Using Acidic Ionic Liquid 1-Butyl-3-methylimidazolium Hydrogen Sulfate in Selective Nitration of Phenols under Mild Conditions

H. Tajik\textsuperscript{a,b,*}, K. Niknam\textsuperscript{b} and F. Parsa\textsuperscript{a}

\textsuperscript{a}Chemistry Department, University of Guilan, Guilan, Iran

\textsuperscript{b}Chemistry Department, Faculty of Sciences, Persian Gulf University, Boushehr, 75169, Iran

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Selective nitration of phenols with sodium nitrate was carried out in the presence of acidic ionic liquid 1-butyl-3-methylimidazolium hydrogen sulfate at room temperature in good to high yields and short reaction times. The use of inexpensive and relatively non-toxic acidic reagent is an advantage of this method.

Keyword: Acidic ionic liquids, [bmim][HSO\textsubscript{4}], Nitrophenols, Sodium nitrate, Phenol

INTRODUCTION

The ambient temperature ionic liquids especially those based on 1,3-dialkylimidazolium cations have gained considerable interest as promising alternative green solvents in organic synthesis [1]. These ionic liquids have several interesting properties such as excellent chemical and thermal stability, non-volatility, non-coordinating nature, good solvating capability, wide liquid range and ease of recycling. Furthermore, their hydrophobicities/hydrophilicities can be tuned by appropriate modification of the cation or anion [1,2]. Therefore, room temperature ionic liquids have found wide uses in catalytic and non-catalytic reactions [3]. In addition, the synthesis of task-specific ionic liquids, which have a functional group in their framework, may expand the application of ionic liquids in organic chemistry [4-6]. Due to their unique properties such as non-volatility and reusability, acidic ionic liquids have been successfully used in many organic reactions [5-9].

Nitration of organic substrates is a widely studied reaction of great industrial significance as many nitro-compounds are extensively used as intermediates for the manufacture of plastics, dyes, perfumes, drugs and pharmaceuticals. ortho-Nitrophenol, for example, is an important starting material used in the synthesis of useful compounds [10]. Nitration normally requires the use of corrosive liquid phase nitric acid-sulfuric acid mixture, leading to an excessive waste stream. In addition, nitration reactions are not usually regioselective and some over-nitration or competitive oxidation may occur [10,11]. Furthermore, several other nitrating agents, including concentrated nitric acid, acid anhydrides or triflates [12], peroxy nitrite [13,14], metal nitrates, sodium nitrite [15] and nitrogen oxides [16], have been utilized in many investigations. Catalytic nitration of aromatic hydrocarbons with concentrated nitric acid in the presence of solid acids has afforded a good regioselectivity [17-20]. In some cases, the reaction has been performed in expensive media such as ionic liquids [21] and microemulsions [22].

In the nitration of phenols, concentrated nitric acid or mixed acids are promising that always associated with the formation of some di-nitro compounds, oxidized products, and unspecified resinous compounds. Noteworthy, in most of the cases, the typical yield of the direct nitration never exceeds 60% because of the side reactions mentioned above. These
limitations make the existing processes uneconomical. Therefore, it is worthwhile to consider an alternative highly selective nitration process. Thus, in this paper we report the in situ generation of HNO₃ by using a mild nitrating agent including a combination of 1-butyl-3-methylimidazolium hydrogen sulfate ([bmim][HSO₄]) as an acidic ionic liquid, and sodium nitrate. Recently, ([bmim][HSO₄]) was prepared and used as an acidic ionic liquid catalyst in the organic reactions such as acetalization, thioacetalization [7] and the synthesis of coumarines [23].

EXPERIMENTAL

General
Chemicals were purchased from Fluka, Merck and Aldrich chemical companies. The nitration products were characterized by comparison of their spectral (IR and H NMR), TLC and physical data with the authentic samples.

Synthesis of Acidic Ionic Liquid [bmim][HSO₄] at Room Temperature
The 1-butyl-3-methylimidazolium hydrogen sulfate was synthesized according the reported procedure for 1-hexyl-3-methylimidazolium hydrogen sulfate ([hmim][HSO₄]) [5]. The [bmim][HSO₄] derived from chloride salt (Scheme 1) was obtained by a dropwise addition of one equivalent of concentrated sulfuric acid (97%) to a cooled solution of butyl methyl imidazolium chloride (1 equivalent) in anhydrous methylene chloride. The mixture was refluxed for 48 h and the HCl by-product formed in the reaction was collected by dissolving it in deionized water at 0 °C (the acidity of the aqueous solution was measured by titration with NaOH as a control for completion of the reaction). After completion of the reaction, the solution was cooled to room temperature and dichloromethane was removed in a rotary evaporator. The ionic liquid was dried under high vacuum (10⁻² Torr) at 70 °C for 6 h.

Mononitration of Phenol (1) with [bmim][HSO₄] and NaNO₃. A Typical Procedure
A solution of compound 1 (0.188 g, 2 mmol), [bmim][HSO₄] (0.572 g, 2 mmol) and NaNO₃ (0.170 g, 2 mmol) in CH₃CN (8 ml) was magnetically stirred at room temperature. After completion of the reaction, 30 min, CH₃CN was removed and the residue was extracted with diethyl ether to separate the product from the ionic liquid. Diethyl ether was removed by simple distillation heated on a water bath at 35-40 °C. The resulting residue was a mixture of 2- and 4-nitrophenols. Addition of n-pentane to the residue dissolved 2-nitrophenol and left 4-nitrophenol (3) which is insoluble in n-pentane which was separated by filtration to give 4-nitrophenol in 30% yield (0.09 g); m.p.: 110-113 °C {Lit. [16] m.p.: 114 °C}. The n-pentane fraction was dried over a water bath at 35-40 °C to give 2-nitrophenol (4) in 66% (0.20 g); m.p.: 44-45 °C {Lit. [16] m.p.: 44 °C} (Table 1, Scheme 2).

Mononitration of 4-Chlorophenol (4e) with [bmim][HSO₄] and NaNO₃. A Typical Procedure
A solution of compound 4e (0.257 g, 2 mmol), [bmim][HSO₄] (0.572 g, 2 mmol) and NaNO₃ (0.170 g, 2 mmol) in CH₃CN (8 ml) was magnetically stirred at room temperature. The reaction was completed after 20 min. Then acetonitrile was removed and the residue was extracted with diethyl ether to separate the ionic liquid. Diethyl ether was removed on a water bath (35-40 °C) under simple distillation. The yield was 0.27 g, (85%) of crystalline pale yellow solid (5e), m.p.: 89-90 °C {Lit. [16] m.p.: 91 °C}. ¹H NMR (FT-90 MHz, CDCl₃, TMS): δ 7.12 (dd, 1H), 7.42 (dd, 1H), 8.02 (s, 1H), 10.31 (b, 1H).

RESULTS AND DISCUSSION

Phenol was selected as a model compound for the nitration in the presence of 1-butyl-3-methylimidazolium hydrogen sulfate ([bmim][HSO₄]) as an acidic ionic liquid, and NaNO₃.

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\text{Me}^+\text{N}^{+}\text{Bu}^- + \text{H}_{2}\text{SO}_4 \xrightarrow{\text{CH}_2\text{Cl}_2} \text{Me}^+\text{N}^{+}\text{Bu}^- + \text{HSO}_4^- + \text{HCl}
\]

Scheme 1. Preparation of 1-butyl-3-methylimidazolium hydrogen sulfate [bmim][HSO₄]