

Synthesis and Characterization of Benzimidazolium Salts as Novel Ionic Liquids and their Catalytic Behavior in the Reaction of Alkylation

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Abstract: A new series of ionic liquids have been prepared containing benzimidazolium cation (abbreviated as Bim). These salts were characterized by DSC, NMR, elemental analysis and thermogravimetric analysis. They showed different properties compared to imidazolium cation due to the introduction of benzene ring. The alkylation of benzene/diphenyl ether with 1-dodecene was carried in C₄eBimBr-AlCl₃ ionic liquids showing high catalytic activity when the mole ratio of C₄eBimB:AlCl₃ was 1:2.

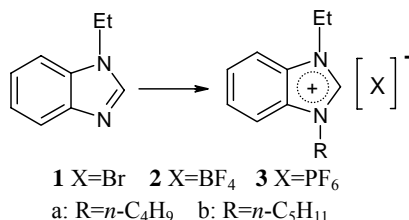
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Recently, ionic liquids have attracted growing attention as versatile materials for catalysis, organic synthesis and electrochemistry¹ due to their particular properties, such as negligible vapor pressure, wide liquid range, large electrochemical window, *etc.* Benzene/diphenyl alkylation with long chain olefin were two important industrial reactions, and the reactions catalyzed by RTILs were reported². Relatively, there were fewer materials on the formation mechanism of ionic liquids with lower melting points and the relationship between the structural features of an ionic liquid and its useful properties. It is very important to expand the utility of ionic liquids and investigate the physicochemical parameters for this versatility, so that their potential application in chemical industry process can come true. Here, we report one series of novel RTILs based on benzimidazolium cation with favorable catalytic performance used in the alkylation of benzene/diphenyl ether with 1-dodecene (**Scheme1**).

Experimental

C₄eBimBr:1-Ethylbenzimidazolium was added to a 100 mL three-necked flask with a reflux condenser followed by addition of 50 mL toluene. Then equal molar freshly distilled bromobutane was added dropwise and the solution was stirred at 70 °C for 24 h until two phase formed, the upper phase, containing unreacted starting material, was decanted and the bottom phase was washed with fresh toluene (25 mL×2). At the end, any remaining toluene was removed by ratovapor at 70 °C for 6 h.

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Scheme 1 Structure of new salts**Table 1** Thermal analysis data of new salts

entry	ILs	MP(°C)	Td(°C)
1a	C ₄ eBimBr	74	246
1b	C ₅ eBimBr	-	254
2a	C ₄ eBimBF ₄	57	320
2b	C ₅ eBimBF ₄	38	340
3a	C ₄ eBimPF ₆	135	357
3b	C ₅ eBimPF ₆	72	349

¹HNMR (500Hz, CDCl₃, δ_{ppm}): 0.97(m, 3H, J=18Hz, CH₃), 1.44(t, 2H, J=15Hz, CH₂), 1.76(t, 3H, J=15Hz, CH₃), 2.04(t, 2H, J=14Hz, CH₂), 4.66(t, 2H, J=15Hz, CH₂), 4.73(m, 2H, J=22Hz, CH₂), 7.70(m, 2H, J=25Hz, 2CH), 7.74(m, 2H, J=14Hz, 2CH), 11.57(s, 1H, N-H). Elemental analysis calcd. for C₁₂H₁₈N₂Br(270): C 55.12, H 6.71, N 9.89; Found C 54.87, H 6.49, N 10.27.

C₅eBimBr: The synthesis followed the same procedure as for C₄eBimBr described above with exception of the bromopentane instead of bromobutane.

C₄eBimPF₆: C₄eBimBr was transferred to a plastic container followed by addition of deionized water. The magnetically stirred solution was cooled in ice bath and 60% HPF₆ in a 1:1.1 (molar ratio) was added slowly. The mixture was stirred in ice bath for 12 h. The product precipitated as a white waxy solid and was collected by filtration. The white solid was washed with quantitative fresh deionized water and then dried *in vacuo* at 70 °C for 6 h.

¹HNMR (500Hz, CDCl₃, δ_{ppm}): 0.97 (m, 3H, J=18Hz, CH₃), 1.44(t, 2H, J=15Hz, CH₂), 1.76(t, 3H, J=15Hz, CH₃), 2.04(t, 2H, J=14Hz, CH₂), 4.66(t, 2H, J=15Hz, CH₂), 4.73(m, 2H, J=22Hz, CH₂), 7.70(m, 2H, J=25Hz, 2CH), 7.74(m, 2H, J=14Hz, 2CH), 11.57(s, 1H, N-H). Elemental analysis calcd. for C₁₂H₁₈N₂PF₆ (335): C 44.83, H 5.46, N 8.05; Found C 45.00, H 5.41, N 7.96.

C₅eBimPF₆: The same procedure was used as indicated for C₄eBimPF₆.

C₄eBimBF₄: The same procedure was used as indicated for C₄eBimPF₆ with exception of the use of 40% HBF₄ instead of 60% HPF₆.

