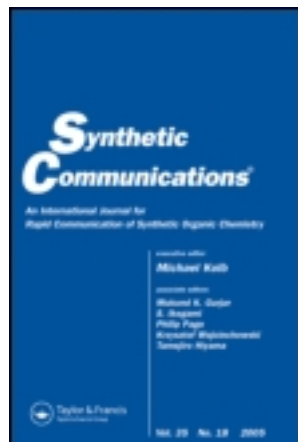


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AROMATIC COMPOUNDS MANNICH REACTION USING ECONOMICAL ACIDIC IONIC LIQUIDS BASED ON MORPHOLINIUM SALTS AS DUAL SOLVENT-CATALYSTS

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Economical acidic ionic liquids containing an alkanesulfonic acid group in a morpholinium cation were found to be effective catalysts for the Mannich reactions of various kinds of aromatic aldehydes, acetophenone and aromatic amines at mild reaction conditions. The satisfactory results were obtained with short reaction time, good yields of the Mannich bases and simplicity in the experimental procedure. These ionic liquids could be recycled and reused for up to five times without considerable decreasing in the catalytic activity.

Keywords: Catalysts; economical ionic liquids; Mannich reaction; solvent-free conditions

INTRODUCTION

Mannich reaction is one of the most classical and important carbon-carbon bond-forming reactions in organic synthesis for the preparation of β -amino carbonyl compounds, which in turn are important synthetic intermediates for various pharmaceuticals and natural products.^[1–3] The conventional catalysts for the classical three-component Mannich reaction of ketones, aldehydes and amines involve mainly mineral and organic acids like proline,^[4] *p*-dodecylbenzenesulfonic acid,^[5] HBF₄,^[6,7] and some Lewis acids,^[8–10] which often suffer from the disadvantages of harsh reaction conditions, toxicity and difficulty, long reaction times in the process. Nowadays, some new synthetic methods for the Mannich reaction have been developed to improve and modify this reaction by microwave^[11] or ultrasound irradiation.^[12]

Meanwhile, it has been noted that this reaction could also be promoted by a wide array of catalysts, such as rare earth perfluorooctane,^[13–15] ionic liquids,^[16–19] salts,^[20–22] proline,^[23–25] and others.^[26–28] However, most of these catalysts also have many disadvantages, that is expensive, requiring atmosphere sensitive reagents, regulatory constraints and so on. As a result, development of the cheap, green catalysts and methodologies remain an ever challenging objective.

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In recent years, with increasing environmental concerns and the regulatory constraints faced in the industry, more attention has been paid to the synthesis of task-specific ionic liquids, which have functional groups and their applications acted as both catalyst and solvent in chemical research.^[29–34] However, traditional task-specific ionic liquids with the cation of imidazole are expensive, which hinders their applications in the chemical industry. Therefore, the synthesis and application of economical task-specific ionic liquids are still in demand. In our previous work, in order to extend the scope and decrease the cost of ionic liquids, some relatively economical task-specific ionic liquids have been synthesized and their applications in Knoevenagel condensation reaction, esterification reactions have also been investigated, respectively.^[35,36]

Herein, we have discovered that some cheap Brønsted acidic ionic liquids that bear an SO₃H group in a morpholinium cation, and subsequently used them as catalyst and solvent for the one-pot three-component Mannich reaction of aromatic aldehydes, aromatic amines and acetophenone under relatively mild conditions.

