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IONIC LIQUID–CATALYZED INTERNAL REDOX ESTERIFICATION REACTION

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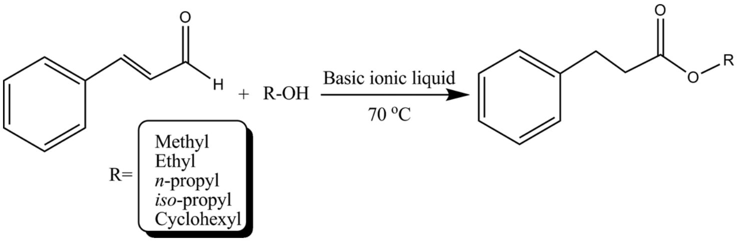
GRAPHICAL ABSTRACT



Abstract *The internal redox esterification of α,β-unsaturated aldehydes and alcohols was carried out using different ionic liquids (ILs) as catalysts and reaction solvents. The basic ionic liquid, 1-butyl-3-methylimidazolium acetate ([bmim]OAc), exhibited the best activity for this reaction. The influences of the amount of ionic liquid catalyst and reaction time on yield of saturated ester have been investigated. The results showed that ionic liquid anions have a crucial effect on the redox esterification of α,β-unsaturated aldehydes and alcohols. The nucleophilic carbenes generated in situ from the ionic liquid cation were believed to be actual active species for this reactions.*

Keywords Basic ionic liquids; carbene; redox esterificartion; α,β-unsaturated aldehydes

INTRODUCTION

Metal-free-catalyzed processes are interesting alternatives to classical organic transformations because they are often more economical and environmentally friendly. The protonation of α,β-unsaturated aldehydes is an important method for the formation of saturated esters starting from α,β-unsaturated aldehydes giving a C=C double bond and a carbonyl group, which are interesting building blocks for the synthesis of natural products and pharmaceuticals. These reactions are usually catalyzed by deprotonation of azolium salts such as thiazolium, imidazolium, and

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triazolium salts in the presence of bases such as NaOH, NaH, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), K_2CO_3, MeONa, and Et_3N.[1–4]

Several processes for the redox esterification reaction have been put forward, including protonation of a nucleophilic homoenolate where the resulting activated carbonyl unit was trapped by a nucleophile, which contributed to good to excellent yields of a broad scope of the saturated esters by addition an excess of phenol as a Brønsted acid.[5] The choice of the bases was found to be critical in this type of reaction.[6] The weaker bases can allow protonation of the homoenolate and subsequent generation of activated carboxylates. When diisopropylethylamine (DIPEA) was used in the reaction of α,β-unsaturated aldehydes with an alcohol, the initially generated homoenolate was protonated more rapidly than the carbon–carbon bond formation of the homoenolate. Additionally, the solvent polarity also played an important role in generating homoenolate equivalents from α,β-unsaturated aldehydes.[7] For example, weak to middle polar solvents such as tetrahydrofuran, (THF), CH_2Cl_2, and PhMe favored forming homoenolate equivalents to obtain saturated esters.

The room-temperature ionic liquids are a kind of environmentally friendly catalysts[8–10] and reagents,[11,12] because of their adjustable physical and chemical properties, and get attention from scholars from various fields such as synthesis,[13] catalysis, separation, and electrochemistry. Interest in basic ionic liquids is driven by internal alkalinity, which suggests that basic ionic liquids could substitute for inorganic bases. There are two main types of application of basic ionic liquids: alkaline catalyst and specific adsorbent agent that uses the basic center to realize the separation process. Until now most research into catalytic properties of basic ionic liquids has been focused on hydroxide-based ionic liquids ([bmim]OH), as reported by Mehnert,[14] which catalyze many types of reaction including the Mannich reaction,[15] Michael addition reaction,[16–19] Knoevenagel reaction,[20] and Markovnikov addition reaction.[21]

