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Ionic Liquid Catalysed Synthesis of β-Hydroxy Ketones

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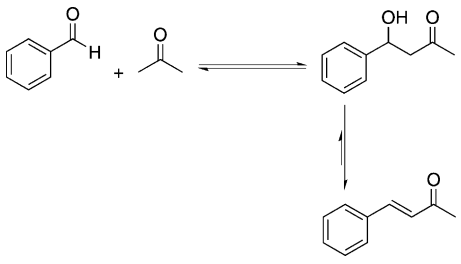
Different acidic ionic liquids (ILs; namely, 1-methylimidazolium tetrafluoroborate, 1-methylimidazolium trifluoroacetate, *N*-methyl-2-pyrrolidone hydrogen sulfate, *N*,*N*,*N*-trioctyl-*n*-butanesulfonic acid ammonium hydrogen sulfate, 1-methyl-3-(3-sulfobutyl)imidazolium hydrogen sulfate) and basic ILs (namely, 1,1,3,3-tetramethylguanidinium lactate and choline hydroxide) were tested as catalysts for the aldol reaction. The choline hydroxide catalysed reaction gave high yield (94.3%) and selectivity of the 4-hydroxy-4-phenylbutan-2-one after a short reaction time (15 min) at 0 °C. This article demonstrates the potential of choline hydroxide, which is a derivative of choline and a naturally occurring water-soluble essential nutrient, as a highly active and selective green catalyst.

Introduction

Ionic liquids (ILs) combine two properties of great value, namely, solvation power and catalytic activity. ILs are considered to be designer solvents because their solvation power can be manipulated by using suitable cations and anions in accordance with the reaction requirements.[1–13] Therefore, ILs are extensively used as solvents and co-solvents for chemical and enzymatic reactions.[1–11]

ILs with catalytic properties are known as task-specific ionic liquids (TSILs).[12,13] TSILs are usually designed by tethering functional groups to one or both of the ions.[12,13] TSILs or functionalised acidic and basic ILs have been used for different organic reactions, namely, esterification, transesterification, the pinacol rearrangement, the Biginelli reaction and the Knoevenagel reaction.[14–25] More recently, acidic ILs have been used for acetalisation, etherisation, and condensation reactions.[26] Herein, we focus on the acid- and base-catalysed aldol reaction, an essential C–C bond-forming reaction (Scheme 1).[27–30]

In general, aldol reactions are industrially carried out by using KOH, NaOH, and $Ca(OH)_2$ as catalysts.[31–33] In this context, the synthesis of aldol condensation products by using a mixture of neutral imidazolium ILs with NaOH,[34,35] 1,1,3,3-tetramethylguanidinium lactate[20,21] and choline hydroxide immobilised on MgO[22] is reported. However, these processes often lead to the formation of α,β-unsaturated ketones (dehydrated products).[22,31–35] In addition, functionalised ILs derived from a chiral pyrrolidine unit[36] and mixtures of different imidazolium-based ILs with L-proline[37] are used for aldol reactions.



Scheme 1. The aldol reaction leads to the formation of β-hydroxy ketones and α,β-unsaturated ketones.

The aldol reaction leading to the formation of the versatile β-hydroxy ketone moiety is of great interest because β-hydroxy ketones are building blocks for diols, amino alcohols, lactones, and polyketides, which are known for their high biological activity.[27–30] Although ILs are considered to be green reagents, recent investigations also showed toxicity and ecotoxic effects.[2,11,38–40] In this context, the use of a catalytic amount of these ILs can reduce the risk of environmental impact significantly.

Acidic and basic ILs are used in various capacities in organic synthesis. However, a systematic investigation of such ILs for the production of β-hydroxy ketones has not been performed yet.