RESULTS AND DISCUSSION

The Mannich reaction among benzaldehyde, acetophenone and aniline was chosen as a model reaction to test the catalytic activities of these three Brønsted acidic ionic liquids, [MPA][TFA], [MPA][HSO₄] and [MMPA][PTSA] and no other solvents were added as initial explorations. The results are summarized in Table 1. It was demonstrated that no β-Amino carbonyl compound was observed in the absence

Table 1. Mannich reaction of aromatic aldehydes, acetophenone and aromatic amines catalyzed by acidic ionic liquids

Entry	R ₁	R ₂	Ionic liquid (mol%)	Time (h)	Yields (%)
1	H	H	None	12	0
2	H	H	[MPA][HSO ₄]	3	No reaction
3	H	H	[MPPA][CF ₃ COO] (25)	2	89
4	H	H	[MMPA][PTSA] (25)	2	78
5 ^a	H	H	[MPPA][CF ₃ COO] (25)	2	82
6	H	H	[MPPA][CF ₃ COO] (5)	4	67
7	H	H	[MPPA][CF ₃ COO] (10)	3.5	75
8	H	H	[MPPA][CF ₃ COO] (15)	2.5	82
9	H	H	[MPPA][CF ₃ COO] (20)	2	86
10	H	H	[MPPA][CF ₃ COO] (30)	2	87
11	H	H	[MPPA][CF ₃ COO] (50)	2	87
12	<i>p</i> -CH ₃	H	[MPPA][CF ₃ COO] (25)	1.5	91
13	<i>p</i> -CH ₃ O	H	[MPPA][CF ₃ COO] (25)	1	93
14 ^b	<i>p</i> -NO ₂	H	[MPPA][CF ₃ COO] (25)	5	62
15	H	<i>p</i> -CH ₃ O	[MPPA][CF ₃ COO] (25)	1.5	93
16	H	<i>p</i> -CH ₃	[MPPA][CF ₃ COO] (25)	2	92
17	H	<i>p</i> -NO ₂	[MPPA][CF ₃ COO] (25)	6	70

Reaction condition: 10 mmol aromatic benzaldehyde, 10 mmol acetophenone and 10 mmol aromatic amine; temperature = 25 °C. Two drops of water (3.33 mmol) was added to the reaction mixtures.

^aTwo drops of water was not added.

^b15 mmol acetophenone and 15 mmol aniline was added to stir well.

of ionic liquids used as dual solvent and catalyst. [MPA][TFA] or [MMPA][PTSA] could catalyze this reaction. However, [MPA][HSO₄] reacted readily with aniline due to its strong acidity and no Mannich product was obtained (entry 2, Table 1). In addition, a small amount of water could promote the yield of product in the Mannich reaction catalyzed by these two acidic ionic liquids. This experimental phenomenon was in accord with the result from the literature.^[17] On comparing the results obtained by using [MPA][TFA] and [MMPA][PTSA], it is observed that the catalytic activity of [MPA][TFA] is higher than that of [MMPA][PTSA].

To optimize the reaction conditions, we examined the effect of the amount of acidic ionic liquid on yield of the Mannich base using the Mannich reaction of benzaldehyde, acetophenone and aniline catalyzed by [MPA][TFA] as a model reaction. From the data of Table 1, we can see that the amount of the acidic ionic liquid affected the yield of product significantly. The yield of the product increased with the amount of [MPA][TFA] when ionic liquid was not enough in the reactor, but did not change considerably as the amount of [MPA][TFA] more than 25 mol%. The main reason could be that the acidic active sites increase with the amount of [MPA][TFA], which enhances the reaction rate. The optimized conditions were extended to a series of aromatic aldehyde acceptors and aromatic amines to explore the generality of this catalytic system and the results are also summarized in Table 1. In most cases, the Mannich bases were obtained in good yields. However, when one of three-component was an aliphatic compound, such as propionaldehyde, butyraldehyde, butanone, acetone, propylamine and ethylamine, the Mannich reaction did not take place in the presence of the catalyst even if the reaction time was prolonged. Furthermore, the yield of the product was very low when cyclohexanone was using as a ketone donor.

