

Ionic liquid i.e. 1-Pentyl-3-methylimidazolium bromide mediated synthesis of 2-phenylbenzoxazole

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Abstract: An efficient and green synthesis of 2-phenylbenzoxazole have been carried out by a simple condensation of 2-aminophenol and aromatic aldehyde in an inexpensive ionic liquid i.e. 1-pentyl-3-methylimidazolium bromide ([pmIm]Br) by microwave irradiation under solvent free condition. Initially, imidazolium based ionic liquid i.e. 1-Pentyl-3-methylimidazolium bromide [pmIm]Br have been synthesized by microwave irradiation from 1-methylimidazole and n-pentyl bromide. The structure of newly synthesized ionic liquid and 2-phenylbenzoxazole have been confirmed by spectral studies such as UV-Vis, FT-IR and ¹H-NMR spectroscopy techniques. Ionic liquid i. e. [pmIm]Br as a reaction media offers several advantages including non-toxic, non-corrosive, shorter reaction time, high yield of the products, mild reaction conditions as well as simple experimental and isolation procedures.

Keywords: Ionic liquid, Microwave, [pmIm]Br, Imidazolium, Catalyst-free, Green chemistry

I. INTRODUCTION

The development of green and environmentally benign green synthetic procedures is one of the apex priorities for today's researchers. It's a matter of great necessity to exploit substitutes for organic solvents and highly effective nontoxic green catalysts to reduce environmental pollution. Ionic liquids as green solvents have become a point of interest of recent synthetic green chemistry because of their particular nontoxic and green characters. Among green synthesis technologies modern synthetic design demands high efficiency in terms of minimization of synthetic steps together with maximization of complexity of molecules [1, 2].

Ionic liquids means the organic liquids completely composed of ions at room or near room temperature. They have particular characters such as environment friendly, recycled use, very low vapour tension, non-flammability, high thermal stability, high polarity and non-volatility. They provide new chemical reaction surroundings for chemists and have been used in chemical separation, electrochemistry and so on [3, 4]. The application of microwave irradiation in synthetic chemistry is a fast-growing research area since this method has opened up the possibility of realizing the fast synthesis of organic compounds. From the perspective of microwave chemistry, the strong polar nature of ionic liquids makes them ideal reaction medium in microwave-assisted organic reactions [5-8].

Ionic liquids have previously been reported as alternative 'green' solvents for extensive range of reactions. However, in addition to likely concerns about the recyclability of ionic liquids there have also been concerns hoist over the biodegradability or ecological perseverance of ionic liquids [9]. A series of imidazolium compounds were shown to be inadequately biodegradable and it was established that bacteria did not use them as a starting place of carbon under the circumstances of the investigation making them potentially constant pollutants [10].

The 2-arylbenzothiazole and 2-phenylbenzoxazole nucleus constitutes the core unit of many therapeutic agents including antitumour drugs. Thus, synthesis of these heterocyclic systems is of much interest and a number of procedures have been developed [9]. However, many of these procedures are associated with one or more disadvantages such as involving expensive and toxic catalysts, hazardous and carcinogenic organic solvents like nitrobenzene, acetonitrile, dioxane for reactions, multistep process and non-recovery of the catalyst [10, 11].

Hence, a simple, green and efficient procedure avoiding these drawbacks will be of much use. Ionic liquids usually divided into two classes, i.e., pyridine class and imidazole class. It is difficult for ionic liquids with pyridine matrix to be decomposed. However, it is very easy for ionic liquids with imidazole matrix to be decomposed and their toxicity is very low. The application of them can better reduce environmental pollution [12]. Therefore, imidazole class of ionic liquid is very important in research and application of ionic liquids. By microwave irradiation, imidazolium ionic liquids i.e. 1-Butyl-3-methylimidazolium bromide ([bmim]Br), 1-propyl-3-methylimidazolium bromide ([pmim]Br), 1-hexyl-3-

methylimidazolium bromide ([c6mim]Br) were synthesized, respectively from 1-methylimidazole and organic bromide (1-bromobutane, 1-bromopropane, 1-bromohexane) have been synthesized [13].

Therefore, We report here a green synthesis of 2-phenylbenzoxazole by the condensation of 2-aminophenol and benzaldehyde in ionic liquid, 1-pentyl-3-methylimidazolium bromide ([pmIm]Br) under microwave irradiation without requiring any other solvent and catalyst (Scheme 1 and 2) [14, 15]. So far, no research work has been carried out for the green synthesis of 2-phenylbenzoxazole by using ionic liquid i. e. 1-Pentyl-3-methylimidazolium bromide. Therefore, the current research paper is organized as follows, Section I contains the introduction about different ionic liquid and its utility in green synthesis of 2-arylbenzothiazole and 2-phenylbenzoxazole. Section II contains the experimental procedure and scheme for the synthesis of 1-Pentyl-3-methylimidazolium bromide and phenylbenzoxazole. Section III contains the spectral interpretation of newly synthesized products and some experimental mechanistic details with future directions and planning. Section IV contains the conclusive remarks of research work.