Herein, we report the use of a set of functionalised Brønsted acidic (Scheme 2) and basic ILs (Scheme 3) as catalysts and co-solvents along with a benign organic solvent for the synthesis of β-hydroxy ketones. In particular, our focus is on the use of choline hydroxide, which is a derivative of choline and a naturally occurring, water-soluble essential nutrient, as a catalyst.[41]

Results and Discussion

Different acidic (Scheme 2), namely, 1-methylimidazolium tetrafluoroborate ([Hmim][BF_4]), 1-methylimidazolium trifluoroacetate ([Hmim][TFA]), *N*-methyl-2-pyrrolidone hydrogen sulfate ([NMP][HSO_4]), *N*,*N*,*N*-trioctyl-*n*-butanesulfonic acid ammonium hydrogen sulfate ([TOBSA][HSO_4]), 1-methyl-3-(3-sulfobutyl)imidazolium hydrogen sulfate ([HSO_3-BMIm][HSO_4]), and basic (Scheme 3) ILs, namely, 1,1,3,3-tetramethylguanidinium lactate

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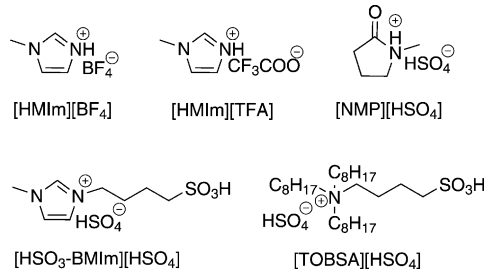
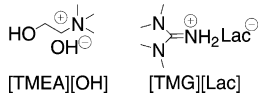


Scheme 2. Acidic ILs used for the aldol reaction. [Hmim][BF_4] = 1-methylimidazolium tetrafluoroborate, [Hmim][TFA] = 1-methylimidazolium trifluoroacetate, [NMP][HSO_4] = *N*-methyl-2-pyrrolidone hydrogen sulfate, [TOBSA]-[HSO_4] = *N*,*N*,*N*-trioctyl-*n*-butanesulfonic acid ammonium hydrogen sulfate, and [HSO_3-BMIm][HSO_4] = 1-methyl-3-(3-sulfobutyl)imidazolium hydrogen sulfate.



Scheme 3. Basic IL used for the aldol reaction. [TMG]-[Lac] = 1,1,3,3 tetramethylguanidinium lactate.

([TMG][Lac]) and choline hydroxide, were tested for the aldol reaction of benzaldehyde with acetone at room temperature (Table 1). All of the reaction mixtures were biphasic and stirred vigorously during the course of the reaction.

The choice of acidic ILs was based on successful applications in other reactions[14–20] and to ensure comparison with earlier reports, whereas the basic ILs were selected as catalysts owing to their environmental friendliness because they were derived from natural resources, such as choline and lactic acid.

The imidazolium cation containing acidic IL [HMIm][BF_4] gave 20.8% conversion of benzaldehyde with 88.9% selectivity to 4-hydroxy-4-phenylbutan-2-one (Table 1, entry 1). On the other hand, no product was observed when changing the counterion to TFA (Table 1, entry 2).

[NMP][HSO_4] gave 12.6% conversion of benzaldehyde with 55.5% selectivity to 4-hydroxy-4-phenylbutan-2-one (Table 1, entry 3). The sulfonic acid functionalised ILs [TOBSA][HSO_4] and [HSO_3-BMIm][HSO_4] gave high conversions (97.7 and 80.4%), whereas the selectivity to 4-hydroxy-4-phenylbutan-2-one was only 42.6 and 34.7%, respectively (Table 1, entries 4 and 5).

Two basic ILs, [TMG][Lac] and choline hydroxide, were used for the aldol reaction of benzaldehyde with acetone. It is important to note that these two ILs are derivatives of lactic acid and choline; these are naturally occurring substances found primarily in food materials. It was observed that [TMG][Lac] did not catalyse the reaction of benzaldehyde and acetone (Table 1, entry 6).[21] Even after 24 h no product was detected. Earlier reports on [TMG][Lac] always utilised 4-nitrobenzaldehyde as the substrate; this highlights the importance of the nitro group as an activating group when using this catalyst.[21]

In contrast, using choline hydroxide as a catalyst gave 92.3% conversion and 50.2% selectivity to the desired 4-hydroxy-4-phenylbutan-2-one were achieved at room temperature (Table 1, entry 7). This is in line with the earlier reports on the synthesis of aldol condensation products using choline hydroxide impregnated on MgO and NaOH-containing, imidazolium-based tetrafluoroborate and hexafluorophophate ILs.[22,34,35] However, in those cases, the elimination product was the dominant product.