In addition to the hydroxyl anion ionic liquids, carboxylate-based ionic liquids have been recognized because the thermal and chemical stability of carboxylate-based ionic liquids are greater than those of [bmim]OH. The basic ionic liquid 1-butyl-3-methylimidazolium (L)-lactate ([bmim]lactate) not only catalyzed the Adler–Diels reaction between ethyl acrylate and cyclopentadiene (in which rate enhancements and selectivities were similar to those of reactions performed in lithium perchlorate–diethyl ether mixtures) but also was separated and reused more easily.[22] *O*-Acetylation of alcohols and saccharides using a dicyanamide ionic liquid as a catalyst was a rapid, clean, and mild approach.[23] Furthermore, the basic ionic liquid is not only an excellent solvent for a range of hydroxylated compounds but also an effective base catalyst for *O*-acetylation. Lewis basic ionic liquids such as 1-butyl-4-aza-1-azaniabicyclo[2.2.2]octane bromide ($[C_4DABCO]Br$) as the catalyst also can bring about activation of CO_2[24] and be a recyclable and efficient catalyst for selective synthesis of 5-aryl-2-oxazolidinones from aziridines and CO_2 without utilization of any organic solvent or additive, and high conversion and chemo- and regioselectivity were attained.

In this study, several neutral ionic liquids and basic ionic liquids were synthesized and used in the redox esterification between α,β-unsaturated aldehydes and alcohols. Obviously, ionic liquids are much cheaper and more stable than carbene catalysts given by azolium salts in the presence of a strong base.[25,26] Furthermore, basic ionic liquids can act as not only a catalyst but also a solvent and base promoter in the present system. The results showed that by using 1-butyl-3-methylimidazolium acetate ([bmim]OAc) as catalyst for redox esterification, high conversion of α,β-unsaturated aldehydes and good yield of saturated ester were obtained. The reaction mechanism is also discussed in this work.

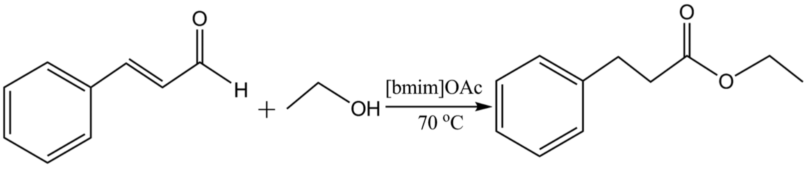
RESULTS AND DISCUSSION

Effect of Ionic Liquid on Redox Esterification Reaction

Ionic liquids were prepared according to the procedure reported in the literature.[27] In initial efforts to evaluate different conditions, we employed cinnamaldehyde and ethanol as model substrates. The reactions were studied using cinnamaldehyde (1 mmol) and ethanol (3 mmol) in ionic liquid (0.5 mmol) without any other base additives (Scheme 1).

Table 1 shows the effect of ionic liquid catalysts on redox esterification reaction. Ionic liquids such as 1-butyl-3-methylimidazolium acetate ([bmim]OAc), 1-butyl-3-methylimidazolium dicyanamide ([bmim]N(CN)$_2$), 1-butyl-3-methylimidazolium lactate ([bmim]lactate), and 1-butyl-3-methylimidazolium dimethylglycinate ([bmim]DMG) afforded greater activity than other ionic liquids studied in this work (Table 1, entries 1–7, 9). In particular, [bmim]OAc (Table 1, entry 4) exhibited excellent performance for redox esterification of α,β-unsaturated aldehyde. Nevertheless, when we utilized the strong basic ionic liquid [bmim]OH as a catalyst, the liquid extracts did not contain the desired products after reaction, and the high-molecular-weight products were obtained possibly because the basicity of [bmim]OH was so strong so that side reaction became dominant. In addition, pure imidazolium hydroxide is unstable under reaction conditions unless stabilized by the presence of a proton donor such as a protic solvent (e.g., water, methanol, etc.).[28] In contrast, [bmim][OAc] is a relatively stable ionic liquid,[29] suggesting that the equilibrium proposed in Scheme 2 can be effectively tuned by appropriate choice of anions.[30]

As shown in Table 1 (entries 10 and 11), the reaction did not occur in pure water or ethanol without ionic liquids, which indicated that the ionic liquid catalyst was absolutely necessary for this reaction. Moreover, it can be seen that the cations and especially anions of the ionic liquids have significant effects on redox esterification of cinnamaldehyde. The neutral ionic liquids such as [bmim]PF$_6$ and [bmim]Cl did not afford any desired products (Table 1, entries 1 and 2). When the 2-position proton in imidazilium cation was substituted by the methyl group, the reaction did not happen as well even though the anion was same (Table 1, entries



