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Journal of Molecular Catalysis A: Chemical 268 (2007) 107–111
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
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A novel ionic liquid supported organocatalyst of pyrrolidine amide: Synthesis and catalyzed Claisen–Schmidt reaction

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Received 7 March 2006; received in revised form 18 November 2006; accepted 21 November 2006
Available online 26 November 2006

Abstract

A novel organocatalyst of pyrrolidine amide based on room temperature ionic liquid (RTIL) has been developed to perform Claisen–Schmidt reaction with acetone or cyclic ketone and various aromatic aldehydes at room temperature under free-solvent condition. The (*E*)-α,β-unsaturated ketone products were obtained in good yields. The ionic liquid supported pyrrolidine amide catalyst can be readily recovered and reused successfully without any significant loss of catalytic activity.

Keywords: Ionic liquid; Pyrrolidine amide; α,β-Unsaturated ketone; Organocatalyst

1. Introduction

Room temperature ionic liquids (RTILs) have been drawing much attention in the last years. Their negligible vapor pressure, excellent thermal stabilities and their polar and non-coordinating properties, especially the provision of a simple and effective method of recovering products and recycling catalysts and have made them solvents of choice for green chemistry [1,2]. Furthermore, they can enhance the rate and increase the selectivity of a number of valuable reactions. Based upon these advantages, RTILs are not only gaining greater attention as solvents for organic synthesis but also increasingly finding applications in other areas as well [3,1c].

One of the more recent developments is the use of RTILs as homogeneous supports much of this interest has been in the area of homogeneous supported catalyst [4,5], such as vanadyl salen complexes [6] and ruthenium metathesis catalysts [7]. These species were not only catalytically active, but also were readily retained in RTIL layers and thereby recycled. In terms of nonmetallic reagents, besides the quinuclidine [8], the only existing reports all deal with either sulfonic acids [9] or sulfonyl chlorides [10] supported on RTILs, the former of which are recyclable acid catalysts, while the later are consumed reagents for Friedel–Crafts alkylations or Beckman rearrangements. But the idea of supporting organic small molecules catalyst to an ionic liquid core is far less studied. In light of these results, we envisioned that application of this strategy by introduction of an ionic liquid directly bound to the organocatalyst should avoid the problem of catalyst leaching. Moreover, the resulting ionic liquid supported catalyst should be completely soluble in ketone and would allow the Claisen–Schmidt condensation reaction to be carried out under standard homogeneous conditions.

Herein, we report the synthesis of an alkyl imidazolium salt supported pyrrolidine amide organocatalyst L-1 and its use and recycling in Claisen–Schmidt condensation reaction. It was prepared based on L-proline and this bifunctional molecule having a basic pyrrolidine and a significantly acidic amide moiety could function the same ways as L-proline does for promoting reactions, synchronously having speciality of ionic liquid could easy to separated and recycled. The route for the synthesis of the L-1 is illustrated in Scheme 1. Starting from the commercially available Boc-proline (**1**), acylation of the Boc-proline carboxyl group with 2-bromo-ethylamine hydrobromide and afforded **2** in 86% yield. Subsequent alkylation of 1-methylimidazole with **2** and afforded **3** in 93% yield. Deprotection and following anion exchange in water with $NaBF_4$, afforded the desired tetrafluoroborate imidazolium salt L-1 in 98% yield. which was purified by redissolved in the medley liquids of THF and ethanol, then acetone, filtrated to removal the byproduct of NaBr and afforded

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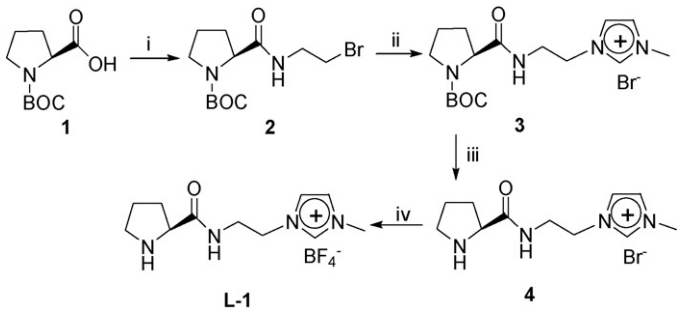
1381-1169/$ – see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.molcata.2006.11.039



Scheme 1. Synthesis organocatalyst of pyrrolidine amide L-1. Reaction conditions: (i) $BrCH_2CH_2NH_2{\cdot}HBr$, NEt_3, THF, 5–10 °C then room temperature; (ii) 1-methylimiazole, CH_3CN, reflux; (iii) CF_3COOH, CH_2Cl_2, 30 min; (iv) $NaBF_4$, H_2O, 6–8 h.

pure ionic liquid (IL) catalyst L-1 as an air-stable pale-yellow and transparent liquid.