As can also be known from Table 1, the substitutional group of the reactants was crucial to the yield of Mannich bases. So far as aromatic aldehydes were concerned, the yield of Mannich base for the Mannich reaction using *p*-methylbenzaldehyde as a aldehyde donor was higher than that using benzaldehyde, but lower than that using *p*-methoxybenzaldehyde (entries 12, 13, and 14, Table 1). Moreover, in case of aromatic amines, it is noteworthy that the reactivity order of aromatic amines was *p*-methoxyaniline > *p*-methylaniline > aniline > *p*-nitroaniline (entries 15, 16, and 17, Table 1). The main reason could be that the exist of electron-donating group could be favorable to increasing its nucleophilic ability which determined the Mannich reaction speed. Unfortunately, the reaction using cyclohexyl amine or

Table 2. Reusing of the acidic ionic liquid [MPA][TFA]^a

Entry	Run	Yields (%)
1	Fresh	89
2	1	86
3	2	85
4	3	87
5	4	84
6	5	86

^a10 mmol benzaldehyde, 10 mmol aniline, and 10 mmol acetophenone, 2.5 mmol [MPA][TFA], temperature = 25 °C, time = 2 h.

2,4-xylylene as an amine compound did not take place even after prolonging the reaction time up to 24 h under this optimized conditions as examined through TLC.

The recycling of the acidic ionic liquid, [MPA][TFA] was also investigated. In the model reaction among benzaldehyde, acetophenone and aniline, the results listed in Table 2 showed that the [MPA][TFA] could be reused for five times without lowering of the catalytic activity. Meanwhile, no large difference was observed compared the IR of the reused ionic liquid with that of fresh ionic liquid. Therefore, the structure of the ionic liquid did not change during the process of the Mannich reaction.

CONCLUSION

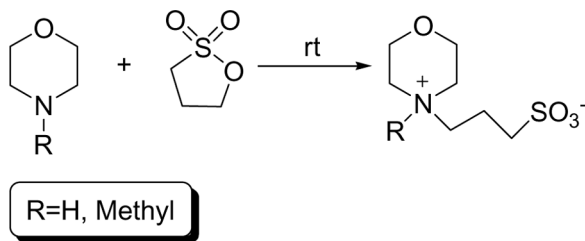
In summary, an efficient protocol for Mannich reaction of aromatic aldehydes, aromatic amines and aromatic ketones used economical acidic ionic liquids based on morpholinium salts as potential catalysts was developed. This method avoids the use of acid or basic catalysts and environmentally unfavorable volatile organic solvents (VOCs). The most attractive part of this work is that the cation was the cheap morpholinium sulfone, not triphenyl phosphonium sulfone or imidazolium sulfone. Therefore, we believe that this work would have potential application in green chemical industry.

EXPERIMENTAL

^1H NMR were measured on a Bruker DRX500 (500 MHz) spectrometer in D_2O with TMS as internal standard. The IR spectra were run on a Nicolette spectrometer (KBr). Melting points were taken on a hot-plate microscope apparatus and were not corrected. All yields refer to isolated products after purification. All chemicals (AR grade) were commercially available and used without further purification.

Synthesis of Morpholinium Propane Sulfonate (MPS) and N-Methylmorpholinium Propane Sulfonate (MMPS)

To a solution of morpholine or N-methylmorpholine (0.10 mol) in anhydrous acetone was added 1,3-propane-sulfone (0.10 mol) in portions within 30 min, and then the mixture was stirred for 3 h at room temperature (25°C). A white precipitate thus was formed, and subsequently filtered and washed with anhydrous acetone at 0°C . The white solid product was dried *in vacuo* at 60°C for 48 h to give morpholinium propane sulfonate or N-methylmorpholinium propane sulfonate. The yield of morpholinium propane sulfonate was 96%, m.p. $236\text{--}238^\circ\text{C}$ and the yield of N-methylmorpholinium propane sulfonate was 87%, m.p. $>280^\circ\text{C}$. MPS: ^1H NMR (500 MHz, D_2O): $\delta = 4.12$ (s, 1H, -NH), 3.72–4.00 (m, 4H, -CH₂-O-CH₂-), 3.32–3.54 (m, 2H, -CH₂-SO₃⁻), 3.12–3.26 (m, 4H, -CH₂-N⁺-CH₂-), 2.75–2.92 (t, 2H, -N⁺-CH₂-), 2.06–2.12 (m, 2H, -CH₂-), MMPS: ^1H NMR (500 MHz, D_2O): $\delta = 3.95$ (m, 4H, -CH₂-O-CH₂-), 3.52–3.55 (m, 2H, -CH₂-SO₃⁻), 3.40–3.48 (m, 4H, -CH₂-N⁺-CH₂-), 3.13 (s, 3H, -CH₃), 2.89–2.91 (t, 2H, -N⁺-CH₂-), 2.14–2.17 (m, 2H, -CH₂-).



