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# Functionalized ionic liquid as the recyclable catalyst for Mannich-type reaction in aqueous media

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ABSTRACT

A novel functionalized ionic liquid 3-(N,N-dimethyldodecylammonium)propanesulfonic acid hydrogen sulfate ([DDPA][$HSO_4$]) was prepared. The ionic liquid could be used as a Brønsted acid–surfactant-combined catalyst for one-pot three-component Mannich-type reaction at room temperature in water. The heterogeneous catalytic procedure was simple and the catalyst could be reused at least six times without noticeably decreasing the catalytic activity.

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## 1. Introduction

The Mannich-type reaction is one of the most important fundamental carbon–carbon bond-forming reactions for the preparation of drugs and biologically active compounds [1,2]. Lewis acids [3–5], Lewis base [6], Brønsted acids [7–9], rare metal salts [10,11] or organic compounds [12–14] have been investigated as the catalysts for Mannich-type reaction over the past decades. However, the search for the new readily available and green catalysts is still being actively pursued.

In recent years, ionic liquids have attracted extensive interest in the context of green synthesis nowadays, of which functionalized ionic liquids have been one of the hottest topics. Combining the useful characteristics of solid acids and mineral acids, Brønsted acidic task-specific ionic liquids (TSILs) are designed to replace traditional mineral liquid acid catalysts, such as sulfuric acid and hydrochloric acid in chemical processes [15–17]. Using TSILs as catalysts for Mannich-type reaction have also been reported in these years [18–20]. However, TSILs with imidazole or triphenylphosphine as the cation are relatively expensive, which hinders their industrial applications. Furthermore, the commonly used dialkylimidazolium ionic liquids (bmimX) showed negligible biodegradability in the Closed Bottle Test (OECD 301 D), and the typical ionic liquids consist of halogen containing anions (such as $[PF_6]^-$, $[BF_4]^-$, $[CF_3COO]^-$, $[CF_3SO_3]^-$ or $[(CF_3SO_2)_2N]^-$) which in some regard limits their “greenness” [21–24]. Thus, it is necessary to synthesize less expensive and halogen-free ionic liquids, which can be used straightforwardly with the simple procedure.

We are especially interested in preparation and developing the potential use of efficient, simple and biodegradable TSILs catalysts. In our previous work some novel $SO_3H$-functional halogen-free acidic ionic liquids have been prepared and their catalytic activities for acid-catalyzed reactions have also been investigated [25–28]. In continuation of our work, we reported here a novel Brønsted acid–surfactant-combined halogen-free ionic liquid [DDPA][$HSO_4$] that bears a propane sulfonic acid group in an acyclic dimethyldodecylammonium cation (Scheme 1), and its use in the heterogeneous catalysis procedure of one-pot three-component Mannich-type reaction in aqueous media was also investigated.

## 2. Experimental

### 2.1. Materials and methods

Melting points were determined on X-6 microscope melting apparatus and reported uncorrected. $^1H$ NMR spectra were recorded on Bruker DRX300 (300 MHz). Elemental analyses were recorded on Perkin–Elmer C spectrometer. Mass spectra were obtained with automated FININIGAN TSQ QUANTUM ULTRA AM (Thermal) LC/MS spectrometer. All chemicals (AR grade) were commercially available and used directly without further purification.

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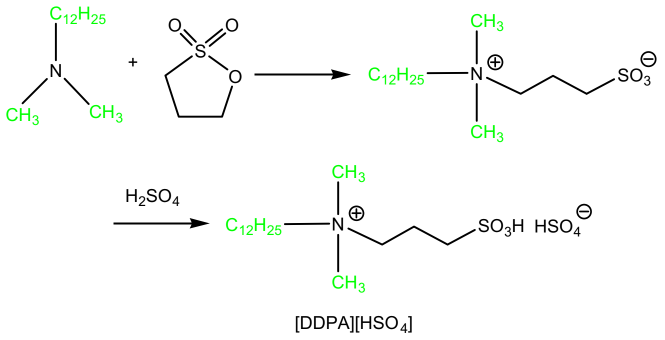


**Scheme 1.** Structure of the ionic liquid [DDPA][$HSO_4$].

### 2.2. Preparation of $SO_3H$-functional halogen-free acidic ionic liquid [DDPA][$HSO_4$]

The $SO_3H$-functionalized ionic liquid [DDPA][$HSO_4$] was prepared according to our previous method [28] with some changes. The structure of [DDPA][$HSO_4$] was analyzed by $^1$H NMR, elemental analyses and MS spectral data (Scheme 1).

To a solution of 13.3 g N,N-dimethyl-N-dodecyl amine (0.10 mol) in 30 mL 1,2-dichloroethane was added 12.2 g 1,3-propanesultone (0.10 mol) in portion within 15 mim, and then the mixture was stirred under nitrogen for 2 h at 55–60 °C. When cooled to room temperature, a white precipitate thus formed was then filtered and washed with petroleum ether. The product was refined from a mixture of water, ethanol and ether, there was obtained 98% yield of white solid product, mp 320–322 °C (decomposing) with darkening at 300 °C.

The mixture of 13.3 g N,N-dimethyl-N-dodecylammonium propane sulfonate (0.10 mol) and 10.0 g sulfuric acid solutions (98%) (0.10 mol) was stirred for 2 h at 80 °C. Then, the combined solution was dried in a vacuum at 100 °C. The produced [DDPA][$HSO_4$] was washed repeatedly with diethyl ether to remove unreacted material and dried in a vacuum again, and then the [DDPA][$HSO_4$] was obtained quantitatively and in high purity as colorless oil.

