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Acidic ionic liquid $[NMP]H_2PO_4$ as dual solvent-catalyst for synthesis of β-alkoxyketones by the oxa-Michael addition reactions

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ABSTRACT

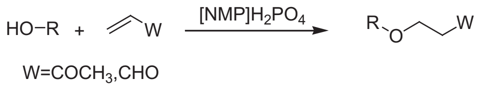
Acidic ionic liquid *N*-methyl-2-pyrrolidonium dihydrogen phosphate $[NMP]H_2PO_4$ was prepared and used as efficient catalyst and reaction medium to synthesize β-alkoxyketones by the oxa-Michael addition reactions for the first time. The effect of anions and cations, amount of ionic liquid on the reaction was investigated. Various alcohols and phenols proceeded smoothly and led to corresponding β-alkoxyketones with high yields under mild reaction conditions, O-selectivity addition of aminoethanols was also achieved in this paper. Compared with traditional imidazolium ionic liquids, $[NMP]H_2PO_4$ gave the better results. The ionic liquid was stable and could be reused at least five times with a slight loss of activity.

1. Introduction

The synthesis of β-alkoxyketones has attracted a great deal of attention from both academia and industry since they are building blocks and structural motifs of many natural products. The oxa-Michael addition reactions of alcohols to α, β-unsaturated compounds provide a direct protocol to construct β-alkoxyketones.[1] However, the reaction proceeds less efficiently because of the low reactivity and reversibility.[2] Strong bases or acids, red mercury oxide, boron trifluoride etherate, and a few transition metals (e.g., Pd, Cu, V) have been used as catalysts, but these synthetic methods are limited due to their drawbacks, such as violent reaction conditions and hazardous results to environment.[3–5] A lot of effort have been made and a new strategy with chiral phosphoric acid as catalyst to perform enantioselective oxa-Michael addition reaction was developed recently.[6]

Room-temperature ionic liquids (RTIL) have been applied in many areas because of their unique physical and chemical properties, such as good solvating ability, variable polarity, negligible vapor pressure, and ease of recyclability in recent years.[7–10] Some acidic ionic liquids have been successfully used in esterification reaction,[11] cleavages of ethers,[12] Friedel–Crafts alkylation reaction,[13] hydrolytic reaction,[14] Beckmann rearrangement,[15] Mannich reaction,[16] Saucy–Marbet reaction,[17] selective alkylation of phenol,[18] and arene carbonylation.[19] Although there are many publications utilizing basic and chiral ionic liquids in Michael addition reactions,[20–23] relevant reports about oxa-Michael addition reactions using acidic ionic liquids as catalysts are relatively scarce. Furthermore, imidazolium ionic liquids are the most frequently used among these reports. But the application of imidazolium ionic liquids is restricted due to the expensive cost and high toxicity.[24] Recently, some non-imidazolium ionic liquids have been prepared and applied in heck reaction, esterification, preparation of azides, oxidative desulfurization, and biodiesel synthesis.[25] However, preparation and application of novel acidic ionic liquids for oxa-Michael addition reactions are still highly desirable.

With a wish to establish more simple and practical reaction conditions, we have prepared and applied a series of acidic ionic liquids in the oxa-Michael addition reactions, satisfactory results were obtained when $[NMP]H_2PO_4$ was used (Scheme 1). To the best of our knowledge, we represent the first example of oxa-Michael reactions in acidic ionic liquid. The acidic ionic liquid $[NMP]H_2PO_4$ was used as a novel, recyclable, and efficient catalyst as well as reaction medium for oxa-Michael addition reactions.



Scheme 1. The oxa-Michael addition reactions promoted by $[NMP]H_2PO_4$.