¹HNMR(500Hz, CDCl₃, δ_{ppm}): 0.99(t, 3H, J=5Hz, CH₃), 1.44(m, 2H, J=23Hz, CH₂), 1.68(m, 3H, J=39Hz, CH₃), 2.00(t, 2H, J=15Hz, CH₂), 4.49(t, 2H, J=15Hz, CH₂), 4.55(d,

2H, $J=7\text{Hz}$, CH_2), 7.67(m, 2H, $J=25\text{Hz}$, 2CH), 7.74(m, 2H, $J=13\text{Hz}$, 2CH), 9.61(s, 1H, N-H). Elemental analysis calcd. for $\text{C}_{12}\text{H}_{18}\text{N}_2\text{BF}_4$ (276.81 : C 53.83, H 6.56, N 9.66; Found C 53.79, H 6.64, N 9.54.

$\text{C}_5\text{eBimBF}_4$: The same procedure was used as indicated for $\text{C}_4\text{eBimBF}_4$.

Results and Discussion

In the DSC curves, C_4eBimBr (**Figure 1**) showed multiple phase behavior. In this case, the sample seemed to have quenched, without crystallization to a glass state. A glass transition was observed at $-34\text{ }^\circ\text{C}$. Then a broad crystallization peak appeared at $31\text{ }^\circ\text{C}$ on heating, as commonly observed in "marginal glass formers". At $61\text{ }^\circ\text{C}$, C_4eBimBr exhibited a solid-solid transition and finally melted at $74\text{ }^\circ\text{C}$. The similar phenomenon has been reported for the N-methyl-N-butylpyrrolidinium hexafluorophosphate salts³ and quaternary ammonium imide salts⁴. C_5eBimBr only displayed a glass transition at $-30\text{ }^\circ\text{C}$ and its melting point was not observed in the DSC curve when heated. The melting points of new salts were listed in **Table 1**. From **Table 1**, it was clear that both the cation and anion significantly influenced the melting point of these compounds. The melting points of salts containing lower symmetry such as C_5eBimX were lower than that of C_4eBimX containing higher symmetry. For each cation, the melting point followed the trend $\text{BF}_4^- < \text{Br}^- < \text{PF}_6^-$, which was somewhat different from imidazolium salts. The thermogravimetric data of new ionic liquids were shown in **Table 1** and **Figure 2**. They displayed high thermal stability. The $\text{C}_5\text{eBimPF}_6$ did not show weight loss to $340\text{ }^\circ\text{C}$ (**Figure 2**).

C_4eBimBr integrating with anhydrous AlCl_3 showed excellent catalytic activity in the reactions of benzene/diphenyl ether alkylation with 1-dodecene, when the mole ratio of $\text{C}_4\text{eBimBr}:\text{AlCl}_3$ was 1:2. Both the reactions carried out at atmospheric pressure, the 1-dodecene was totally converted in the reaction of benzene alkylation in 5 minutes at room temperature, while the conversion was 84% in the reaction of diphenyl ether alkylation in 2 hours at $50\text{ }^\circ\text{C}$; the selectivity in the former was 57.7% (2-LAB + 3-LAB

Figure 1 The DSC curve for $[\text{C}_4\text{eBim}][\text{Br}]$ and $[\text{C}_5\text{eBim}][\text{Br}]$

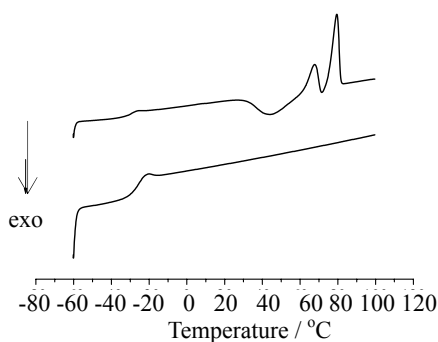
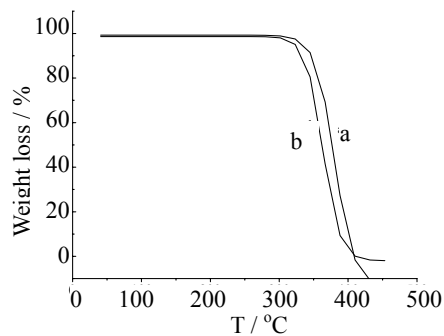


Figure 2 Thermogravimetric curve for novel ionic liquids



(a) $\text{C}_5\text{eBimPF}_6$ and (b) $\text{C}_4\text{eBimBF}_4$

isomers) and the mono alkyl diphenyl ether was 100% in the latter which were superior to the previous results⁵. Furthermore, the catalyst was utilized repeatedly over five times with the conversion and selectivity nearly unchanged. Further work is in progress in our group.

In summary, new ionic liquids based on benzimidazolium reported in this paper had low melting point and interesting phase behavior. They also showed peculiar solubility and thermal stability, which can expand the utility of RTILs chemistry. As a new kind of medium in alkylation, they showed extremely high catalytic activity. Simultaneously, the ability to reuse the ionic liquid also has been demonstrated.

Acknowledgments

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