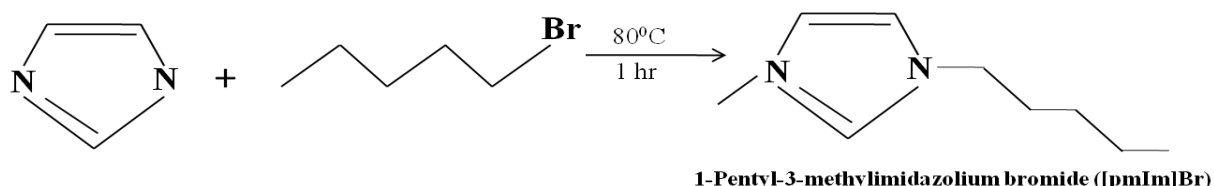
II. EXPERIMENTAL

Materials:

AR grade *N*-Methyl imidazole, *n*-pentyl bromide, 2-aminophenol, benzaldehyde and other required chemicals were purchased from SD Fine Chemicals Limited and used without further purification. UV-Visible spectra of 1-pentyl-3-methylimidazolium were recorded by preparing solution in dimethylsulphoxide on Shimadzu, UV-Visible double beam spectrophotometer in the range of 200-850 nm. Infrared spectra was recorded using KBr pellet in nujol mull on Perkin-Elmer-spectrum RX-I spectrophotometer in the range of 4000-500 cm^{-1} . $^1\text{H-NMR}$ studies were performed in solvent, methanol, on Bruker Advance-II 400 MHz proton NMR spectrophotometer. All the analytical and spectral studies were carried out at Sophisticated Analytical Instrumentation Facility (SAIF) Punjab University, Chandigarh. All solvents and reagents were used as received and all reactions were run in oven-dried glassware. The homogeneity of the products was checked on TLC plates coated with silica gel-G and visualized by exposure to iodine vapors.

Synthesis of ionic liquid i. e. 1-Pentyl-3-methylimidazolium bromide ([pmIm]Br)

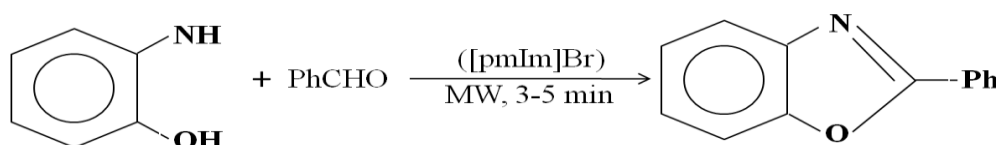
N-Methyl imidazole (1.2 g, 15 mmol) and *n*-pentyl bromide (2.71 g, 18 mmol) were taken in a small round bottom flask. Then the mixture was heated in water bath at 80 °C for an hour, keeping a guard tube at the mouth of the round bottom flask. A clear yellow viscous liquid was formed. It was then cooled and washed with a small amount of ether (1 ml) twice with ether to remove any unreacted bromide and remaining viscous liquid was dried by a vacuum pump. (Scheme 1).



Scheme 1: Synthesis of 1-Pentyl-3-methylimidazolium bromide ([pmIm]Br)

Synthesis of 2-phenylbenzoxazole

A mixture of benzaldehyde (1.0 g) and 2-amino-thiophenol (1.25 g,) was heated in microwave oven (10% power, 120 W) in presence of ionic liquid [pmIm]Br (500 mg) for 3 mins. After being cooled the reaction mixture was extracted with ether and the ether extract was evaporated to leave the crude product which was recrystallized from ethanol-water (4:1) to give a white solid (Scheme 2).



Scheme 2: Synthesis of 2-phenylbenzoxazole

III. RESULT AND DISCUSSION

1) Ionic liquid i. e. 1-Pentyl-3-methylimidazolium bromide ([pmIm]Br)

UV-Visible: The UV-vis spectrum of ([pmIm]Br) was measured by Shimadzu, UV-Visible double beam spectrophotometer in the range of 200-850 nm. The sample was placed in 1 cm quartz colorimetric vessel to be measured after it was dissolved

in methanol. In the measure of UV-vis spectrum, the solvent was used to not only dissolve ionic liquid but also decrease polymerization of high viscous and strong conducting ions. Methanol was used as solvent in these experiments and the sample concentration is $2.8 \times 10^{-4} \text{ mol L}^{-1}$. The UV-vis absorption spectra of ([pmIm]Br) measured at room temperature were shown in Fig. 1. Obviously, the light transmittances of ionic liquids increased at 250 nm and there were obvious inflexions. The inflexions had trend to move in shortwave direction. This was because the interaction between anion and cation decreased while ionic liquid formed [16].