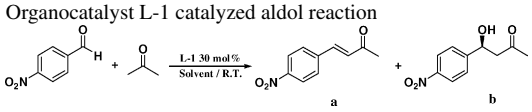
The broad utility of α,β-unsaturated carbonyl compounds in organic synthesis has continued to attract considerable synthetic interest in developing new methods for their syntheses [11]. Generally, these compounds are prepared by the Claisen–Schmidt condensation from aromatic aldehydes and ketones [12,13]. However, this method suffers from drawbacks of the narrow substrate diversity and several side reactions under relatively strong basic conditions [12,13]. As an alternative, the pyrrolidine imide organocatalyst catalyzed aldehydes and ketones condensation reaction have been described by Wang et al. but the catalyst cannot recycled and reused [14]. Pilar performed the Claisen–Schmidt condensation in the 1-butyl-3-methylimidazolium hexafluorophosphate [(bmim)PF_6], but they still used the traditional strong basic conditions [15]. The novel IL supported organocatalyst L-1 we synthesized was successful applicated to the direct catalysis of the Claisen–Schmidt condensative reaction between unmodified ketones and aldehydes under mild reaction conditions and obtained excellencent results. Importantly, isolation of the pure product was easily accomplished by extraction with diethyl ether, and the IL-cat. L-1 was reused for the next cycle of metathesis. From an atom economic and environment friendly point of view, it has obviously predominance.

2. Results and discussion

In an initial study, we expected to apply L-1 to the direct catalysis of the aldol condensation reaction. The reaction of 4-nitrobenzaldehyde with acetone was carried out in the presence of L-1 (30 mol%) at room temperature in DMSO. Surprisingly, it did not result in the formation of the desired condensation product 'b' (Table 1). In contrast, the further dehydration product, α,β-unsaturated ketone 'a' with (*E*)-configuration was obtained as the major product in excellent yield (Table 1, entry 4). Based on this observation, we thought that L-1 was an effective catalyst for direct preparation of the synthetically useful α,β-unsaturated carbonyl compounds from simple aldehydes and ketones.

First, we examined the solvent effect in this reaction: change the solvent from DMSO to the other solvents, the process revealed that solvents played a significant role in the formation of α,β-unsaturated ketone 'a' and condensation product 'b'. The dehydration product 'a' was produced exclusively in polar solvents, such as acetone, DMSO and DMF (Table 1, entries 3–5). However, in the other three solvents, the aldol product 'b' was obtained along with the formation of dehydration product 'a' (Table 1, entries 1 and 5). However, under free-solvent conditions, when to add 30 mol% L-1 and excessived acetone to reaction system, the significant results occured and the dehydration product 'a' was formed in 92% yield within a shorten time. In the decreasing of L-1 30–20 mol%, similar result was

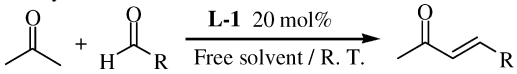
Table 1
Organocatalyst L-1 catalyzed aldol reaction

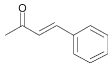
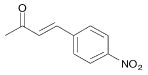
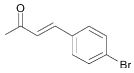
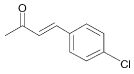
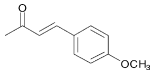
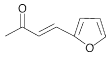
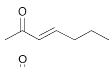


Entry	Solvent	*T* (h)	Yield for a[a,b] (%)	Yield for b[a,b] (%)
1	CH_2Cl_2	48	42	26
2	DMF	36	84	n.d.[c]
3	DMSO	36	89	n.d.
4	Acetone	24	91	n.d.
5	CH_3OH	72	56	18
6	Free solvent	24	92	n.d.