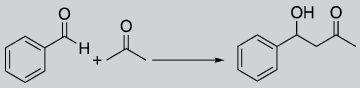
The formation of an α,β-unsaturated ketone (4-phenylbut-3-en-2-one) from the β-hydroxy ketone (4-hydroxy-4-phenylbutan-2-one) is a thermodynamically controlled process.[27–29] Therefore, the aldol reaction was carried out at 0 °C. The formation of 4-phenylbut-3-en-2-one was then suppressed to 1.3% (Table 1, entry 8). A conversion of 36.2% was observed with high selectivity (96.4%). Notably, during the choline hydroxide catalysed reaction the formation of an α,β-unsaturated ketone can be detected visually because the IL phase turns yellow with an increase in the concentration of 4-phenylbut-3-en-2-one (Figure 1).

The effect of increasing the concentration of acetone on the formation of 4-hydroxy-4-phenylbutan-2-one was investigated by using acetone as the solvent. The three most active and selective catalysts, namely, choline hydroxide, [HSO_3-BMIm][HSO_4] and [TOBSA][HSO_4], were chosen for this purpose.

The choline hydroxide catalysed reaction gave a high yield (94.3%) of the 4-hydroxy-4-phenylbutan-2-one after a short reaction time (15 min, Figure 2). The amount of 4-hydroxy-4-phenylbutan-2-one remained constant until 20 min (95%). After 0.5 h, the yield of 4-hydroxy-4-phenylbutan-2-one decreased slightly to 94% because dehydration gave 4-phenylbut-3-en-2-one (Figure 2).

Under similar reaction conditions, established basic catalysts, that is, $Ca(OH)_2$, KOH, and NaOH, were compared with choline hydroxide for the aldol reaction (Table 2). NaOH and KOH gave only 4 and 6.2% of 4-hydroxy-4-phenylbutan-2-one and 93 and 96% of 4-phenylbut-3-en-2-one, respectively. $Ca(OH)_2$ gave 58.5% of aldol with 95.8% selectivity. It is clear that choline hydroxide, with yields as high as 94% and

Table 1. The use of different ILs for the aldol reaction.



Entry	IL	Time [h]	Temperature [°C]	Conversion [%][a]	Aldol [%][b]	Selectivity [%][c]
1	[HMIm][BF_4]	24	25	20.8	18.5	88.9
2	[HMIm][TFA]	24	25	nd[d]	nd	–
3	[NMP][HSO_4]	24	25	12.6	7	55.5
4	[TOBSA][HSO_4]	24	25	97.7	41.7	42.6
5	[HSO_3-BMIm][HSO_4]	24	25	80.4	27.9	34.7
6	[TMG] [Lac]	24	25	nd	nd	–
7	Choline hydroxide	2	25	92.3	46.4	50.2
8	Choline hydroxide	2	0	36.2	34.9	96.4

[a] Conversion of benzaldehyde to β-hydroxy ketone and α,β-unsaturated ketone, as determined by using HPLC. [b] Amount β-hydroxy ketone, as determined by using HPLC. [c] Selectivity to aldol was determined by dividing the percentage of aldol with conversion. [d] Not detected.

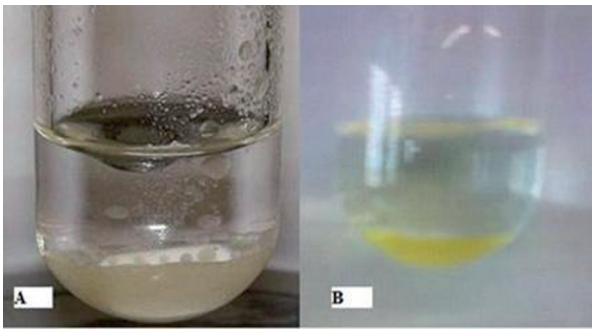


Figure 1. Reaction mixture of choline hydroxide catalysed aldol reaction at 0 °C after 30 min (A) and at 25 °C after 2 h (B). The reaction at 25 °C is pale yellow in colour because of the formation of 4-phenylbut-3-en-2-one.