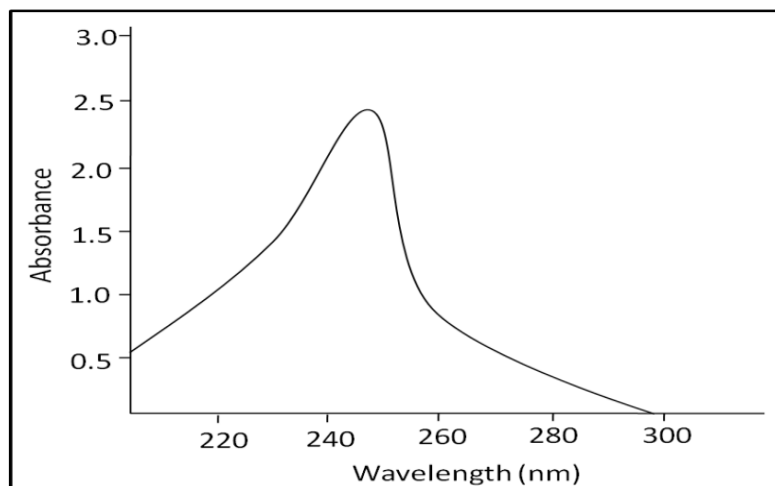


Fig 1: UV-Visible spectra of 1-Pentyl-3-methylimidazolium bromide ([pmIm]Br)

FT-IR Analysis: A structure of the ([pmIm]Br) was analyzed by fourier transform infrared spectroscopy (FT-IR) using KBr pellet in nujol mull on Perkin-Elmer-spectrum RX-I spectrophotometer in the range of $4000\text{--}500 \text{ cm}^{-1}$. The results were shown in Figure 2. The peaks of wave numbers of 2957.69 cm^{-1} and 2864.96 cm^{-1} are the aliphatic asymmetric and symmetric (C–H) stretching vibration is due to methyl groups. A broad peak in the range $3389.31\text{--}3082.91 \text{ cm}^{-1}$ is due to quaternary amine salt formation with bromine. Wave numbers 1614.94 cm^{-1} and 1568.42 cm^{-1} are due to C=C and C=N stretching. Peak at wave number 829 cm^{-1} is due to C–N stretching vibration. Based on FTIR analysis, it was observed that synthesized IL was ([pmIm]Br) [17, 18].

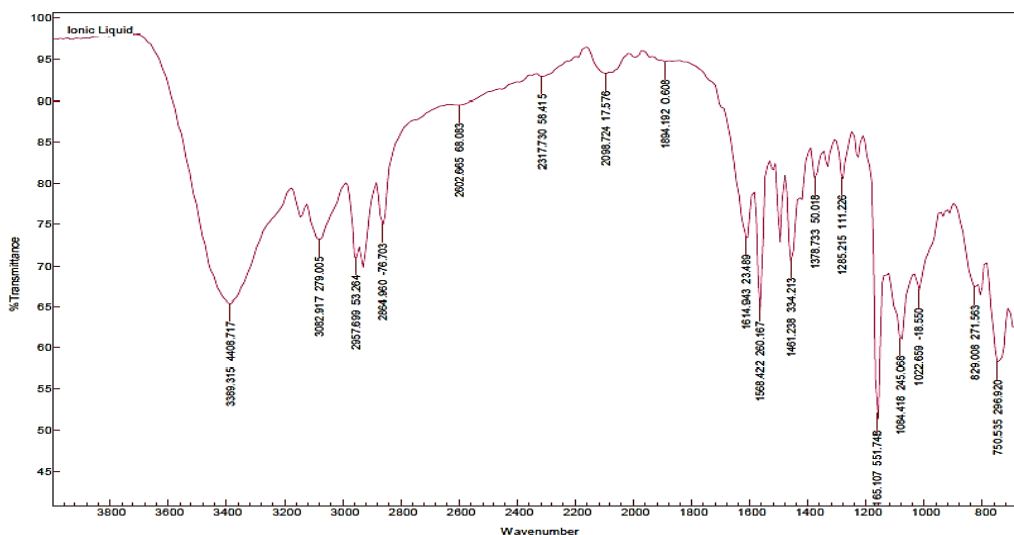


Fig. 2: FT-IR spectra of 1-Pentyl-3-methylimidazolium bromide

¹H-NMR:

¹H-NMR spectra as shown in Figure 3 in ppm (δ) from the internal standard (TMS, 0.0 ppm), chemical shift (multiplicity, integration) were reported.

