recorded in ppm using tetramethylsilane as reference and  $\text{CDCl}_3$  as solvent. Fourier transform infrared (FT-IR) spectra were recorded using an Agilent technology FT-IR spectrophotometer in wavenumber ( $\text{cm}^{-1}$ ). Elemental analyses were carried out with a PerkinElmer Series 11 (CHNS/O) Analyzer 2400.

### Synthesis of 1-benzyl Imidazole (1a)

Imidazole (10.0 mmol, 0.68 g), potassium hydroxide (12.0 mmol, 0.67 g), and acetonitrile (80.0 ml) were added to a 250 ml two necked round bottom flask and stirred for 1 hour at room temperature. To the stirred mixture, benzyl bromide (11.0 mmol) was added, the mixture was refluxed under magnetic stirring at  $80^\circ\text{C}$  for 24 hours. After the completion of the reaction, the solvent was allowed to evaporate in a fume hood and the crude product was extracted twice with ethyl acetate (30 ml) and distilled water (20 ml). The separated organic layer was dried and washed several times with n-hexane to obtain thick brown oil. The product was further purified using silica gel column chromatography with ethylacetate/diethyl ether (70:30) as eluent (Ibrahim *et al.*, 2018b; Nguyen *et al.*, 2017).

### 1-Benzylimidazole (1a)

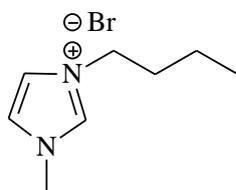


Thick brown oil; 0.97 g, Yield (61%),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 5.01 (s, 2H  $\text{NCH}_2$ ), 6.83 (s, 1H  $\text{NCH}$ ), 7.01 (s, 1H  $\text{CCHN}$ ), 7.26 ( $\text{CDCl}_3$ ), 7.28 - 7.07 (m, 5H Ar-H), 7.49 (s, 1H  $\text{NCHN}$ ). **FT-IR** ( $\nu$   $\text{cm}^{-1}$ ); C=N 1659.34, C=C aromatic 1451.48, =C-H aromatic 3029.87, C-N 1033.50, C-N 1074.27, mono substituted benzene 713.11. Anal. Calcd for ( $\text{C}_{10}\text{H}_{10}\text{N}_2$ ) Calc.; C (75.94), H (6.32), N (17.70). Found; C (77.01), H (6.21), N (17.14).

### Solvent Free Synthesis of the Ionic Liquids (2a and 2b)

To a 25 mL round bottom flask, 1-alkyl imidazole (0.50 mL) and n-bromobutane (4.00 mL) were introduced. The mixture was heated to  $70^\circ\text{C}$ . The temperature was maintained under magnetic stirring for 16 h. After completion of the reaction, the mixture was cooled down to room temperature. The oily product was separated from excess bromobutane by decantation. The product obtained as thick brown oil was dried and kept in a closed container before further use (Ibrahim, 2018; Nguyen, 2017).

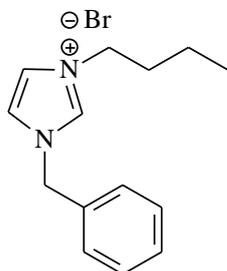
### 1-methyl-3-butyl imidazolium bromide (2a)



Brown oil, 95% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 10.08 (s, 1H,  $\text{NCHN}$ ), 7.70 (s, 1H,  $\text{NCHC}$ ), 7.58 (s, 1H,  $\text{CCHN}$ ), 4.363 (t,  $J = 6.4$  Hz, 2H  $\text{NCH}_2\text{C}$ ), 4.13 (s, 3H,  $\text{NCH}_3$ ), 1.92 (m, 2H,  $\text{CH}_2$ ), 1.41 (m, 2H,  $\text{CH}_2$ ), 0.97 (t,  $J = 6.8$  Hz,

3H,  $\text{CCH}_3$ ), **FT-IR** (Neat) ( $\nu$   $\text{cm}^{-1}$ ); C=N 1629, C=C 1566, C-N 1167,  $\text{CH}_3$  2929; **Anal.** Calcd (found) for  $\text{C}_8\text{H}_{15}\text{BrN}_2$ ; C 43.84(43.08) H 6.85(6.77) N 12.78(12.51).