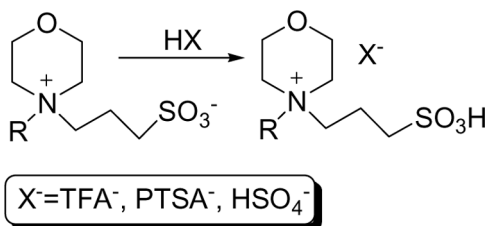
Scheme 1. Synthesis approach of MPS and MMPS.

Synthesis of Acidic Ionic Liquids, [MPA][TFA](Morpholinium Propanesulfonic Acid Ammonium Trifluoroacetate), [MPA][HSO₄](Morpholinium Propanesulfonic Acid Ammonium Hydrogen Sulfate), and [MMPA][PTSA](N-Methylmorpholinium Propanesulfonic Acid Ammonium P-Toluenesulfonate)³⁷

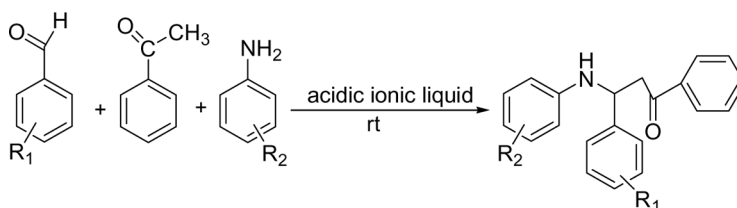
Equal molar of MPS or MMPS and sulfuric acid (96%), trifluoroacetic acid or fluoboric acid (40%) were mixed and stirred at specific temperature for specific time. Then the combined solution was evaporated *in vacuo* at 85 °C for 2 h to remove the water. The product was washed with diethyl ether three times and then dried under vacuum at 60 °C for 48 h. The [MPA][X] (X⁻=HSO₄⁻, CF₃COO⁻) and [MMPA][X] (X=PTSA⁻) were obtained in 89%, 84%, and 86%, respectively. Since these brønsted acidic ionic liquids were synthesized in accordance with the procedures previously reported in the literature, no further characterization was done.

Typical Procedure for Mannich Reaction Among Aromatic Aldehydes, Acetophenone, and Aromatic Amines

In a typical reaction, to a mixture of aromatic aldehyde (10 mmol), acetophenone (10 mmol) and aromatic amine (10 mmol) was added acidic ionic liquids (2.5 mmol) as catalyst and solvent. The mixture were stirred at room temperature (25 °C) in a 50 ml round-bottomed flask equipped with a magnetic stirrer. After a certain time the reaction mixture became viscous and close to solid. Then the solid was washed with water (5 ml × 3) and recrystallized from anhydrous ethanol. The products was vacuum dried for 6 h at 50 °C and identified by ¹H NMR and physical data (m.p.) with those reported in the open literature. The unreacted starting



Scheme 2. Synthesis of economic ionic liquids.



Scheme 3. Mannich reactions in ionic liquids.

materials in the filtrate were separated from the ionic liquids by extracting with ether. The left water layer containing ionic liquids was vacuum dried at 80 °C for 4 h to remove water and reused in the next run.

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