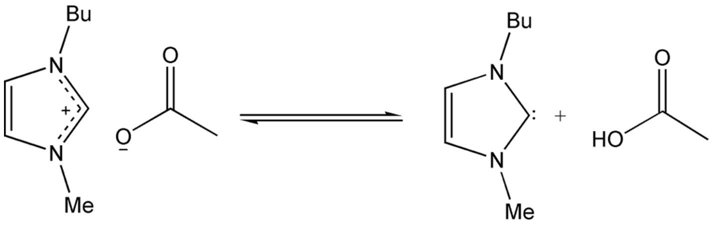
Scheme 1. Redox esterification reaction between cinnamaldehyde and ethanol.

Table 1. Comparison of different catalysts for reduction esterification of cinnamaldehyde with ethanol in ionic liquids[a]

Entry	Catalyst/solvent	t (h)	Conversion (%)	Selectivity (%)
1	[bmim]PF_6	2	0	0
2	[bmim]Cl	2	0	0
3	[bmmim]OAc	2	0	0
4	[bmim]OAc	2	99	100
5	[bmim]$N(CN)_2$	2	50	30
6	[bmim]Lactate	2	15	100
7	[bmim]DMG	2	17	100
8	[bmim]DMG	12	94	100
9	[bmim]OH[b]	2	—	—
10	H_2O	2	0	0
11	Ethanol	2	0	0

[a]All reactions were carried out with cinnamaldehyde and ethanol in ionic liquids. Reaction conditions: cinnamaldehyde/ethanol = 1:3 (molar radio), ionic liquids 0.5 mmol, cinnamaldehyde 1.0 mmol, T = 70 °C.
[b]High-molecular-weight side products were produced.

3 and 4). This probably indicates that the substrate cinnamaldehyde had a strong interaction with the proton on the 2-position of imidazolium ring.[31] It was also demonstrated that [bmim]OAc ionic liquid can afford greater conversion and yield than other basic ionic liquids such as [bmim]$N(CN)_2$, [bmim]lactate, and [bmim]DMG (Table 1, entries 5–8). It suggests that the basicity of ionic liquids had a significant impact on the conversion of the umpolung reaction of cinnamaldehyde. From previous reports,[32] we knew that the basicity of ionic liquids decreased in the following order: [bmim]OH > [bmim]DMG > [bmim]OAc > [bmim]$N(CN)_2$ > [bmim]Cl > [bmim]PF_6. The reason for the high reactivity of [bmim]OAc for this reaction is that [bmim]OAc is Lewis basic ionic liquid[33] and might promote the formation of a nucleophilic carbene catalyst in the process of redox esterification reaction as displayed in Scheme 2. On the other hand, dimethylglycine anion could not facilitate the carbene formation, possibly because of its steric hindrance. Moreover, strong Brønsted basic ionic liquid [bmim]OH showed no reactivity for the redox esterification reaction. It is known that a weak base is more favorable than a strong base for the imidazolium or triazolium salt–catalyzed umpolung reaction, which is in good agreement with our results.[6] In summary, the results showed



Scheme 2. Possible acid–base equilibrium between the constitutive ions of a 1,3-dialkylimidazolium ionic liquid.

Table 2. Effects of the amounts of [bmim]OAc on the reaction[a]

Entry	IL/sub.	Yield (%)
1	1:10	0
2	1:4	25
3	1:2	99
4	1:1	99

[a]All reactions were carried out with cinnamaldehyde and ethanol in ionic liquid. Reaction conditions: cinnamaldehyde/ethanol = 1:3 (molar radio), ionic liquids 0.5 mmol, T = 70 °C, t = 2 h.

that [bmim]OAc was an excellent catalyst and solvent for redox esterification of cinnamaldehyde.

The efficiency of the reaction was also affected by the added amount of [bmim]OAc (Table 2). The conversion of cinnamaldehyde increased with the molar ratio of [bmim]OAc to cinnamaldehyde, and the conversion of cinnamaldehyde was obtained up to 99% when the molar ratio was 1:2, but more amounts of the IL catalyst did not increase the yield noticeably (Table 2, entries 3, 4).