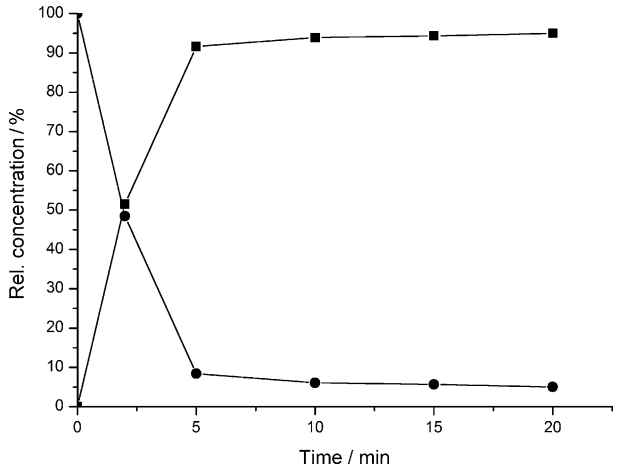


Figure 2. Formation of 4-hydroxy-4-phenylbutan-2-one (■) during the choline hydroxide catalysed aldol reaction of benzaldehyde (●) with acetone.

excellent selectivity (97%) to β-hydroxy ketone, outperforms the other reagents.

On the other hand, under similar reaction conditions, the [HSO_3-BMIm][HSO_4]-catalysed aldol reaction gave 7.9% conversion (100% selectivity, Figure 3) and the [TOBSA][HSO_4]-catalysed aldol reaction gave 47% conversion (62% selectivity, Figure 4) after 0.5 h.

[HSO_3-BMIm][HSO_4]- and [TOBSA][HSO_4]-catalysed aldol reactions were continued for 25 h. Less hydrophobic [HSO_3-BMIm]-[HSO_4] gave only 32% conversion (78% selectivity, Figure 3) after 25 h, whereas the highly hydrophobic [TOBSA][HSO_4]-catalysed aldol reaction gave somewhat better conversion (72%) of benzaldehyde and only 59% selectivity to 4-hydroxy-4-phenylbutan-2-one after 25 h (Figure 4).

Table 2. Comparison of $Ca(OH)_2$, KOH, NaOH, and choline hydroxide catalysts for the aldol reaction.

Catalyst	Conversion [%][a]	Aldol [%][b]	Selectivity [%][c]
KOH	99.7	4	3.6
NaOH	99.5	6.2	6.2
$Ca(OH)_2$	61	58.5	95.8
Choline hydroxide	97	94	97

[a] Conversion of benzaldehyde to β-hydroxy ketone and α,β-unsaturated ketone, as determined by using HPLC. [b] Amounts of β-hydroxy ketone and 4-phenylbut-3-en-2-one were determined by using HPLC. [c] Selectivity to aldol was determined by dividing the percentage of aldol with conversion.

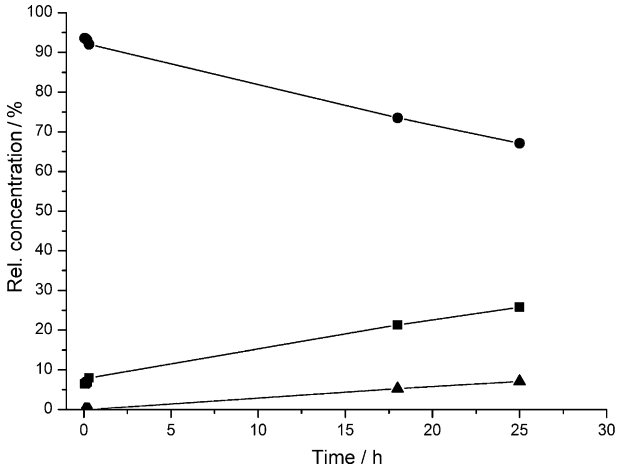


Figure 3. Formation of 4-hydroxy-4-phenylbutan-2-one (■) and 4-phenylbut-3-en-2-one (▲) during the [HSO_3-BMIm][HSO_4]-catalysed aldol reaction of benzaldehyde (●) with acetone.