[a] Reaction conditions: A mixture of 4-nitrobenzaldehyde (0.1 mmol), acetone (1.0 mL) and catalyst L-1 30 mmol% was vigorously stirred in room temperature. The resulting mixture was then directly purified by silica gel chromatography.
[b] Isolated yield based on aldehyde.
[c] Not detected.

Table 2
L-1 catalyzed Claisen–Schmidt reaction between acetone and various aldehydes[a]



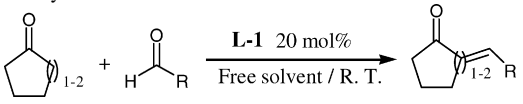
Entry	Product	*T* (h)	Yield (%)[b]
1		36	81
2		24	92
3		36	88
4		48	83
5		48	84
6		36	78
7		24	82
8		24	86

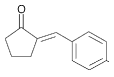
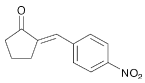
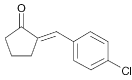
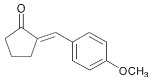
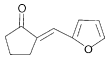
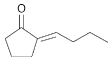
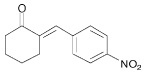
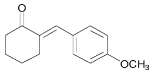
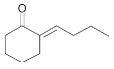
[a] Reaction conditions: A mixture of aldehyde (0.1 mmol), ketone (1.0 mL) and catalyst L-1 20 mmol% was vigorously stirred for 24–48 h. The resulting mixture was then extracted with ether and condensed, the residue directly purified by silica gel chromatography.
[b] Isolated yield based on aldehyde.

obtained, the reaction yield has no obvious change. When to reduce the L-1 loading to 10 mol%, the reaction was extended to 72 h. Based on these observations, it prompted us to prepare α,β-unsaturated ketone by adding 20 mol% catalyst to 0.1 mmol aldehydes and 1.0 mL acetone mixture under free-solvent conditions at room temperature.

Under the optimal reaction conditions, the reactions between acetone and various aldehydes were conducted at room temperature, the results are summarized in (Table 2). Aliphatic, heteroaromatic, and aromatic aldehydes with different structural features were found to be suitable substrates. The reactions proceeded smoothly and stereoselectively to afford (*E*)-α,β-unsaturated ketone in good to high yields. It was found that electronic effect on the reactions was very limited. For example, benzaldehydes having electron-donating and electron-withdrawing groups afforded products both in high yields (Table 2).

Table 3
L-1 catalyzed Claisen–Schmidt reaction between cyclopentanone and various aldehydes[a]



Entry	Product	*T* (h)	Yield (%)[b]
1		16	88
2		16	96
3		16	92
4		16	89
5		16	81
6		16	94
7		16	92
8		16	91
9		24	87
10		16	93
11		16	92

[a] Reaction conditions: A mixture of aldehyde (0.1 mmol), ketone (1.0 mL) and catalyst L-1 20 mmol% was vigorously stirred for 16–24 h. The resulting mixture was then extracted with ether and condensed, the residue directly purified by silica gel chromatography.
[b] Isolated yield based on aldehyde.

Table 4
L-1 recycling and reuse in Claisen–Schmidt reaction between acetone and 4-nitrobenzaldehyde[a]

Catalyst	Cycle						
	1	2	3	4	5	6	7
L-1 (% recyl.)	99	99	98	98	97	97	96
Prod. (% conv.)[b]	>98	>98	>97	>98	>97	>95	>91

[a] Reaction conditions: A mixture of aldehyde (0.1 mmol), ketone (1.0 mL) and catalyst L-1 20 mmol% was vigorously stirred for 16–24 h.
[b] % conv. based on gas chromatogram.

We also investigated the reaction between cyclopentanone and 4-nitrobenzaldehyde. It was carried out in cyclopentanone (1.0 mL) and 4-nitrobenzaldehyde (0.1 mmol) in the presence of 20 mol% L-1 under the same reaction conditions. No less than we expected, the organocatalyst L-1 catalyzed reaction was tolerant of not only acylic ketones, but also cyclic systems (Table 3). Much higher yields (96%, Table 3) were obtained. Following, reactions with other aldehyde substrates were proceeded in good yields. In comparison with the classical reaction [12,14], the method is cleanly and environmentally friendly. Generally, higher yields were obtained within a same time.