The reaction kinetics was plotted as shown in Fig. 1. The conversion of cinnamaldehyde and the yield for the saturated ester were increased with reaction time by using [bmim]OAc, [bmim]N(CN)$_2$, and [bmim]DMG ionic liquids as catalysts and reaction solvents. The conversion achieved 96% at 70 °C after reaction for only 1 h with [bmim]OAc, which was much greater than that using other basic imidazolium ionic liquid catalysts such as [bmim]N(CN)$_2$ and [bmim]DMG ionic liquids, indicating that the [bmim]OAc was a very efficient catalyst for this reaction. No obvious increasing in the yield of ester was obtained when the reaction time was more than 1 h. The advantages of the ionic liquid catalyst [bmim]OAc are that it is much

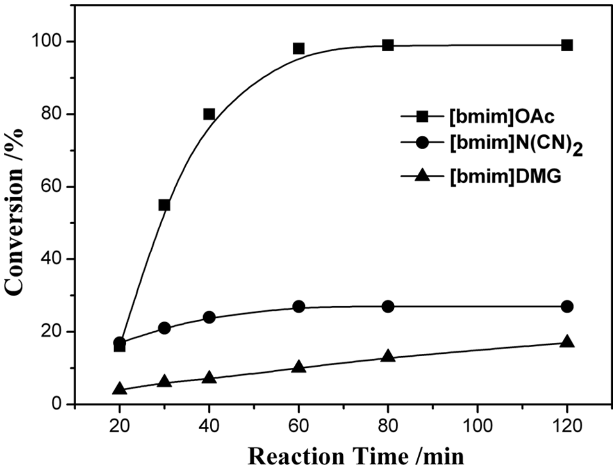


Figure 1. Time profile of redox esterification between cinnamaldehyde and ethanol catalyzed by [bmim]OAc, [bmim]N(CN)$_2$, and [bmim]DMG. Reaction conditions: ethanol (3 mmol), cinnamaldehyde (1 mmol), IL catalyst (0.5 mmol), T = 70 °C.

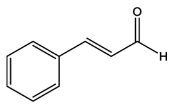
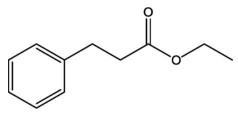
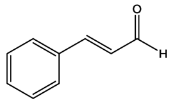
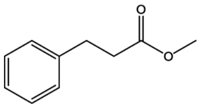
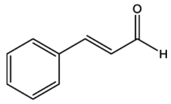
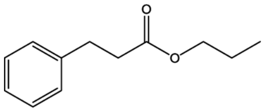
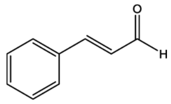
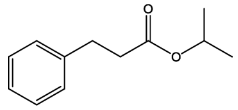
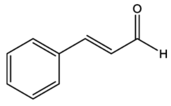
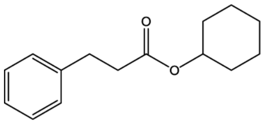
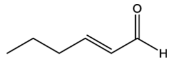
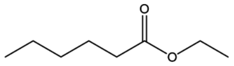
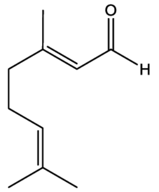
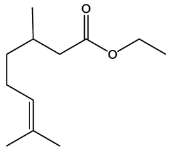
cheaper and simpler than the previous reported carbene catalysts given by azolium salts in the presence of a strong base.[5]

Survey of Different α,β-Unsaturated Aldehydes

Encouraged by these interesting results, we proceeded to examine the ability of other aldehydes to act as substrates and react with different alcohols. As shown in Table 3, with [bmim]OAc as the catalyst, most of the aldehydes can be converted efficiently into the corresponding saturated ester under mild conditions.

