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Synthesis and Characteristics of Important Ionic Liquid Intermediate 1-butyl-3-methylimidazolium Chloride

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Abstract 1-butyl-3-methylimidazolium chloride was synthesized by N-methylimidazole and 1-chlorobutane, and the optimum reaction process was established. The chemical structure of 1-butyl-3-methylimidazolium chloride was characterized and confirmed by nuclear magnetic resonance spectrum, and the melting point and melting heat of ion liquid intermediate were measured by differential scanning calorimetry. The results showed that high purity 1-Butyl -3-methylimidazolium chloride was prepared.

Key words ionic liquid, 1-butyl-3-methylimidazolium chloride; N-methylimidazole

Introduction

The great leader Comrade **Kim Jong Il** said as follows.

"**While directing our main efforts to the key sectors of science and technology, we must develop the new spheres of science and technology, including lasers, and actively introduce the latest achievements of science and technology into the new factories and projects for technical improvement.**"("**KIM JONG IL** SELECTED WORKS" Vol. 12 P. 202)

Recently, a new class of solvent has emerged-ionic liquids, which solvents are often fluid at room temperature, and consist entirely of ionic species. The ionic liquids unusual properties, such as high polarity, negligible vapor pressure, high ionic conductivity, and thermal stability make them as attractive environmentally benign solvents for organic chemical reactions, polymer synthesis, extractions and separations, and electrochemical applications[1－4].

The first room-temperature ionic liquid(ILs) $[EtNH_3][NO_3]$(m.p. 12℃) was discovered in 1914 and in 1990, the new water-stable ILs based on imidazolium have been continuously developed and have received more and more attention due to their unique physical and chemical properties[5, 6].

1-Butyl-3-methylimidazolium chloride (BMIC) have been used as an intermediate for preparing the numbers of ILs such as 1-butyl-3-methylimidazolium tetrafluoroborate, 1-ethyl-3-methylimidazolium tetrafluoroborate.

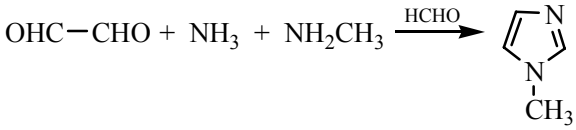
In this article, we reported a simple and novel method to synthesize a starting material; N-methylimidazole and the considerable synthetic conditions to prepare important ILs intermediate; BMIC.

1. Experimental Method

Methylamine, glyoxal, formaldehyde, ammonia solution and 1-chlorobutane were used. All chemicals used in this study were of analytical grade.

1.1. Synthesis of N-methylimidazole

The methods for preparation of N-methylimidazole are the step cyclization and substitution of imidazole. We have used the methods by step cyclization.

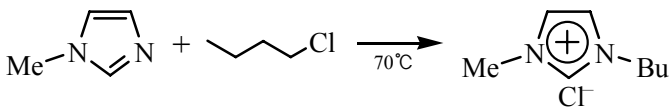


A three-necked flask is equipped with a water bath, an internal thermometer adapter, an overhead mechanical stirrer and a reflux condenser.

A mixture of 145mL of 30% strength aqueous glyoxal solution(1.0mol) and 75mL of 40% strength aqueous formaldehyde solution(1.0mol), and a mixture of 80mL of 40% strength aqueous methylamine solution(1.0mol) and the defined parts of 4.5% strength aqueous ammonia are themselves mixed for 30min in a stirred flask. The temperature of the flask was kept around 60℃ through the completion of the reaction, which took about 4～5h. After completion of the reaction, the water is removed through the rotary evaporator. The distillate is obtained under reduced pressure (20mmHg) at 80℃, analyzed by using liquid chromatography("SIL-10A"). The influence of reactive conditions are measured by varying the adding amounts of aqueous ammonia, the mode of addition, and reactive temperatures. The structural analysis was performed by using Fourier transform infrared spectrometer ("IR-BRO400").