¹H-NMR (300MHz, CDCl₃): δ (ppm) 7.9 (1H, d), 3.39 (3H, s), 2.5 (1H, s), 8.1 (2H, sextet) 8.1 (2H, sextet), 7.4 (2H, t), 7.5 (2H, heptate), 4.2 (3H, t).

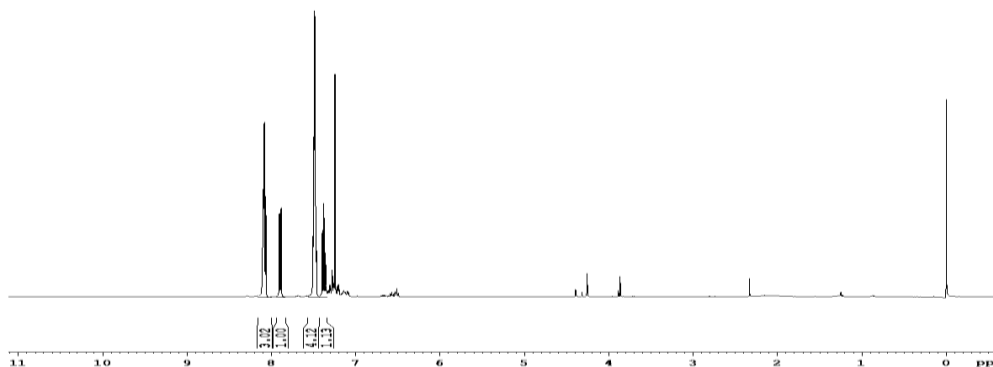


Fig. 3: $^1\text{H-NMR}$ spectra of 1-Pentyl-3-methylimidazolium bromide

2) 2-phenylbenzoxazole

FT-IR: The FTIR-spectrum of 2-phenylbenzoxazole is represented in Figure 4. C=N stretching bands are observed in the range $1676\text{--}1596\text{ cm}^{-1}$. The C-N stretching vibrations are observed in the region at $1311\text{--}1248\text{ cm}^{-1}$ due to stretching of the phenyl carbon–nitrogen bond. As expected the asymmetric C-O-C vibration produce strong band at 1160 cm^{-1} in the IR region. The symmetric C-O-C stretching vibration is observed at 1072 cm^{-1} in the IR spectrum. The existence of one or more aromatic rings in the structure is normally readily determined from the C-H and C=C ring related vibrations. The C-H stretching occurs above 3000 cm^{-1} and is typically exhibited as a multiplicity of weak to moderate bands, compared with the aliphatic C-H stretch. A medium band, displayed between $1650.0\text{--}1660.2\text{ cm}^{-1}$, may be due to stretching vibration of $>\text{C}=\text{C}<$ in aromatics [19-21]. The presence of disubstitution of aromatic ring is recognized from the weak band appearing at 850.7 and 965.4 cm^{-1} .