The electron-deficient cinnamaldehyde afforded the best reactivity among the aldehydes studied, possibly because the addition of a nucleophilic carbene catalyst

Table 3. Results of reduction esterification of α,β-unsaturated aldehydes with different alcohols using [bmim]OAc as catalyst and solvent[a]

Entry	Aldehydes	Alcohols	Product	t (h)	Conversion (%)	Selectivity (%)
1		Ethanol		1	97	100
2		Methanol		1	97	100
3		n-Propanol		4	98	100
4		Iso-propanol		4	96	100
5		Cyclohexanol		4	85	100
6		Ethanol		6	85	90
7		Ethanol		1	15	0[b]

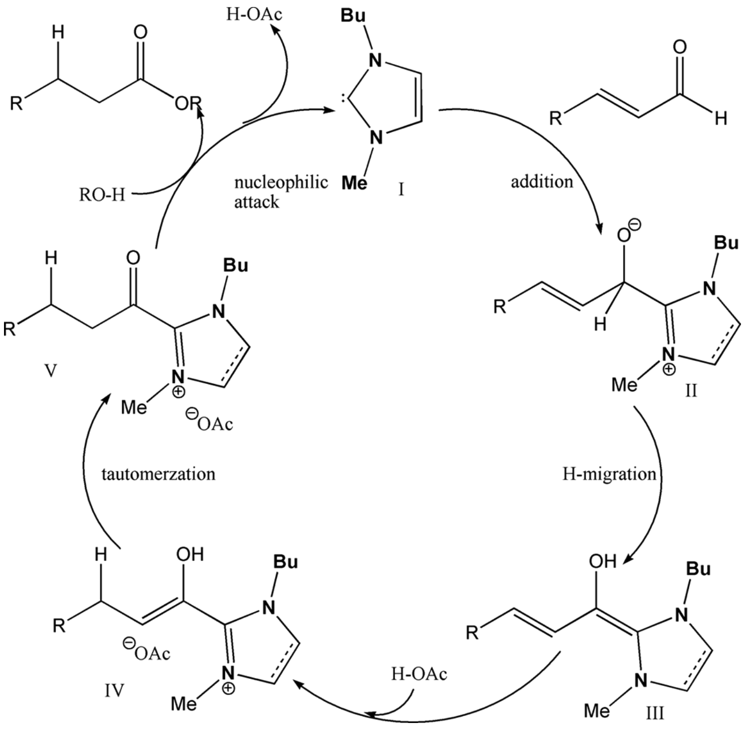
[a] All reactions were carried out with α,β-unsaturated aldehyde with alcohol in [bmim]OAc. Reaction conditions: aldehyde/ethanol = 1:3 (molar radio), ionic liquids 0.5 mmol, α,β-unsaturated aldehyde 1 mmol, T = 70 °C.

[b] The isomer of citral(carane 4,5-epoxide) was detected as a side product.

to the carbonyl compound (cinnamaldehyde) became more favorable than nonaromatic aldehydes (Table 3, entries 1, 6, and 7), which was very similar to the previous reports.[5–7] However, the citral was converted to its isomer (carane 4,5-epoxide) (Table 3, entry 7), which indicated that [bmim]OAc catalyst could not activate citral to form the appreciate intermediate. On the other hand, when the same cinnamaldehyde reacted with different alcohols, the reaction afforded a satisfying yield of saturated esters, but the activity decreased with longer alkyl chains of alcohols, which implied that the larger steric hindrance may result in lower reactivity (Table 3, entry 5).[5]

Reaction Mechanism

It has been reported that anions with high basicity (e.g., acetate) enable proton transfer in imidazolium-based ionic liquids, providing an imidazole-2-ylidene derivative (N-heterocyclic carbene, NHC) and an acid (e.g., acetic acid) as shown in Scheme 1.[30] Two neutral species are either attached to each other by a hydrogen bond (NHC–acetic acid complex) or are dissociated, and the fine-tuning of the carbene concentration in the imidazolium-based ionic liquids is possible by using counteranions with different basicity. According to the previous investigation,[30] the NHC–acetic acid complex could be produced in the present ionic liquid catalyst system. As a result, aldehydes and alcohols will then promote the decomposition of



Scheme 3. Proposed mechanism to generate homoenolate equivalent from α,β-unsaturated aldehyde.

Table 4. Reusability results of [Bmim]OAc[a]

Run	Conversion (%)
1	97
2	90
3	30

[a]All reactions were carried out with cinnamaldehyde and ethanol in ionic liquids. Reaction conditions: cinnamaldehyde/ethanol = 1:3 (molar radio), ionic liquids 0.5 mmol, Cinnamaldehyde 1 mmol, T = 70 °C, t = 1 h.

