



Pergamon

Synthesis of methyl orange using ionic liquids

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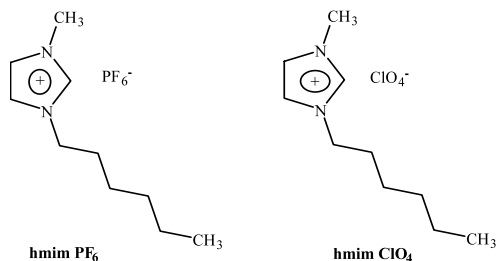
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Abstract—Two ionic liquids were synthesized, each system consisting of the 1-hexyl-3-methylimidazolium ion ([hmim]⁺) as the cation and either hexafluorophosphate ([PF₆]⁻), or perchlorate ([ClO₄]⁻) as the anions. This study involves the synthesis of methyl orange (4-[[[4-dimethylamino]phenyl]-azo] benzene sulfonic acid sodium salt) using the ionic liquids as replacement solvents for the reaction. The advantage of using ionic liquids as substitutes for organic solvents includes: recyclable/reclaimable solvents, stabilization of intermediates and higher product yields. The 1-hexyl-3-methylimidazolium derivatives can be used for syntheses conducted at low temperatures and are less toxic than typical organic solvents.

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Owing to their unique properties, ionic liquids are versatile solvents whose applications include: reaction catalysis,^{1–4} separation technology,⁵ and conductivity studies.^{6,7} These ionic liquids have also been used as replacement solvents and catalysts for several organic reactions. Some of these different types of organic reactions include: Friedel–Crafts reactions,^{8,9} electrophilic aromatic nitration,¹⁰ benzoin condensation,¹¹ biphasic arene hydrogenations,¹² and esterifications.¹³ The current study was initiated to continue the search for new ionic liquids and determine their usefulness in typical organic reactions.

The ionic liquids, ([hmim]⁺[PF₆]⁻) and ([hmim]⁺[ClO₄]⁻) were synthesized and used as alternative solvents in the production of methyl orange (Scheme 1).



Scheme 1.

Keywords: ionic liquids; diazo coupling; helianthin; methyl orange.

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The 1-hexyl-3-methylimidazolium cation was prepared by combining equimolar quantities of 1-methylimidazole and 1-chlorohexane. The reagents are stirred and allowed to react at 70°C for 48 hours. The resulting liquid was then cooled and washed with three 50 mL portions of ethyl acetate to remove unreacted starting material. The residual ethyl acetate was removed by rotary evaporation. The product, 1-hexyl-3-methylimidazolium ion, was combined with 125 mL of water and then slowly reacted with 50 mL of hexafluorophosphoric acid (60% aq) (hmim PF₆) or 9.18 g of sodium perchlorate hydrate (hmim ClO₄). The solutions were then allowed to stir for 12 h to complete the anion replacement reaction. Finally, the ionic liquids were washed with a series of saturated sodium carbonate solutions and water, to remove excess acid or perchlorate. Yield: 95% for both ionic liquids. The 1-hexyl-3-methylimidazolium cation was analyzed and confirmed using both FT-IR and 60 MHz proton FT NMR. ¹H NMR (60 MHz, neat) δ 0.47 (t, 3H), 0.53–1.25 (m, 8H), 1.63 (s, 3H), 3.60 (t, 2H), 8.20 (d, 2H), 10.2 (s, 1H). The ionic liquids were confirmed by an increase in the conductance for each solution when compared with the starting materials indicating the increased presence of charge carrying species. The perchlorate ionic liquid could be thermally unstable or explosive, however, since our reaction temperatures were kept below 70°C there never was an issue.

Synthesis of methyl orange using the ionic liquids:¹⁴

In this reaction, the azo dye methyl orange was prepared by a diazo coupling reaction. Sulfanilic acid (3.6 g) was dissolved in a basic aqueous solution of sodium

carbonate (1.1 gram/50 ml). Sodium nitrite (1.5 g) and chilled 2 M hydrochloric acid (5.0 ml) are then added and stirred. After 10 min the precipitation of the sulfanilic acid as a diazonium salt occurs (white precipitate). The diazonium salt was allowed to react with a solution containing *N,N*-dimethylaniline (2.7 ml) and the ionic liquid (2.0 ml). The mixture was cooled in an ice bath for 15 min to completely form the helianthin precipitate. The helianthin was the first product of the coupling reaction and the red acidic form of methyl orange. At this point the helianthin solid was collected by vacuum filtration. The filtrate contained the ionic liquid which was separated from the aqueous layer and dried over 4–8 mesh molecular sieves. The helianthin solid was finally dissolved in 10.0% sodium hydroxide (30.0 ml) by heating the solution to boiling. After all the helianthin had dissolved, solid sodium chloride (10 g) was added to the solution and cooled in an ice bath to precipitate the final sodium salt (basic form) of methyl orange. The basic form of methyl orange was collected through vacuum filtration and allowed to dry. Acetic acid was used to stabilize the reaction intermediates for the control reactions and the ionic liquids were used in the experimental reactions for the same purpose.

The comparison of percent yields for three replicate trial syntheses of methyl orange run concurrently in acetic acid and in both ionic liquids suggests an increase in product yield. The means and standard deviations show a product yield of 86.94% \pm 1.95 when either ionic liquid was used as the solvent as compared to a product yield of 55.39% \pm 1.66 for the control reaction solvent acetic acid.

In the synthesis of methyl orange the ionic liquids replaced acetic acid as the stabilizer of the charged helianthin intermediate. The product yield results show that the ionic liquid was more effective than the acetic acid at stabilizing the helianthin and increased the product percent yield, when these reactions were run under similar conditions and concurrently. Also, use of the solvent decreased the overall reaction time, the amount of heat required for dissolution of the reactants, and the amount of cooling time required for precipitation of the final product. The methyl orange products were confirmed by using their transition ranges as an acid/base indicator and by UV/vis (461 nm).¹⁵ A 0.01 w/v% aqueous solution was prepared and observed for transition range. Each product demonstrated pH values for the transition range that were within experimental error of the literature values for methyl orange.¹⁵ All experimental transition ranges

were between 2.9 and 4.5 pH units, while the literature reported transition ranges between 3.1 and 4.4 pH units. The ionic liquids were quantitatively recovered (1.5–1.8 ml/2.0 ml) from the product for each reaction and the purity confirmed by proton NMR.

The ionic liquids enhanced the methyl orange reaction mechanism by improving charge stabilization, which allowed an increased product yield of more than 30% when compared to the traditional reaction solvent. Both ionic liquids reacted in a similar fashion and by stabilizing the high-energy charged intermediates they ran at lower temperatures than the control reaction. Future and ongoing work will include more diazo coupling, bromination, oxidation and addition reactions in ionic liquids. The synthesis of new ionic liquids will also be a future goal.

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