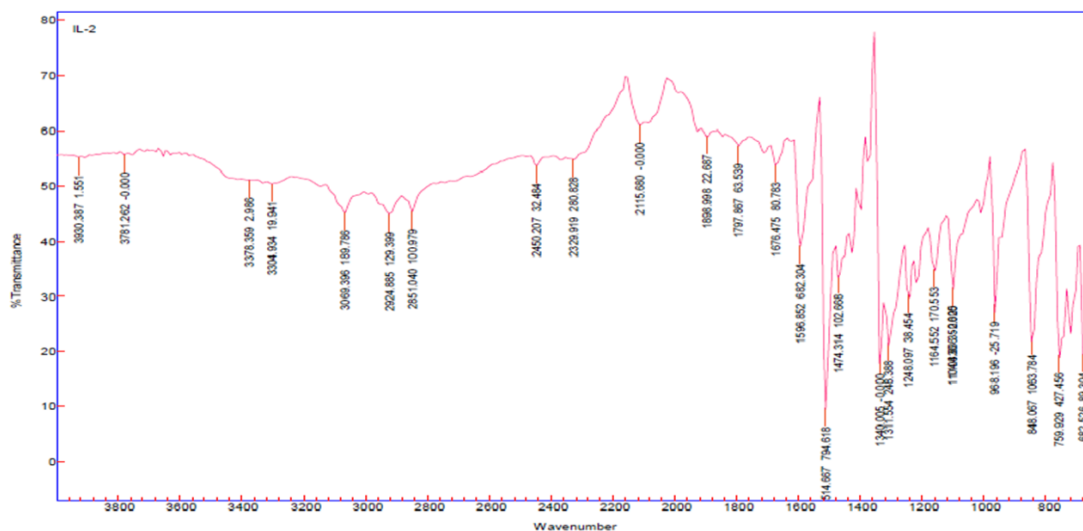


Fig. 4: FT-IR spectra of 2-phenylbenzoxazole

$^1\text{H-NMR}$: $^1\text{H-NMR}$ spectra as shown in Figure 5 in ppm (δ) from the internal standard (TMS, 0.0 ppm), chemical shift (multiplicity, integration) were reported.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.32 - 8.25 (m, 2H), 7.83 - 7.77 (m, 1H), 7.64 - 7.58 (m, 1H), 7.58 - 7.51 (m, 3H), 7.38 (dd, 2H)

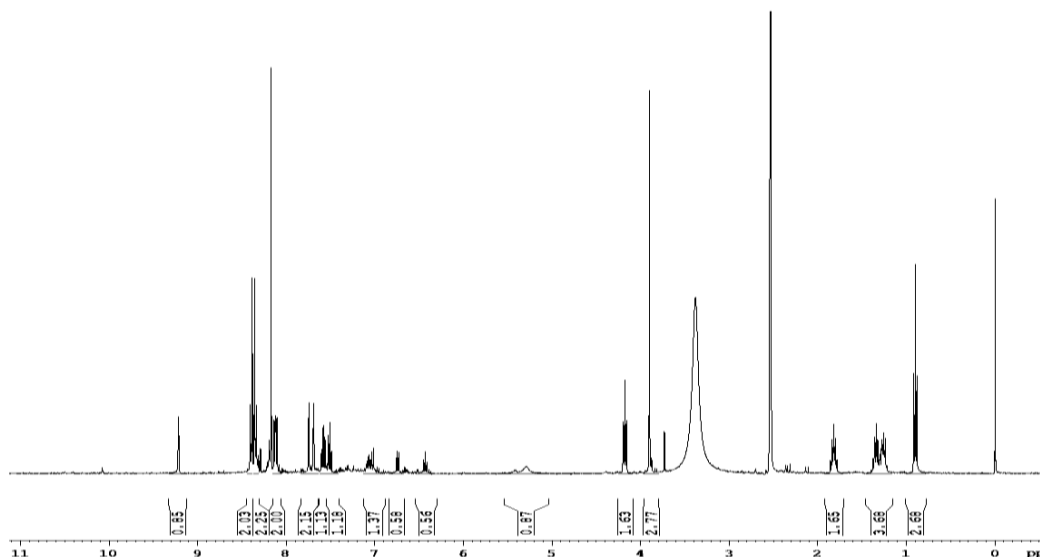


Fig. 5: $^1\text{H-NMR}$ spectra of 2-phenylbenzoxazole

These reactions under microwave are in general, very fast (3–5 min) and clean. For comparison, when all these reactions are carried out by conventional heating ($80\text{ }^\circ\text{C}$) much longer periods (5–7 h) are required. The catalytic activity of ionic liquid, ([pmIm]Br) has been established by the fact that when the reaction is run without ionic liquid no benzoxazole is obtained and the reaction is arrested with the formation of imine. Although mechanism of action of this ionic liquid is yet to be established by further experiments, it may be assumed that the bromide ion of [pmIm]Br is hydrogen-bonding to $-\text{OH}$ increasing the nucleophilicity of oxygen atom. This makes the hydroxyl anion a stronger nucleophile towards efficient condensation with aldehydes followed by cyclization [22-25]. The future aspects of the present work include the experimentation of ionic liquid as a catalyst on different types of organic transformations as well as polymer synthesis.

IV. CONCLUSION

The present synthetic procedure catalyzed by a simple and inexpensive ionic liquid i.e. [pmIm]Br provides an efficient methodology for the synthesis of 2-phenylbenzoxazole by the microwave assisted condensation of 2-aminophenol and aromatic aldehyde. The structures of both the ionic liquid and 2-phenylbenzoxazole have been confirmed by spectral analysis. The spectral values matches well with the proposed structure of ionic liquid and 2-phenylbenzoxazole. The significant advantages of this procedure are: fast reaction; mild reaction condition compatible with a variety of sensitive groups; high yields; atom efficient; cost efficiency providing recyclability of the catalyst and green aspects avoiding the emission of toxic and hazardous solvent, toxic catalyst and waste reaction products.

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