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2. Results and discussion

Initial studies were carried out using the addition of β-phenylethanol to methyl vinyl ketone (MVK) as a model reaction. Table 1 showed the effect of different ionic liquids on the reaction. It was clear that the conversion was heavily influenced by the anions and cations of ionic liquids. In a first set of experiments, ionic liquids of the general [cation][BF_4] and [DMIM]Cl, [BMIM]PF_6 were tested as catalyst and reaction medium (entries 1–5, Table 1). For ionic liquids of the general [cation][BF_4], the conversion decreased as the volume of the cation increased (entries 1–3, Table 1). The [BMIM]PF_6 ionic liquid was less efficient and gave only 33% conversion (entry 4, Table 1). Furthermore, [DMIM]Cl produced the oxa-adduct with lower conversion than [BMIM]BF_4 (entry 5, Table 1). However, the best conversion was still lower than 50% (entry 1, Table 1). In the second set of experiments, two acidic imidazole ionic liquid [BMIM]HSO_4 and [HMIM]HSO_4 were tested (entries 6 and 7, Table 1). Although both imidazolium ionic liquids gave higher conversions, the results still could not meet our needs. In order to obtain higher conversion, some non-imidazolium ionic liquids were prepared and applied in the reaction. Compared with traditional imidazolium ionic liquids, *N*-methyl-2-pyrrolidonium ionic liquid [NMP]HSO_4 produced the oxa-adduct with the better result (entry 8, Table 1). It was found that the conversion decreased slightly when the anion was $PTSA^-$ (entry 9, Table 1). To our delight, a promising result (95% conversion) was achieved when [NMP]H_2PO_4 was employed (entry 10, Table 1). The order of catalytic activity could be related to the solvating ability of *N*-methyl-2-pyrrolidonium ionic liquids.

Table 1
The effect of ionic liquids on the oxa-Michael addition reaction[a]

Entry	Catalyst	Conversion[b] (%)
1	[BMIM]BF_4	47
2	[OMIM]BF_4	27
3	[Bupy]BF_4	38
4	[BMIM]PF_6	33
5	[DMIM]Cl	43
6	[BMIM]HSO_4	54
7	[HMIM]HSO_4	71
8	[NMP]HSO_4	87
9	[NMP]PTSA	84
10	[NMP]H_2PO_4	95

[a] Reactions were carried out on 0.5 mmol scale of β-phenylethanol with 2 equiv of MVK (entries 1–10, Table 1) in 2 mmol ionic liquid at room temperature for 24 h.
[b] Conversion determined by HPLC.

It should be noted that the amount of ionic liquid has an important impact on the reaction. As indicated in Table 2, the conversion was very low when the amount of ionic liquid was 0.1 mmol. After the screening, the optimal amount of ionic liquid was about 2 mmol.

Table 2
The effect of amount of ionic liquid on the oxa-Michael addition reaction[a]

Entry	Catalyst	Amount of catalyst (mmol)	Conversion[b] (%)
1	[NMP]H_2PO_4	2	95
2	[NMP]H_2PO_4	1	90
3	[NMP]H_2PO_4	0.5	82
4	[NMP]H_2PO_4	0.1	30

[a] Reactions were carried out on 0.5 mmol scale of β-phenylethanol with 2 equiv of MVK (entries 1–4, Table 2) in ionic liquid at room temperature for 24 h.
[b] Conversion determined by HPLC.

With the optimized reaction conditions in hand, we then examined the scope and limitations of this strategy for other structurally diverse substrates, the results were summarized in Table 3. β-Phenylethanol produced the oxa-adduct with high yield (entry 1, Table 3). The reactivity of 4-nitrobenzyl alcohol (entry 2, Table 3) was lower due to the effect of substituted group. Sterically hindered secondary alcohols, such as dl-sec-phenethyl alcohol and

Table 3
The oxa-Michael addition promoted by [NMP]H_2PO_4[a]