### 1-benzyl-3-butyl imidazolium bromide (**2b**)



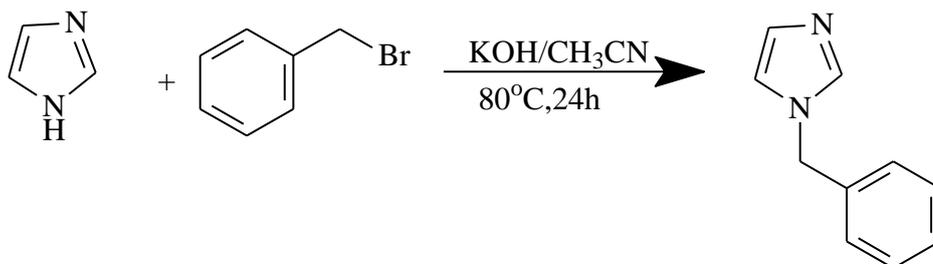
Brownish gummy oil, 0.38 g, Yield (79 %),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.10 (t,  $J = 8.5$  Hz, 3H  $\text{CH}_3$ ), 1.60-1.54 (m, 2H,  $\text{CH}_2$ ), 2.20 - 2.12 (m, 2H  $\text{CH}_2$ ), 4.69 (t,  $J = 7.2$  Hz, 2H,  $\text{NCH}_2$  - Aliphatic), 5.01 (s, 2H  $\text{NCH}_2$ -Aromatic), 6.83 (s, 1H  $\text{CCHN}$ ), 7.26 ( $\text{CDCl}_3$ ), 7.28 - 7.01 (m, 5H Ar-H), 7.49 (s, 1H  $\text{NCHC}$ ), 11.68 (s, 1H  $\text{NCHN}$ ). **FT-IR** ( $\nu$   $\text{cm}^{-1}$ ); C=N 1666.33, C=C aromatic 1451.41, =C-H aromatic 3029.77, C-N 1033.75, C-N 1078.66, C-H aliphatic 2925.80, mono

substituted benzene 702.27. **Anal.** Calcd for ( $\text{C}_{14}\text{H}_{19}\text{N}_2\text{Br}$ ) Calc.; C (56.94), H (6.44), N (9.49). Found; C (56.78), H (6.69), N (9.27).

## RESULTS AND DISCUSSION

### Synthesis of 1-Benzylimidazole

1-Benzylimidazole was synthesized in good yield using the procedure described above and represented in scheme 1.

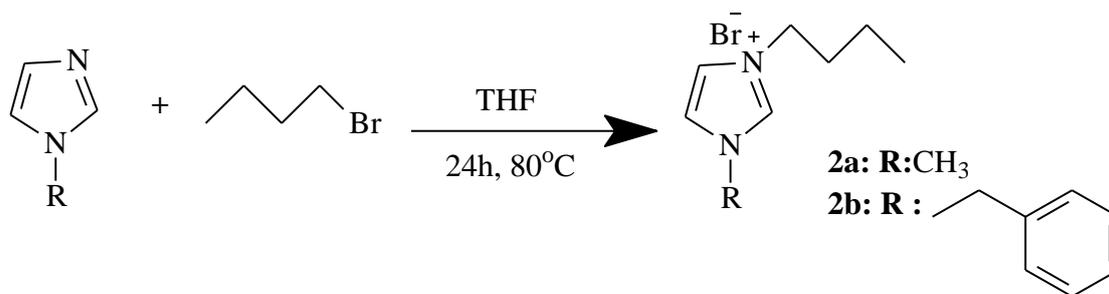


### Scheme 1: Benzylation of imidazole using benzyl bromide

The first step in preparing N-benzyl imidazole using benzyl bromide involves the deprotonation of the Nitrogen atom by using a strong base (potassium hydroxide), so as to make the deprotonated nitrogen nucleophilic enough to attack the primary carbon of the benzyl bromide to generate the corresponding N-benzyl imidazole. It is necessary to start making the  $\text{SP}^2$  nitrogen more nucleophilic by deprotonation through constant stirring at room temperature prior to adding the benzyl bromide into the mixture so as to avoid getting the benzyl group being attached to the other nitrogen instead. The purity of the synthesized product was monitored using thin-layer chromatography and the pure product was obtained through silica gel microcolumn chromatography. The product N-