1.2. Synthesis of 1-butyl-3-methylimidazolium chloride(BMIC)

Approximately 40mL of N-methylimidazole was combined with 60mL of 1-chlorobutane in a round bottom flask. A magnetic stirrer was placed in the flask and constantly stirred the reaction.



The flask was attached to a condenser, through which nitrogen gas was flowed to remove oxygen gas that may interfere with the reaction. The temperature of the flask was kept around 70℃ through the completion of the reaction, which took about 48h. Next, the BMIC was washed with ethyl acetate to remove any excess reactants and any contaminates. The BMIC was mixed with about 20mL of ethyl acetate in a separator funnel and shook together. After a few minutes, the mixture separated into two distinct layers. The top layer was ethyl acetate and all of the contaminants. The bottom layer was BMIC. A lot of the ethyl acetate was removed through the rotary evaporator. The structural analysis was performed by using NMR spectrometer ("XL-2300"), the thermal analysis by using differential scanning calorimetry ("RIGAK-8131").

2. Results and Discussion

2.1. The influences of the reactive conditions on the yields of N-methylimidazole

The influence of the adding amounts of aqueous ammonia, the mode of addition, and reactive

temperatures on the yields of N-methylimidazole are shown in table.

Experiments 1, 2 employed the different adding mode of materials. As shown in table, it can be known that the differences of the yield on the different adding mode of materials are large, because the reaction is quiet exothermic. In using experiment 1, it can be resulted in loss by the easy evaporation of an aqueous ammonia and methylamine solution with a sudden rise of the temperature. Experiments 3, 4 employed the reactions under the different adding amounts of aqueous ammonia. As shown in table, it can be known that the influences of the adding amounts of aqueous ammonia on the yield are not large.

Table. The influences of the reactive conditions on the yields of N-methylimidazole

No.	Experimental method	N-methylimidazole		
		Weight/g	Yield/%	Purity/%
1	Direct mixing, room-temperature reaction	35.6	43.4	97.5
2	Add with stirring at room-temperature, subsequently, room-temperature reaction	58.9	71.8	98.3
3	Add with stirring at room-temperature, subsequently, rise up to 70℃	67.8	82.6	98.6
4	Add with stirring at room-temperature, subsequently, rise up to 70℃, but amount of ammonia varies to 1.2mol	70.4	85.9	98.5

Experiments 1, 2, 3 and 4 employed the reactions under the different temperatures. As shown in table, it can be known that the influences of the different temperatures on the yield are considerably large.

The structure of N-methylimidazole was identified by using Fourier transform infrared spectrometer ("IR-BRO400"). Result is shown in Fig. 1.

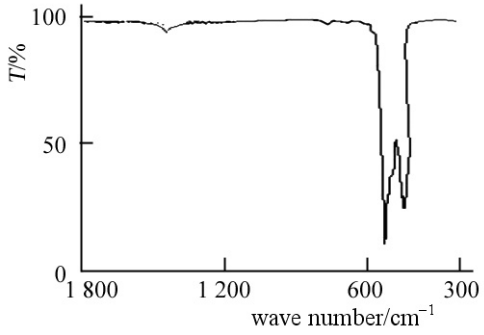


Fig. 1. FTIR of N-methylimidazole

2.2. The synthesis and characterization of BMIC

In the preparation of BMIC, the relation between reactive temperature and N-methylimidazole ($C_4H_6N_2$)/1-chlorobutane(C_4H_9Cl) molar ratio was shown in Fig. 2.

As shown in Fig. 2, it could be known that the yields of the product become higher as increasing the reactive temperature up to 70℃, and rapidly decrease as the temperatures become higher. This reason could be due to the stronger side reactions over the range of 70℃. It was observed that the optimum reactive temperature was in the range of 70℃. It was also studied that the influences of 1-chlorobutane (C_4H_9Cl)/ N-methylimidazole ($C_4H_6N_2$) molar ratio on the yields is not large compared to the

temperature and no changes were observed when higher concentrations of 1.2 molar ratio were employed. It could be known that the optimum molar ratio was in the range of 1.2mol.