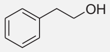
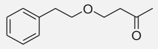
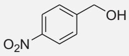
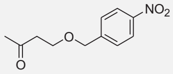
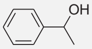
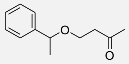
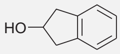
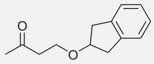
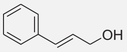
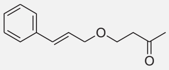
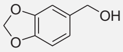
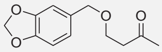
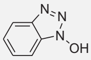
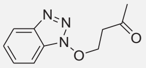
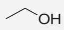
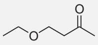
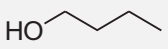
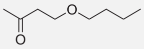
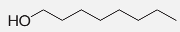
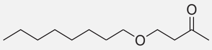
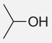
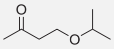
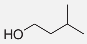
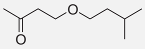
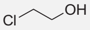
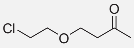
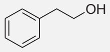
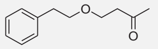
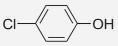
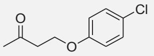
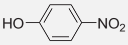
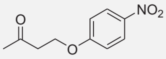
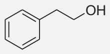
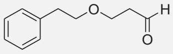
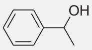
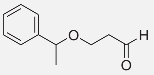
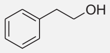
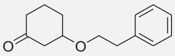
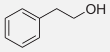
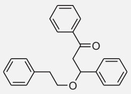
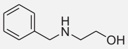
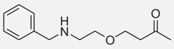
Entry	Substrate	Product	Yield[b] (%)
1			90
2			81
3			71
4			78
5			86
6			83
7			92
8			82
9			63
10			57
11			67
12			61
13			54
14			92[c]
15			48[d]
16			43[d]
17			59[e]
18			48[e]
19			—[f]
20			—[f]
21			93

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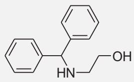
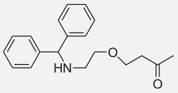
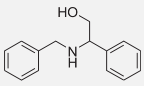
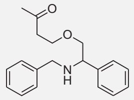
Table 3 (*continued*)

Entry	Substrate	Product	Yield[b] (%)
22			56
23			47

[a] Reactions were carried out on 0.5 mmol scale of substracts with 2 equiv of MVK (entries 1–13, 21–23, Table 3) in 2 mmol ionic liquid at room temperature for 24 h.

[b] Yield of isolated product.

[c] Reactions were carried out on 5 mmol scale of β-phenylethanol with 2 equiv of MVK (entry 14, Table 3) in 2 mmol ionic liquid at room temperature for 24 h. Conversion determined by HPLC.

[d] Reactions were carried out on 0.5 mmol scale of substracts with 2 equiv of MVK (entries 15 and 16, Table 3) in 2 mmol ionic liquid at 50 °C for 24 h.

[e] Reactions were carried out on 0.5 mmol scale of substracts with 2 equiv of acrylaldehyde (entries 17 and 18, Table 3) in 2 mmol ionic liquid at room temperature for 24 h.

[f] No reaction.

2-indanol alcohol (entries 3 and 4, Table 3) showed relatively lower activities compared to β-phenylethanol. Interesting, cinnamyl alcohol provided the oxa-adduct exclusively with good yield under the same reaction conditions (entry 5, Table 3). More complicated heteroaromatic alcohols, such as 3,4-(methylenedioxy) benzyl alcohol and 1-hydroxybenzotrizole could also be used as substrates to obtain the corresponding oxa-Michael adducts with moderate to high yields (entries 6 and 7, Table 3). Aliphatic alcohols were also tested in the reaction. As the carbon chain length of the alcohol moiety increased, the reactivity decreased (entries 8–10, Table 3). Sterically hindered alcohols, such as propan-2-ol and 3-methylbutan-1-ol (entries 11 and 12, Table 3) gave only moderate yields under the same reaction conditions. But the result of propan-2-ol was still superior to the known base-catalysed (12–20%),[26] $BF_3 \cdot OEt_2$-catalysed (34%)[27] and Tsoh-catalysed reaction (45%).[28] The reactivity of 2-chloroethanol (entry 13, Table 3) was lower than ethanol because of the effect of substituted group. Furthermore, 4-chlorophenol and 4-nitrophenol could also give the corresponding oxa-adducts with moderate yields in higher reaction temperature (entries 15 and 16, Table 3). While they could not undergo oxa-Michael addition reactions in the presence of strong acid Tf_2NH due to the competitive interference of Friedel–Crafts-type reaction.[29] A large scale reaction was attempted with 5 mmol of β-phenylethanol and 10 mmol of MVK (ten times larger than other entries) under the same reaction conditions. As shown in Table 3, 92% conversion was obtained, this result revealed this catalyst was practical even for large scale reaction. Acrylaldehyde could also be used as acceptor and reacted with β-phenylethanol and dl-sec-phenethyl alcohol to give the corresponding oxa-adducts with moderate yields (entries 17 and 18, Table 3). Cyclohex-2-enone and chalcone were examined under the same reaction conditions (entries 19 and 20, Table 3), but there were no reaction for both substrates. Elevating the reaction temperature to 50 °C still did not make the oxa-Michael addition happen. This might be due to the nature of their poor activity.