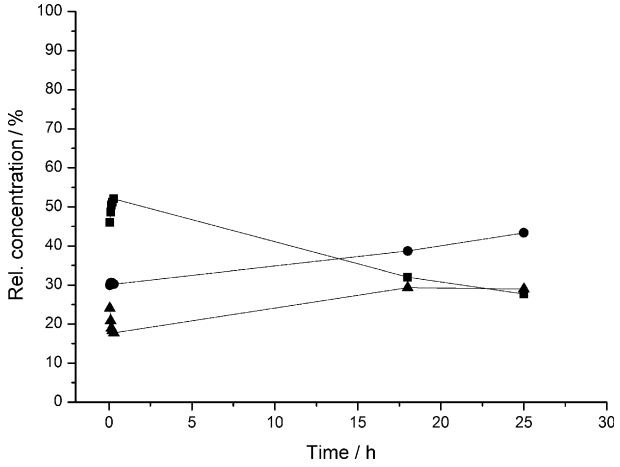
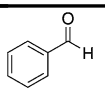
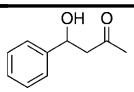
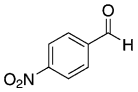
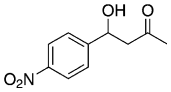
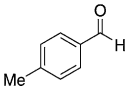
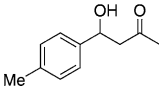
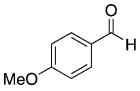
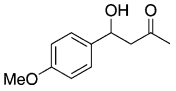
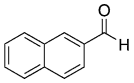
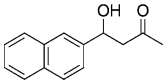
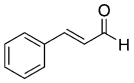
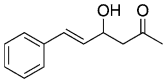
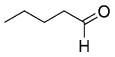
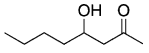
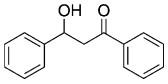


Figure 4. Formation of 4-hydroxy-4-phenylbutan-2-one (●) and 4-phenylbut-3-en-2-one (▲) during the [TOBSA][HSO4]-catalysed aldol reaction of benzaldehyde (■) with acetone.

Clearly, basic choline hydroxide outperforms the acidic ILs as catalysts both in terms of activity and selectivity. Therefore, subsequently, differently substituted aromatic aldehydes were tested under the optimised reaction conditions by using choline hydroxide as the catalyst (Table 3). Aldehydes with strongly electron-withdrawing groups, such as 4-nitrobenzaldehyde, gave 75% of 4-hydroxy-4-(4-nitrophenyl)butan-2-one in a short reaction time (0.15 h) with 20% of 4-(4-nitrophenyl)but-3-en-2-one (Table 3, entry 2).

When using 4-methylbenzaldehyde and 4-methoxylbenzaldehyde as substrates, 76 and 82% of the corresponding aldol products were isolated after a slightly longer reaction (Table 3, entries 3 and 4). Bulky substrate 2-naphthaldehyde gave 79%

Table 3. Aldol reaction of different aldehydes with ketones by using choline hydroxide as the catalyst at 0 °C.

Entry	Aldehyde	Ketone	Reaction time [h]	Product	Isolated yield [%][a]
1			0.25		92
2			0.15		75
3			1.5		76
4			2.5		82
5			1.15		79
6			2		84
7			3		66
8			3.5		45

[a] Isolated yield of the β-hydroxy ketones after column chromatography.

of 4-hydroxy-4-(naphthalen-2-yl)butan-2-one in 1.15 h, whereas cinnamaldehyde gave 84% of 4-hydroxy-6-phenylhex-5-en-2-one in 2 h (Table 3, entries 5 and 6).

To extend the substrate specificity of this reaction toward aliphatic aldehydes, pentanal was used as a substrate. After 3 h, 66% of 4-hydroxyoctan-2-one was isolated (Table 3, entry 7). Remarkably, no self-condensation of pentanal was observed.

Additionally, acetophenone was used as a solvent and substrate. After 3.5 h, only 45% of the desired β-hydroxy ketone (3-hydroxy-1,3-diphenylpropan-1-one) was isolated (Table 3, entry 8). The low selectivity to the product was due to the formation of different side products, namely, 3-hydroxy-1,3-diphenylpropan-1-one, 3-hydroxy-1,3-diphenylbutan-1-one and 1,3-diphenylbut-2-en-1-one.