As we mentioned before, this novel IL organocatalyst obviously predominance is easy to separated and recycled. Excellent conversions were obtained for up to seventh consecutive cycles of recycling and reuse (Table 4). These results show the importance of attaching an imidazolium ionic liquid pattern to the catalyst to obtain its recycling from the reaction system. We have investigated the chemical stability of the IL catalyst L-1 and accomplished the seventh run. A similarly high yield was obtained, which showed that IL catalyst L-1 remains active. It is worthy of noting, when the IL catalyst L-1 lost its activity after repeated use. It could be easy recovered by washed with dichloromethane in water, then removed the water at reduced pressure and catalyzed new reaction.

3. Conclusion

In summary, we have shown that the imidazolium supported pyrrolidine amide organocatalyst is an efficient and recycling catalyst for direct Claisen–Schmidt reaction of aldehydes and ketones. In this regard, the preparation and use of L-1 opens up the possibility of developing structurally and electronically novel catalysts that have high reactitives and stereoselectively to afford (*E*)-α,β-unsaturated ketone. In comparison to the classical Claisen–Schmidt reaction, our catalyzed system offer substantial advantages: (1) it can very efficiently catalyze the reaction for a broad range of substrates (both acyclic- and cyclic ketones) with high yields; (2) the ionic-liquid moiety can act as a phase tag to facilitate recycling and reuse of the catalyst; (3) the modular and tunable features of ionic liquids promise potential developments. Further investigations concerning the effectiveness of L-1 and related catalysts for other reactions are currently underway.

4. Experimental

4.1. General information

All anhydrous solvents (CH_2Cl_2 and THF) were dried by standard techniques and freshly distilled before use. The 2-bromo-ethylamine hydrobromide [16] and Boc-proline [17] prepared according as literature. Infrared (IR) spectra were recorded on a Shimadzu IRPrestige-21 spectrometer. ^1H and ^{13}C NMR spectra were measured on a Varian Mercury-plus 300BB NMR spectrometer at ambient temperature. Spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard, integration, multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, quint: quintet, hept: heptet, m: multiplet, br: broad). For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm) were used. The products were purified by flash column chromatography on silica gel (230–400 mesh).

4.2. Synthesis and characterization of proline-based amide L-1

4.2.1. N-Boc-proline-2-bromo-ethylamide (2)

A mixture of Boc-proline (**1**) (2.15 g, 10.0 mmol) and triethyl amine (2.23 g, 22.0 mmol) in tetrahydrofuran was cooled in an ice-bath. Ethyl chlorformate (1.19 g, 11.0 mmol) was added dropwise with vigorously stirring and the pasty reaction mixture stirred for an additional 30 min (temperature 5–10 °C), obtaining in situ the mixed anhydride. The 2-bromo-ethylamine hydrobromide (2.03 g, 10.0 mmol) was added to this mixture, After 12 h stirring at room temperature. The mixture was filtered and the solid was thoroughly washed with ethyl acetate. The filtrate and wash liquids were evaporated at reduced pressure, the residue was redissolved in ethyl acetate and successively washed with water, an aqueous sodium hydrogen carbonate solution, and brine. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (ethyl acetate/hexane = 1:2 as eluent) to give **2** (2.74 g, 86% yield). ^1H NMR (300 MHz, $CDCl_3$) δ 7.30 and 6.56 (t, J = 8.8 Hz, 1H), 4.23 (t, J = 8.8 Hz, 1H), 3.59 (t, J = 8.4 Hz, 2H), 3.40 (t, J = 7.2 Hz, 2H), 3.29 (t, J = 7.2 Hz, 2H), 2.18 (m, J = 8.4 Hz, 2H), 1.83.64 (t, J = 10.8 Hz, 2H), 1.40 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6 (two peaks overlap), 154.7 (two peaks overlap), 79.5, 60.3 (two peaks overlap), 46.3, 40.45, 30.9, 28.0; IR (neat) 3300, 3085, 2867, 1691, 1658, 1556, 1399, 1244, 1161, 1119, 1088, 974, 771 cm^{-1}.