The Michael addition reaction of *N*-substituted aminoethanols was an important reaction to synthesize many useful compounds. Zhang reported that the addition selectivity of aminoethanols depended on the polarity of the solvent.[30] Aminoethanols could undergo oxa-Michael addition in polar solvents such as DMSO. There was no report about oxa-Michael addition of *N*-substituted aminoethanols with environmentally friendly methodologies. We investigated the reaction of *N*-Benzylethanolamine (entry 21, Table 3) in $[NMP]H_2PO_4$ and the corresponding oxa-adduct was obtained with 93% yield. The result accounted for the first example of oxa-Michael addition of *N*-substituted aminoethanol as the oxygen nucleophile to a Michael acceptor using ionic liquid as catalyst. Other structurally diverse *N*-substituted aminoethanol derivatives were also examined and the corresponding oxa-adducts were produced with moderate yields (entries 22 and 23, Table 3).

The remaining $[NMP]H_2PO_4$ could be reused without any additional operation. The addition reaction of β-phenylethanol to MVK was repeated five times and the results were shown in Table 4. It could be seen that the ionic liquid $[NMP]H_2PO_4$ remained consistent activity and high conversions were obtained.

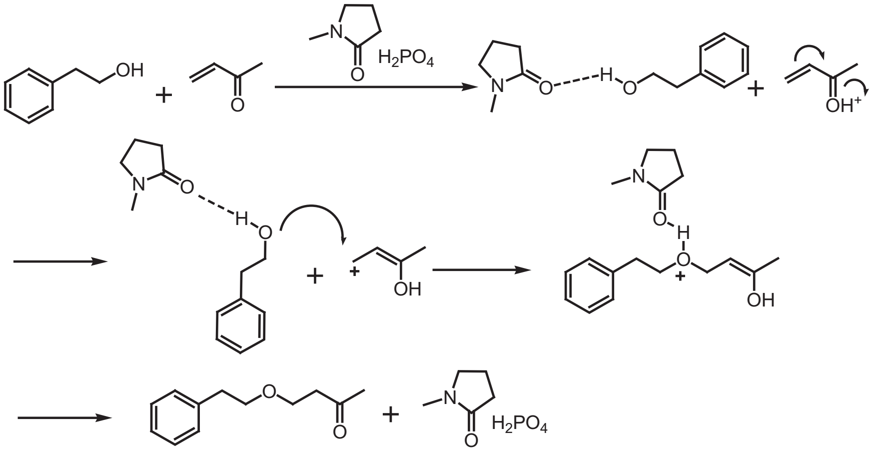
Table 4
Recycling of $[NMP]H_2PO_4$ in the Michael addition of β-phenylethanol to MVK[a]

Run	Conversion[b] (%)
1	95
2	91
3	91
4	92
5	91

[a] Reactions were carried out on 0.5 mmol scale of β-phenylethanol with 2 equiv of MVK (entries 1–5, Table 4) in 2 mmol ionic liquid at room temperature for 24 h.

[b] Conversion determined by HPLC.