Due to the biphasic nature of the system, recycling should be straightforward. Indeed, when recycling of choline hydroxide was carried out, the catalyst could be reused several times (Figure 5). In the first run, 87% of 4-hydroxy-4-phenylbutan-2-one and 7% of 4-phenylbut-3-en-2-one were isolated. In the second and third runs a slight decrease of activity and selectivity was observed. The decrease in conversion was due to some loss of choline hydroxide during product extraction with diethyl ether. On the other hand, not all (elimination) products were removed, which led to a perceived lower selectivity in the second and third runs.

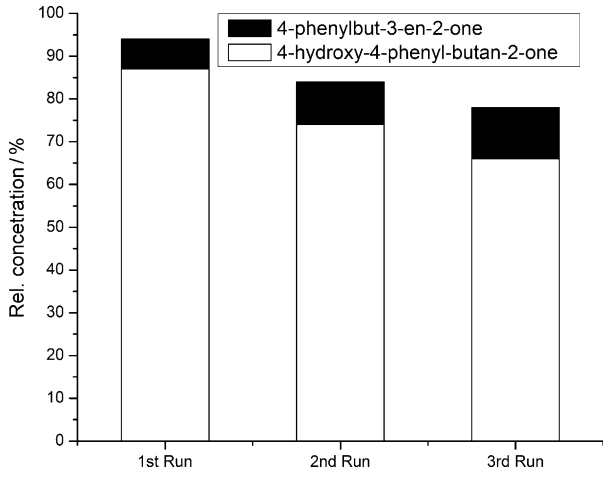


Figure 5. Recyclability of choline hydroxide during the aldol reaction of benzaldehyde with acetone. The reaction conditions used were those shown in Table 3.

It is apparent that choline hydroxide gave high yields of β-hydroxy ketones by the reaction of various aldehydes and ketones. This was remarkable because earlier work described for the aldol condensation, that is, the aldol reaction with subsequent elimination, was the main reaction using choline hydroxide; however, it was performed at higher temperatures.[22] Moreover, for catalyst preparation, the previously described impregnation of choline hydroxide onto MgO[22] and multi-step derivatisation of choline chloride with proline[23] was not necessary; this simplifies the reaction conditions.

Conclusions

Different acidic and basic ILs were tested for the production of β-hydroxy ketones. Three catalysts, $[HSO_3\text{-BMIm}][HSO_4]$, $[TOBSA][HSO_4]$, and choline hydroxide, gave good to excellent selectivities for the desired β-hydroxy ketones. Of these catalysts, choline hydroxide was the most active and selective and also the most environmentally benign. By utilising recyclable choline hydroxide, which is a derivative of a nutrient, as catalyst, a range of aldehydes could be selectively converted into their corresponding β-hydroxy ketones.

Experimental Section

Materials and methods: 1-Methylimidazole, *N*-methyl-2-pyrrolidone, 1,1,3,3-tetramethyl guanidine, 1,4-butanesultone, trioctyl amine, lactic acid, tetrafluoroboric acid, trifluoroacetic acid, and sulfuric

acid were purchased from Acros Organics and Sigma–Aldrich. Choline hydroxide was purchased from Acros Organics. Freshly distilled benzaldehyde and 1-methylimidazole were used for the reactions. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 400 (400 and 100 MHz, respectively) or Varian Unity Inova 300 (300 and 75 MHz, respectively) instruments. All reactions were carried out under N_2 by using standard Schlenk techniques. Thin-layer chromatography (TLC) was performed by using precoated silica gel SIL G/UV 254 plates. The water contents in the ILs were determined by applying Karl–Fischer titrations with a 756/831 KF Coulometer, according to the manufacturer's instructions.

Separation of the formed products was carried out by using HPLC using the following instrument and method: pump: Waters 590; UV detector: Waters 486, flow rate: 1 mL min^{-1}. A Chromolith Speed ROD, RP-18e, 50–4.6 mm, column was used for this purpose with H_2O/CH_3CN (90:10) as the mobile phase. The formed aldol (4-hydroxy-4-phenylbutan-2-one) and dehydrated product (4-phenylbut-3-en-2-one) were quantified by using 1,2,3-trimethoxybenzene as an internal standard. The retention times of 4-hydroxy-4-phenylbutan-2-one, benzaldehyde, 1,2,3-trimethoxybenzene, and 4-phenylbut-3-en-2-one were 3.4, 4.3, 9.9 and 20.2 min. All analyses were performed by diluting 20 μL of sample in 980 μL of HPLC eluent H_2O/CH_3CN (90:10).

