

Synthesis of Task Specific Thiocarbonyl Functionalized Ionic Liquids

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ABSTRACT

A thiocarbonyl functionalized room temperature ionic liquids is synthesized, and characterized as a part of study to explore the expedite use of ionic liquids in nanoparticle synthesis. The synthesis of these ionic liquids is concise and practical due to the easy availability of the starting materials. Both hydrophilic and hydrophobic ionic liquids were prepared. Salt with chloride anion was solid (low melting), while those with PF_6^- and BF_4^- anion were liquids at room temperature.

Key Words: Ionic liquids, thiocarbonyl compounds, nanomaterial synthesis.

1. INTRODUCTION

Today, organic synthesis has reached a remarkable level of competence and even the most complex molecules are accessible.¹ The prerequisites for this success are both the availability of a wide range of efficient synthetic methods² and reagents,³ and the fact that “retrosynthetic analysis”⁴ can provide a framework for the design of a synthetic strategy leading to the desired product in the most efficient and logical way.

However, the demands for green and sustainable synthetic methods in the fields of healthcare and fine chemistry combined with the pressure to produce these substances expeditiously and in an environmentally benign fashion, pose significant challenges to the synthetic chemical community. This objective can be achieved through the development of aqueous synthetic protocols using MW-heating, and use of environmentally benign materials such as ionic liquids. It should also be noted that the rapid development of “Green Chemistry in Organic Synthesis” is due to the recognition that environmentally friendly products and processes will be economical in the long term as they circumvent the need of treating ‘end-of-the-pipe’ pollutants and byproducts generated by conventional synthesis.

In spite of advantages, nanocatalysts are kinetically unstable with respect to agglomeration to the bulk metal and therefore require stabilization. Therefore, to be used they need stabilization by either surface-ligating anions or other ligands. With this it is possible to realize additional control, mostly on the solubility in an appropriate solvent and their isolation.⁵ Combining different stabilizing effects may even improve the performance of nanoparticle catalysts. For example, Finke and co-workers^{6,7} showed that co-stabilization of rhodium nanoparticles with polyoxoanions and tetrabutylammonium cations leads to a high improvement of turnover frequency (TOF) for hydrogenation of olefins and arenes. An important advantage of using ILs in such preparations is that they facilitate inorganic synthesis from highly polar starting materials under ambient conditions and under anhydrous conditions. For instance, in their earlier work, Zheng and others have successfully synthesized pure rutile and rutile-anatase composite TiO_2 nanoparticles via an ionic liquid-assisted method,⁸ and have also prepared a series of shape-controllable ZnO nanocrystals stabilized by different ionic liquids,⁹ which show tunable photoluminescence and high photocatalytic activity.