The melting heat of BMIC were measured by differential scanning calorimetry (DSC). The DSC patterns were recorded at 10℃/min of the rate of temperature rise and －50～200℃ of heating-up interval(Fig. 3).

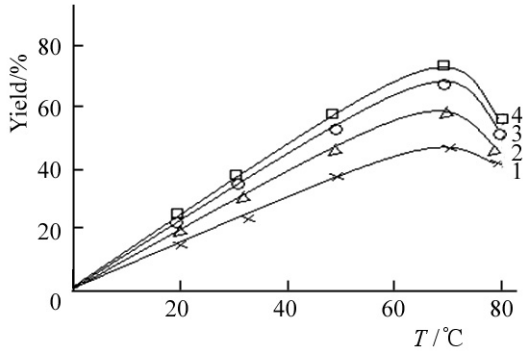


Fig. 2. Relation between reaction temperature and $(C_4H_6N_2)/(C_4H_9Cl)$ molar ratio in the synthesis of BMIC
1－4 $(C_4H_6N_2)/(C_4H_9Cl)$ molar ratio 0.6, 0.8, 1.0, 1.2

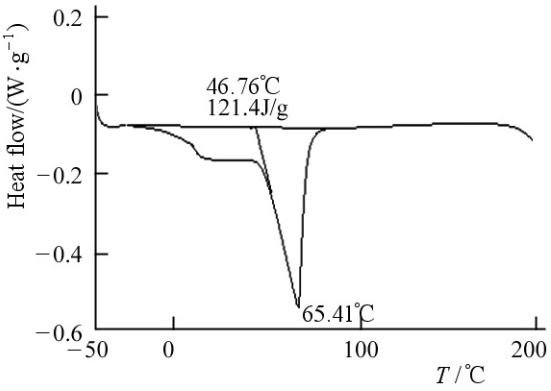


Fig. 3. DSC curve of BMIC sample

As shown in Fig. 3, it could be known that the melting heat($\triangle H$) was 121.4J/g, melting point 65.4℃ and they were in accord well with the literature (66±1℃)[4]. The results showed that high purity 1-butyl-3-methylimidazolium chloride was obtained.

NMR spectroscopy was performed by using tetramethylsilan as a standard materials. The result was shown in Fig. 4.

The product has the following spectral properties.

^1H － NMR ($CDCl_3$, TMS)：δ 10.6(imidazole ring, H^2), δ 7.26(imidazole ring, H^4), δ 7.05(imidazole ring, H^5), δ 4.37(NCH_2), δ 4.08(NCH_3), δ 1.88 (NCH_2CH_2), δ 1.37($NCH_2CH_2CH_2$), δ 0.98($NCH_2CH_2CH_2CH_3$). These spectral data were in accord well with the literature [3].

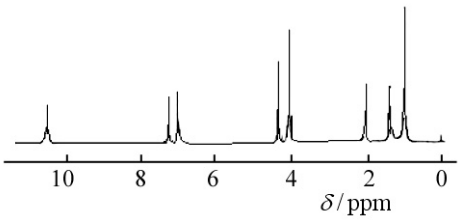


Fig. 4. ^1H-NMR spectroscopy of BMIC sample

Conclusion

N-methylimidazole have been efficiently synthesized by the step cyclization using glyoxal, formaldehyde, methylamine and excess of ammonia as the starting materials.

Ionic Liquid intermediate 1-butyl-3-methylimidazolium chloride have been successfully synthesized under the condition of 1-chlorobutane/N-methylimidazole molar ratio 1.2, reactive temperature 70℃, and reactive times 48h. The melting heat and melting point of BMIC measured by differential scanning calorimetry are $\triangle H$ 121.4J/g, m.p. 65.4℃ and they show that high purity 1-methyl-3-butylimidazolium chloride was obtained. The characterization of 1-butyl-3-methyl imidazolium chloride have been performed through NMR spectroscopy and the results were in good agreement well with the literature.

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