Preparation of ILs: ILs used for this study, namely, [Hmim][BF4][14] (3483 ppm H_2O), [Hmim][TFA][15] (1777 ppm H_2O), [NMP][HSO_4][16,17] (1669 ppm H_2O), [HSO_3-BMIm][HSO_4][18] (513 ppm H_2O), [TOBSA]-[HSO_4][19] (606 ppm H_2O), and [TMG][Lac][20] (1126 ppm H_2O), were prepared and characterised according to reported methods.[14–20] Choline hydroxide had a water content of 451 ppm.

General procedure for the screening of acidic and basic ILs for the aldol reaction: The required IL catalyst (5 mmol) was added to a stirred solution of benzaldehyde (1 mmol, 106 mg), acetone (27 mmol, 2 mL), and dry diethyl ether (29 mmol; 3 mL) under N_2 in a dry 50 mL thermostated Schlenk flask. The reaction was stirred at room temperature for the required time (Table 1).

Choline hydroxide, [TOBSA][HSO_4]-, and [HSO_3-BMIm][HSO_4]-catalysed synthesis of 4-hydroxy-4-phenylbutan-2-one: The IL (4 mmol) was added to a stirred solution of benzaldehyde (1 mmol, 106 mg) in acetone (68 mmol, 5 mL) under N_2 at 0 °C in a dry 50 mL thermostated Schlenk flask. The reaction was stirred for 30 min (choline hydroxide) and 25 h ([TOBSA][HSO_4] and [HSO_3-BMIm][HSO_4]). All analyses were performed by using HPLC by diluting 20 μL of the sample in 980 μL of HPLC eluent (90:10 = H_2O/CH_3CN, Figures 2, 3, and 4).

General procedure for the synthesis of β-hydroxy ketone by using NaOH, KOH, and Ca(OH)$_2$: Ca(OH)$_2$, KOH, or NaOH (4 mmol) was added to a stirred solution of benzaldehyde (1 mmol, 106 mg) and acetone (68 mmol, 5 mL) under N_2 at 0 °C in a dry 25 mL thermostatic Schlenk flask. The reaction was stirred for 30 min. The conversion and selectivity were determined by HPLC, as described earlier.

General procedure for the synthesis of β-hydroxy ketones by using choline hydroxide as a catalyst: Choline hydroxide (4 mmol, 484 mg) was added to the stirred solution of aldehyde (1 mmol, 5 mL) in ketone (68 mmol, 7.94 mL) under N_2 at 0 °C. The reaction was stirred for the required time (Table 2). After the reaction, the solvent was evaporated in vacuo and the residue was extracted with diethyl ether (3×10 mL). The combined organic layers were evaporated and the crude product was purified by using column chromatography with petroleum ether/ethyl acetate (85:15) as the eluent. The isolated yield of the β-hydroxy ketones is given in Table 2. All of the products were characterised by using ^{1}H and ^{13}C NMR spectroscopy and the analytical data are in accordance with the literature.[42–44]

Recycling of choline hydroxide: Choline hydroxide (4 mmol, 484 mg) was added to a stirred solution of benzaldehyde (1 mmol, 106 mg) in acetone (68 mmol, 5 mL) under N_2 at 0 °C. The reaction was stirred for 30 min. After the reaction, the organic layer was separated and choline hydroxide was washed with dry diethyl ether (2×2 mL) under N_2 at 0 °C. Fresh benzaldehyde (1 mmol, 106 mg) and acetone (68 mmol, 5 mL) were added to the IL phase for the second run of the reaction. The third run was performed as described for the second run. The combined organic layers obtained after each run were evaporated separately, and the crude products were purified by using column chromatography with petroleum ether/ethyl acetate (85:15) as the eluent. The isolated yields of 4-hydroxy-4-phenylbutan-2-one and 4-phenylbut-3-en-2-one are presented in Figure 5.

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Keywords: aldol reaction · ionic liquids · organocatalysis · sustainable chemistry

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