benzyl imidazole obtained as thick brown oil at the end of the reaction was isolated in a yield of (61%). From the  $^1\text{H NMR}$  spectrum of **1a**, the methylene protons of the benzyl group were found at 5.02 ppm as singlet peaks. This indicates the successful N-benylation of the imidazole. Also, the signals at chemical shifts 7.01 - 7.28 ppm are indicating the presence of aromatic protons. The result obtained from the elemental analysis shows consistency between the experimental values and the theoretical values. Further, the FT-IR data as well as literature reports (Ibrahim *et al.*, 2018b; and Sahin *et al.*, 2017) of the compound support the presence of the functional groups in the expected structure.

## Synthesis of the Imidazolium Ionic Liquids (IILs)



**Scheme 2:** Alkylation of 1-alkylimidazole with butyl bromide

The 1,3-dialkylatedimidazolium bromides (IILs) **2a** and **2b** were synthesized in good yields (95 and 79 % respectively) from the reaction of a commercially available 1-methylimidazole (**1b**) and 1-benzylimidazole (**1a**) respectively, with butyl bromide (Scheme 2). The <sup>1</sup>H NMR of the 1-Methyl-3-butylimidazolium bromide (Figure 2) and 1-Benzyl-3-butylimidazolium bromide (Figure 3) reveals the presence of downfield signals at 10.08 and 11.681 ppm respectively,

which were assigned to the C-2 proton of the imidazole rings in **2a** and **2b** respectively. So also, the presence of multiple signals around 2.20 - 1.08 ppm was assigned to the CH<sub>3</sub> and CH<sub>2</sub> of the butyl group, which were absent in the proton NMR spectrum of the N-benzylimidazole. This information, coupled with other data obtained from the FT-IR and elemental analyses were used to confirm the formation of the two imidazolium based ionic liquids.

## CONCLUSION

Ionic liquids, 1-Methyl-3-butylimidazolium bromide (**2a**) and 1-Benzyl-3-butylimidazolium bromide (**2b**) were successfully synthesized in excellent isolated yields, from a direct alkylation of the corresponding 1-methyl imidazole using bromobutane as alkylating reagent. The products were confirmed using spectroscopic and analytical techniques. The

method was found to be easy and does not require solvent, additive or catalyst, therefore, the technique is recommended for green synthesis of ionic liquids in commercial quantity. The ionic liquids synthesized have the tendency of being used as ligands in complexes, and as solvents or phase transfer catalysts in organic synthesis.

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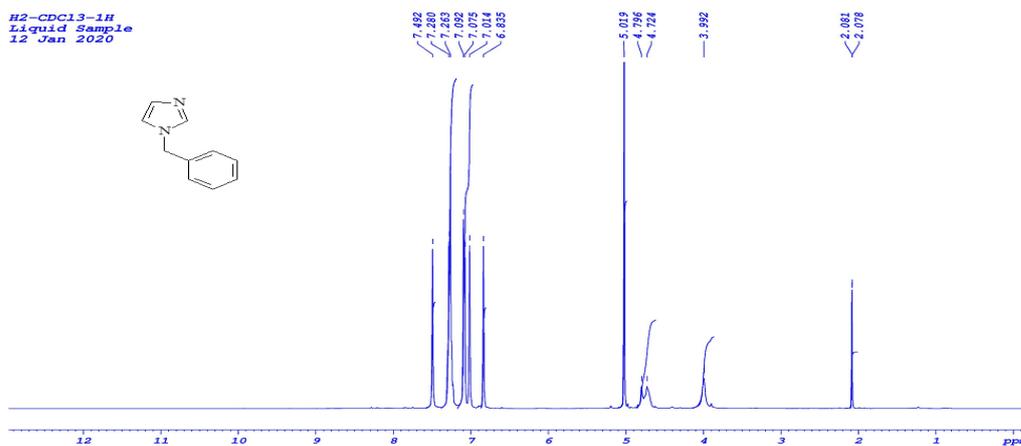