NHC–acetic acid complex and thus form free carbene and acetic acid. As we all know, the acetic acid can act as an electrophile and the nucleophile carbenes are the actual active species for the redox esterification reaction.

On the basis of this discussion, a plausible mechanism is depicted in Scheme 3. Reaction between the NHC produced from proton transfer in the ionic liquid and α,β-unsaturated aldehyde gave rise to a zwitterionic structure I, which involved a formal 1,2-proton shift to generate an extended enediamine intermediate. The normal nucleophilic character of the carbonyl carbon was then extended to the α-position, and in the presence of an electrophile (E-X, CH_3COO-H) should produce enol IV. After tautomerization of IV to activated ester V, the attack of a suitable nucleophile and the regeneration of the nucleophilic catalyst completed the catalytic cycle.

Because the ionic liquids could be separated from the reaction mixture by adding diethyl ether and reused directly as solvent and catalyst, the reusability of the ionic liquid for the reaction was examined, and the results were shown in Table 4. The results showed that the ionic liquid catalyst could be reused three times, although a continuous decrease in catalytic activity was observed. The main reason for the decreasing activity was the loss of ionic liquid in the consecutive runs.

EXPERIMENTAL

Reagents were obtained from commercial sources. Commercially available reagents were further purified before use. Products are all known compounds and identified by gas chromatography–mass spectrometry (GC-MS), and their physical and spectra data were compared with those reported in the literature. The ^{1}H NMR (400-MHz) spectra were recorded on a Bruker Avance-500 NMR spectrometer.

Synthesis of 1-Butyl-3-methylimidazolium Chloride [bmim]Cl and 1-Butyl-2,3-dimethylimidazolium Chloride [bmmim]Cl

[bmim]Cl was prepared and purified by using the procedure described in the literature.[27] The reaction of 1-methylimidazole with an excess of 1-chlorobutane was performed in ethyl acetate at 70 °C for 48 h. The solid product of [bmim]Cl was washed with ethyl acetate and then filtered. The residual solvent was removed by rotary evaporation, and the resulting product was dried at 60 °C under vacuum

for 24 h. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.96$ (t, 3H, $J = 7.30$ Hz, CH_3), 1.40 (m, 2H, CH_2), 1.91 (m, 2H, CH_2), 4.13 (s, 3H, CH_3), 4.35 (t, 2H, $J = 7.30$ Hz, CH_2), 7.47 (s, 1H, imid-H), 7.62 (s, 1H, imid-H), 10.67 (s, 1H, 2-imid-H).

1-Butyl-2,3-dimethylimidazolium chloride [bmmim]Cl was prepared using similar procedures described previously, and gave a white crystal.[34] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.95$ (t, 3H, $J = 7.30$ Hz, CH_3), 1.37 (m, 2H, CH_2), 1.78 (m, 2H, CH_2), 2.74 (s, 3H, CH_3), 3.99 (s, 3H, CH_3), 4.19 (t, 2H, $J = 7.40$ Hz, CH_2), 7.58 (d, 1H, $J = 1.98$ Hz, imid-H), 7.87 (d, 1H, J = 1.98 Hz, imid-H).

Synthesis of 1-Butyl-3-methylimidazolium Acetate [bmim]OAc

These ILs were synthesized and purified by using the procedure described in Refs. 34. Briefly, CH_3CO_2Na was added to a solution of [bmim]Cl in ethanol. The mixture was stirred for 24 h, and the solid NaCl was removed by filtration. After removing ethanol by evaporation under reduced pressure, the viscous liquid [bmim]OAc was dissolved in CH_2Cl_2, filtered to remove residual salt, and then dried under vacuum for 24 h at 60 °C to afford a slightly yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.96$ (t, 3H, $J = 7.40$ Hz, CH_3), 1.40 (q, 2H, CH_2), 1.91 (q, 2H, CH_2), 2.61 (s, 3H, CH_3), 4.13 (s, 3H, CH_3), 4.35 (t, 2H, $J = 7.40$ Hz, CH_2), 7.54 (s, 1H, imid-H), 7.66 (s, 1H, imid-H), 10.20 (s, 1H, 2-imid-H).