4.2.2. N-Boc-proline-2-N-methylimidazole-ethylamide (3)

To a solution of **2** (0.320 g, 1.0 mmol) in CH_3CN was added *N*-methylimidazole (0.123 g, 1.5 mmol). The mixture was stirred for 6 h at reflux temperature. After cooling to room temperature, the reaction mixture was concentrated. The residue was purified by flash column chromatography on silica gel (methanol/dichloromethane = 1:10 as eluent) to give the desired **3** (375 mg, 93% yield). ^1H NMR (300 MHz, $CDCl_3$) δ 9.56 (s, 1H), 8.51 (t, J = 8.4 Hz, 1H), 7.70 (s, 1H), 7.46 (s, 1H), 4.47 (t, J = 8.4 Hz, 2H), 3.84 (t, J = 8.4 Hz, 2H), 3.51 (t, J = 12.2, 1H), 3.38 (t, J = 8.4 Hz, 2H), 2.05 (t, J = 8.4 Hz, 2H), 1.80 (s, 9H), 1.38 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 154.6, 137.7, 123.4 (two peaks overlap), 79.5, 59.9, 48.5, 47.2, 39.1, 36.5, 30.3, 28.3, 24.3; IR (neat) 3300, 3279, 3085, 2867, 1691, 1658, 1556, 1399, 1244, 1161, 1119, 1088, 974, 771 cm^{-1}.

4.2.3. Proline-2-N-methylimidazole-ethylamide (4)

The BOC-protected *N*-carboxamide (**3**) (375 mg) deprotected was performed using 50% TFA in dichloromethane (5 mL) for 1 h at room temperature. After rotary evaporation, TFA salts were removed by triturating the residue with 5 mL of methanol (saturated with ammonia), then the mixture was concentrated and the residue was purified by flash column chromatography on silica gel (methanol/dichloromethane = 1:4 as eluent) to give **4** (204 mg, 98% yield). ^1H NMR (300 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.41 (s, 1H), 7.35 (s, 1H), 4.65 (s, 6H), 4.24 (t, J = 9.2 Hz, 2H), 4.19 (s, 1H), 3.79 (s, 1H), 3.68 (s, 3H), 3.65–3.53 (m, J = 3.6 Hz, 2H), 3.33–3.24 (m, J = 13.5 Hz, 2H), 2.34–2.25 (m, J = 13.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.1, 154.6, 137.4, 123.1, 122.8, 79.5, 59.9, 48.4, 47.1, 39.1, 36.4, 30.2, 28.2; IR (neat) 3300, 3279, 3085, 2867, 1691, 1658, 1630, 1556, 1399, 1244, 1161, 1119, 1088, 974, 771 cm^{-1}.

4.2.4. IL supported pyrrolidine amide L-1

To a solution of **4** (204 mg, 0.68 mmol) in H_2O (10 mL) was added $NaBF_4$ (618 mg, 2.72 mmol). The mixture stirred for 5 h at room temperature. After evaporation of H_2O and the residue was purification of the residue redissolved in the medley liquids of THF and ethanol (1:1), then filtered and the solid was thoroughly washed with medley liquids, the filtrate and wash liquids were evaporated at reduced pressure, the residue redissolved in dichloromethane and again filtrated, removed rudimental salt. The amide L-1 was obtained as the colorless transparent liquid.

4.3. General procedure for Claisen–Schmidt condensation reaction

To a mixture of aldehyde (0.1 mmol) and anhydrous acetone (1.0 mL) was added organocatalyst L-1 (20 mol%). The resulting mixture was stirred at room temperature for 16–48 h. After the reaction was completed (TLC detected), the reaction mixture was added to 2.0 mL H_2O and extracted with diethyl ether (2× 5.0 mL). The organic layer treated with saturated ammonium chloride solution and brine, and then dried over anhydrous Na_2SO_4. After removal of solvent, the residue was purified by flash column chromatography on silicagel (hexane/ethyl acetate = 10:90 as eluent) to give the final product. The organocatalyst L-1 was separated and washed with 2.0 mL dichloromethane, the dichloromethane layer was casted off, after evaporation of H_2O and the recovered L-1 can used to catalyze the next reaction.

Acknowledgements

We thank the NSFC-20021001, NSFC-20572038 and the 'Hundred Scientist Program' from the Chinese Academy of Sciences for the financial support of this work.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2006.11.039.

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