Figure 1. Proton NMR Spectrum of Compound 1b

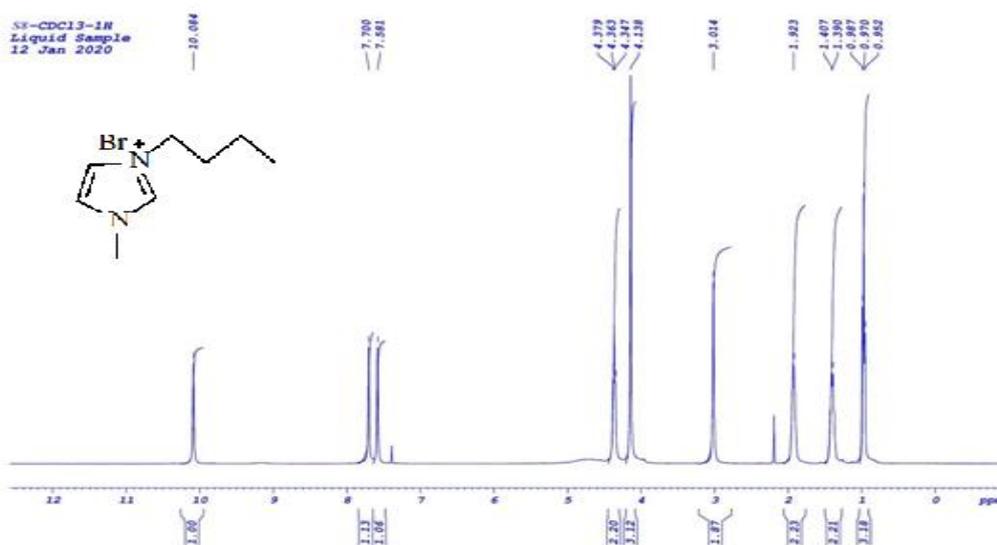


Figure 2. Proton NMR Spectrum of Compound 2b

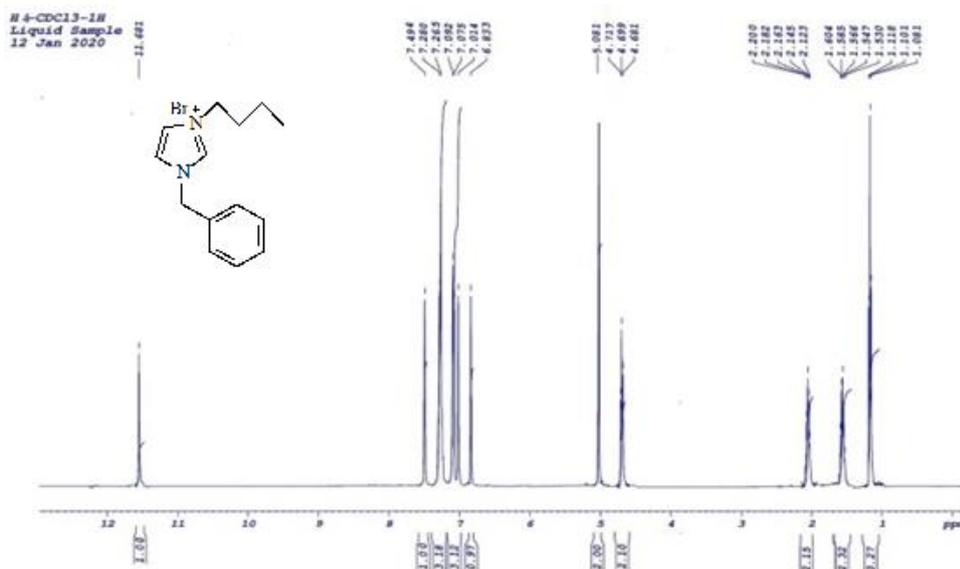


Figure 3. Proton NMR Spectrum of Compound 2b