The high activity of ionic liquid with [NMP]cation could be rationalized by a proposed mechanism (Scheme 2). On the one side, the anion could give proton to activate the MVK. On the other side, the carbonyl moiety of cation could interact with the hydroxyl



Scheme 2. Proposed mechanism for the oxa-Michael addition reaction promoted by $[NMP]H_2PO_4$.

group via H-bond to increase its nucleophilicity. It is expected that such synergistic activation delivers high activity, as demonstrated experimentally.

3. Conclusion

In summary, a simple and efficient method for oxa-Michael addition reaction was developed using novel acidic ionic liquid [NMP]H_2PO_4 as catalyst and reaction medium. Compared with traditional imidazolium ionic liquids, [NMP]H_2PO_4 produced the better results. A series of β-alkoxyketones were obtained with high yields under mild reaction conditions, O-selectivity addition of aminoethanols in ionic liquid were also achieved. The ionic liquid could be reused at least five times with high activity. This protocol provided a better and practical alternative to the existing procedures.

4. Experimental

4.1. Materials and general methods

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ with a Bruker AVANCE DMX 500 spectrometer at 400 MHz and 100 MHz, respectively. Chemical shifts are reported in parts per million (δ), relative to tetramethylsilane (TMS) as the internal standard. IR spectra were measured with a Nicolet Nexus FTIR 670 spectrophotometer. All reactions were carried out with efficient stirring in a round bottom flask at room temperature, unless otherwise stated, and monitored by TLC. Methyl vinyl ketone was distilled before use, other chemicals were obtained from commercial suppliers and were used without further purification.

4.2. General procedure for the synthesis of acidic ionic liquid

[NMP]H_2PO_4 was prepared by a dropwise addition of 1 equiv of phosphoric acid to cooled *N*-methyl-2-pyrrolidinone. After the addition, the reaction was stirred for 24 h at 80 °C. Then the water was removed by heating the residue at 80 °C in high vacuum until the weight of the residue remained constant. The ionic liquid was characterized by ^1H NMR. ^1H NMR (400 MHz, $CDCl_3$): 1.87 (m, 2H), 2.15 (t, 2H), 2.66 (s, 3H), 3.29 (t, 2H).

4.3. Typical procedure for Michael addition of alcohols to methyl vinyl ketone

To a mixture of β-phenylethanol (0.5 mmol, 61 mg) in [NMP] H_2PO_4 (2 mmol), MVK (1 mmol, 70 mg) was added. After addition, the reaction was stirred for 24 h at room temperature. The reaction was monitored by TLC. After the completion of reaction, reaction mixture was extracted with toluene. The ionic liquid could be further washed with toluene and reused several times without further purification. The solvent was evaporated and the product was isolated by column chromatography. IR (neat): 2867, 1716, 1496, 1361, 1169, 1112, 749, 700, 655 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=2.15 (s, 3H), 2.67 (t, 2H), 2.87 (t, 2H), 3.65 (t, 2H), 3.71 (t, 2H), 7.20–7.29 (m, 5H).

4.4. Typical procedure for Michael addition of *N*-substituted aminoethanols to methyl vinyl ketone

To a mixture of *N*-Benzylethanolamine (0.5 mmol, 75 mg) in [NMP]H_2PO_4 (2 mmol), MVK (1 mmol, 70 mg) was added. After addition, the reaction was stirred for 24 h at room temperature. Then the mixture was neutralized with saturated $NaHCO_3$ solution, extracted with ethyl acetate, dried over anhydrous sodium sulfate. The solvent was evaporated and the product was isolated by column chromatography. IR (neat): 2926, 1712, 1453, 1360, 1261, 1170, 1041, 799, 735, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=2.17 (s, 3H), 2.67 (t, 2H), 2.78 (t, 2H), 3.56(t, 2H), 3.69 (t, 2H), 3.80 (s, 2H), 7.31–7.32 (m, 5H).

Supplementary data

Supplementary data for this article can be found in the online version, at doi:10.1016/j.tet.2010.08.017. These data include MOL files and InChIKeys of the most important compounds described in this article.

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