2. RESULT & DISCUSSION

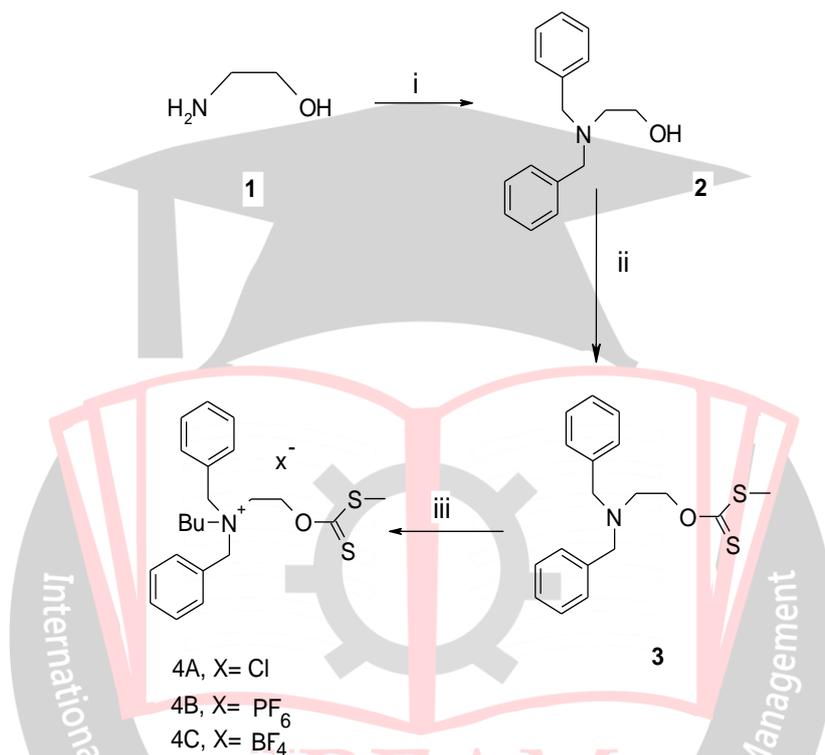
The first step of the synthesis involved addition of benzyl chloride to amino group of 2-amino ethanol. In order to block amino group, initially the reaction was carried out with excess amount of benzyl chloride. However, this approach was found to be more troublesome than anticipated as in this step a mixture of *mono* and *bis*-addition products were formed. This led to reduced yield of desired *bis*-addition product and difficulty of isolation of desired product surfaced. Also in work-up procedure the difficulty of removal of excess benzyl chloride prevailed. Taking into account this problem the reaction was carried out in presence of potassium iodide and quantitative yield of *bis*-addition product **2** was obtained without use of excess of benzyl chloride. Again to ease work up procedure, considering water miscibility of ethanol amine, reaction was planned with excess of amino ethanol. This facilitated total consumption of benzyl chloride at the end and easy removal of excess of unreacted amino ethanol by washings of organic layer with water get pure compound **2**.

Having this intermediate **2** in hand, the attention was then focused on synthesis of **3**. Various methods were tried to convert titary amine **2** to **3**. It was observed that maintaining low reaction temperature was the key for this step. The intermediate **3** and catalytic amounts of imidazole dissolved in Dry THF was added slowly to sodium hydride maintaining the reaction temperature at 0°C . After stirring for 30 min, carbon disulphide was added dropwise

maintaining temperature at 0°C. (this slow addition was crucial as addition at once led to very low yield of 29 %). Again after stirring for half an hour excess quantity of methyl iodide was added dropwise. Excess of sodium hydride was quenched by addition of acetic acid. The product was extracted in ether and organic layer was evaporated to get crude product. The crude product was purified by column chromatography to obtain key intermediate **3** in 84% yield.

The next step of the synthesis involved the transformation of **3** into ionic liquid. The alkylation reaction was carried out under reflux in toluene for 48 h to form the chloride salt **4A** in 91% yield and high purity. The chloride salt was converted to ionic liquids **4B** and **4C** by anion exchange of **4A** with different anions (BF_4^- and PF_6^-).

Thiocarbonyl functionalized ionic liquids **4A**, **4B** and **4C** possess Cl^- , PF_6^- and BF_4^- as anions respectively. Salt that contain the Cl^- anion was solid (low melting), while those with PF_6^- and BF_4^- anion were liquids at room temperature and found to be readily soluble in common solvents, such as alcohols, CH_2Cl_2 , ethyl acetate, DMF and DMSO. However, these salts were immiscible with ether and hexane.



Reaction conditions : (i) Benzyl chloride, Ethanol amine (excess), KI, DCM, reflux 6 h; (ii) NaH, THF, CS_2 , CH_3I , 0 °C, to R.T., 2 h; (iii) n-BuCl, acetonitrile, 80 °C. (to get 4A) followed by KPF_6 , acetone, 24 h, R. T. (to get 4B).

3. CONCLUSION

In conclusion, three thiocarbonyl functionalized ionic liquids are designed, synthesized and characterized. These ionic liquids are prepared in view to employ them in nanoparticle synthesis as stabilizing agents. The synthesis of these ionic liquids is concise and practical due to the commercial availability of the starting materials. The prepared compounds were characterized by NMR analysis.

4. REFERENCES

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