The selected spectral data for $SO_3H$-functionalized halogen-free [DDPA][$HSO_4$]:

3-(N,N-dimethyldodecylammonium)propanesulfonic acid hydrogen sulfate ([DDPA][$HSO_4$]) $^1$HNMR (300 MHz, $D_2O$): $\delta$0.53 (t, 3H, $J = 6.62$ Hz, —$CH_3$), 0.95–1.02 (m, 18H, —$(CH_2)_9$—), 1.42 (m, 2H, —C—$CH_2$—C—N), 1.83–1.87 (m, 2H, —C—$CH_2$—C—$SO_3$), 2.60 (t, 2H, $J = 6.91$ Hz, —$CH_2$—$SO_3$), 2.77 (s, 6H, N—$CH_3$), 2.98 (t, $J = 7.95$ Hz, 2H, —C—$CH_2$—N), 3.14 (t, $J = 8.25$ Hz, 2H, —$CH_2$—C—C—$SO_3$). Anal. Calcd. For CHNOS: C, 47.09; H, 9.07; N, 3.23; Found: C, 46.82; H, 9.08; N, 3.09. MS (*m*/*z*): 432.18 ($M^+-1$).

### 2.3. General procedure for the Mannich reaction catalyzed by [DDPA][$HSO_4$]

In a typical experiment, to a round-bottomed flask charged with [DDPA][$HSO_4$] (1 mmol) in 15 mL of water was added aldehyde (10 mmol) **1**, aniline (10 mmol) **2**, ketone (10 mmol) **3** under stirring. The mixture was then stirred for a certain time at room temperature (Scheme 2). On completion (monitored by TLC), the precipitated crude product was collected by filtration and recrystallized from ethanol–acetone (v/v = 1:1) to afford pure Mannich base **4**. The filtrate containing [DDPA][$HSO_4$] could be reused directly in the next run without further purification. The products were identified by $^1$HNMR, and physical data (m.p.) with those reported in the literatures.

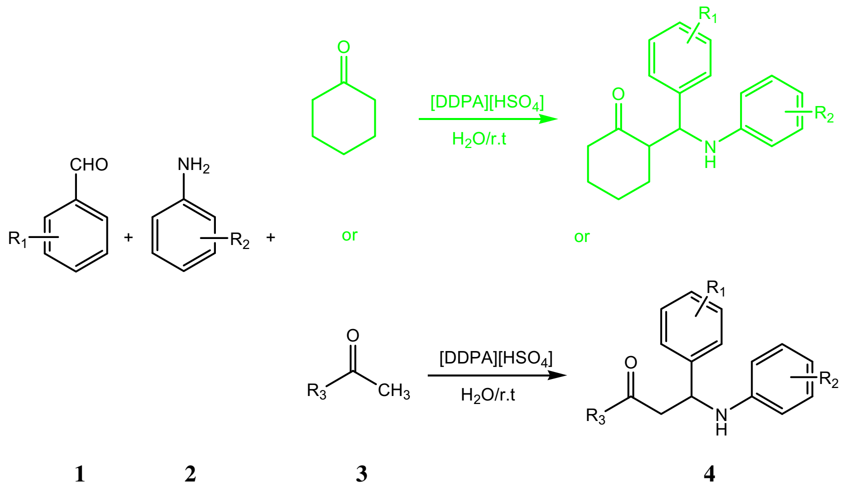
The selected data for Mannich base **4a**:

2-(Phenyl(phenylamino)methyl)cyclohexanone (**4a**, $C_9H_{21}NO$). White crystals; m.p. 116–117 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 1.57$–1.72 (m, 2H), 1.84–1.90 (m, 4H), 2.31–2.42 (m, 2H), 2.73–2.75 (m, 1H), 4.60–4.62 (d, 1H), 4.78–4.80 (br, 1H), 6.51–6.54 (d, 2H), 6.59–6.62 (m, 1H), 7.02–7.05 (m, 2H), 7.19–7.24 (m, 1H), 7.26–7.31 (m, 2H), 7.33–7.37 (d, 2H).

## 3. Results and discussion

The preparation of the catalyst [DDPA][$HSO_4$] was made up of two-step atom economic reaction. The biodegradable surfactant zwitterionic-type precursor (N,N-dimethyl-N-dodecylammonium propane sulfonate) was prepared through a one-step direct sulfonation reaction of N,N-dimethyl-N-dodecyl amine and 1,3-propanesulfone. The zwitterions acidification was accomplished by mixing of zwitterions with sulfuric acid (98%, aq.) to convert the pendant sulfonate group into [DDPA][$HSO_4$]. The chemical yields for both the zwitterions formation and acidification steps were essentially quantitative since neither reaction produced byproducts, the [DDPA][$HSO_4$] synthesis was 100% atom-efficient.

The ionic liquid bears a $SO_3$-functional group in the cation and has a structure of quaternary ammonium salt group which is generally used as phase-transfer catalyst (PTC). The solubility experiment showed that the $SO_3$-functionalized ionic liquid is miscible with water and relatively readily soluble in polar solvents such as methanol, ethanol, and acetone, and they are partially immisci-



**Scheme 2.** Mannich-type reaction catalyzed by the [DDPA][$HSO_4$].

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