Other ionic liquids were prepared using the procedures described previously.[34]

1-Butyl-3-methylimidazolium Hexafluorophosphate [bmim]PF_6

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.99$ (t, 3H, $J = 7.30$ Hz, CH_3), 1.36 (m, 2H, CH_2), 1.86 (m, 2H, CH_2), 3.94 (s, 3H, CH_3), 4.16 (t, 2H, $J = 7.30$ Hz, CH_2), 7.10 (s, 1H, imid-H), 7.25 (s, 1H, imid-H), 8.68 (s, 1H, 2-imid-H).

1-Butyl-3-methylimidazolium Dicyanamide [bmim]DCA

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.99$ (t, 3H, $J = 7.40$ Hz, CH_3), 1.41 (m, 2H, CH_2), 1.92 (m, 2H, CH_2), 4.03 (s, 3H, CH_3), 4.26 (t, 2H, $J = 7.40$ Hz, CH_3), 7.30 (s, 1H, imid-H), 7.45 (s, 1H, imid-H), 9.17 (s, 1H, 2-imid-H).

1-Butyl-3-methylimidazolium Lactate [bmim]Lactate

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.96$ (t, 3H, $J = 7.40$ Hz, CH_3), 1.35 (d, 3H, $J = 1.98$ Hz, Lac-β-CH_3), 1.40 (m, 2H, CH_2), 1.90 (m, 2H, CH_2), 4.05 (s, 3H, NCH_3), 4.17 (t, 2H, $J = 7.40$ Hz, NCH_2), 4.28 (q, 1H, Lac-α -CH), 7.49 (s, 1H, imid-H), 7.58 (s, 1H, imid-H), 9.72 (s, 1H, 2-imid-H).

1-Butyl-3-methylimidazolium Dimethylglycine [bmim]DMG

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.95$ (t, 3H, $J = 7.3$ Hz, CH_3), 1.39 (m, 2H, CH_2), 1.89 (m, 2H, CH_2), 2.97 (s, 3H, CH_3), 3.70 (s, 2H, CH_2), 4.11 (s, 3H, N-CH_3), 4.32 (t, 2H, $J = 7.3$ Hz, CH_2), 7.45 (s, 1H, imid-H), 7.59 (s, 1H, imid-H), 9.71 (s, 1H, 2-imid-H).

General Procedure for Redox Esterification of Cinnamaldehyde and Ethanol with Ionic Liquids

In a typical experiment, [bmim]OAc (0.5 mmol) was charged into a 25-ml Schlenk flask with a magnetic stirrer and a reflux condenser followed by the addition of cinnamaldehyde (1 mmol). The mixture was stirred for 5 min at room temperature following addition of ethanol (3 mmol). The mixture was heated to 70 °C and stirred for 1 h. After reaction for a desired time, followed by cooling to ambient temperature, the products were isolated by liquid–liquid extract with diethyl ether. The liquid extract of the reaction was removed and analyzed by GC-MS. The remaining catalyst was washed with diethyl ether three times, the solvent was removed under vacuum, and the catalyst was used in the next run.

CONCLUSION

In summary, it has been demonstrated that basic ionic liquids could behave as the efficient catalyst and solvent for the redox esterification reaction between α,β-unsaturated aldehydes and alcohols without any additional bases. The ionic liquid anions are found to affect the catalytic activity significantly. Lewis base ionic liquid [bmim]OAc afford the best catalytic activity, in comparison with other ionic liquids such as [bmim]Cl, [bmim]PF_6, [bmim]$N(CN)_2$, [bmmim]OAc, [bmim]lactate, and [bmim]DMG. The N-heterocyclic carbenes derived in situ from 1-butyl-3-methylimidazolium acetate are active species for generating homoenolate species from α,β-unsaturated aldehydes. These nucleophilic intermediates can be protonated by acetic acid, and the resulting activated carbonyl unit is trapped with an alcohol nucleophile to afford a saturated ester. Further investigation of the recycling of the ionic liquid catalyst for this reaction are being actively pursued in our laboratory.

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