



Microwave-assisted heteropolyanion-based ionic liquids catalyzed transamidation of non-activated carboxamides with amines under solvent-free conditions



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ABSTRACT

An environmentally benign and highly efficient protocol for the transamidation of non-activated carboxamides with amines using heteropolyanion-based ionic liquids as catalysts under microwave-assisted and solvent-free conditions has been developed. As evaluated by the reactions of a structurally diverse set of amides and amines, the scope and utility of the transamidation proved to be quite general. Operational simplicity, solvent-free media, the potential reusability of catalysts and wide functional group tolerance are attractive features. This method provides a much improved protocol over the existing methods.

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1. Introduction

Amide bond is a widely prevalent linkage in numerous bioactive products,¹ as well as biological and synthetic polymers (i.e., proteins and nylons).² Amides also act as fundamental building blocks for the synthesis of pharmaceuticals, agrochemicals, polymers and materials.³ Traditional amide formation relies on activation of a carboxylic acid derivative (acyl halide, anhydride, ester or acid) using a coupling reagent and subsequent coupling of the activated species with an amine, but there are limitations, such as using stoichiometric amounts of coupling reagents, poor atom efficiency, large quantities of potentially hazardous waste and difficulties in purification.⁴ These drawbacks have promoted the development of numerous alternative amide formation methods in recent years.⁵ Amongst various catalytic methods, transamidation of amide with amine is potentially an attractive alternative tool for the direct amide bond formation. However, due to the relatively high inertness of the amide bond in contrast with other acyl donors, transamidation is hindered under thermal and noncatalytic conditions.⁶ Although lipase-catalyzed transformation has been reported, this protocol requires high substrate specificity, highly

evolved enzymes and long reaction time.⁷ Moreover, great advances have recently been made to develop more convenient procedures to achieve transformation at relatively lower temperatures by using activating reagents or catalysts.^{8,9} Several metal species have been reported to promote transamidation reactions in the last two decades, including AlCl_3 ,^{8a} $\text{Sc}(\text{OTf})_3$,^{8b} HfCl_4 ,^{8c} lanthanide catalysts,^{8d} $\text{Ti}(\text{NMe}_2)_4$,^{8e} $\text{Cu}(\text{OAc})_2$,^{8f} CeO_2 ,^{8g} Cp_2ZrCl_2 ,^{8h} sulfated tungstate,⁸ⁱ Nb_2O_5 ,^{8j} $\text{Mn}(\text{II})$ complex,^{8k} and $\text{Fe}(\text{III})$ -salt.^{8l,m} In addition, very recently some metal-free catalysts, such as *N,N*-dialkylformamide dimethyl acetals,^{9a} imidazole,^{9b} hydroxylamine hydrochloride,^{9c} boric acid,^{9d} ammonium-salt,^{9e} borate esters,^{9f,9g} *L*-proline,^{9h} hypervalent iodine⁹ⁱ and benzotriazole^{9j} as well as microwave irradiation^{9k,l} have come to the forefront offering enough impetus to improvement. Although the existing methods have their own advantages, the resulting transamidations suffer from certain demerits, such as stoichiometric amount of the catalysts, harsh reaction conditions, long reaction times, low selectivities and limited substrate scopes. Moreover, some of the catalysts have the difficulties in separation from the reaction mass and recycling. Therefore there is a clear need for more efficient and greener methods for transamidation with a broad substrate suitability.

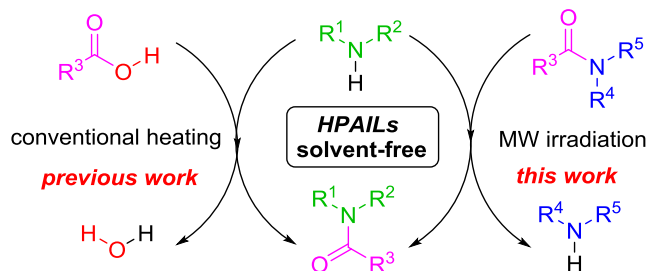
Over the past decades, ionic liquids (ILs) have attracted much interest as efficient and eco-friendly reaction media and/or catalysts due to their excellent properties such as negligible vapour

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pressure, ease of recovery and reuse.¹⁰ Amongst them a series of heteropolyanion-based ILs (HPAILs) have been recently prepared as hybrid materials by combining Keggin heteropolyanions with 'task-specific' ILs (TSILs) cations containing special functional groups.¹¹ HPAILs usually have high melting points, thermal stability and chemical stability owing to the large volume and high valence of heteropolyanions and hydrogen bonding net-works existing in the compounds, and that is consistent with the requirements of a solid acid catalyst. So far, HPAILs have turned out to be an eco-benign, high-efficient and recyclable catalyst for acid-catalyzed¹² or oxidative organic transformations¹³ due to their advantages, such as operationally simplicity, no toxicity, easily isolation and reusability.

On the other hand, 'non-classical' methods have been developed in organic synthesis to improve yields, selectivity and experimental conditions during the last few years.¹⁴ Amongst them microwave (MW)-assisted technology has blossomed into a useful tool for a variety of applications in organic synthesis due to their unique advantages, such as the significant rate enhancements, yield and selectivity improvements, very simplified ease of manipulation and work-up as well as less environmental polluting processes.¹⁵ Although MW-assisted reactions in organic solvents have developed rapidly, the focus is now shifted to environmentally friendlier methods, which explore the using of MW irradiation in conjunction with solvent-free conditions or benign reaction media.¹⁶

Recently, our group has introduced HPAILs as eco-benign and highly efficient catalysts for condensation between carboxylic acids and amines to obtain amides.¹⁷ We envisioned that HPAILs could potentially catalyze the transamidation reaction. To the best of our knowledge, ILs promoted transamidation has not been reported to date. In our continuing efforts in developing efficient and green protocols for catalytic methods for amide bonds formation, we wish to describe herein the first MW-assisted HPAILs catalyzed transamidation of non-activated carboxamides with amines under solvent-free conditions (Scheme 1).



Scheme 1. HPAILs catalyzed amidation reactions developed by our group.

2. Results and discussions

Our study is mainly focused on *N*-substituted imidazole, pyridine and triethylamine based HPAILs, which have already been used as catalysts for many different organic transformations.^{12,13,17} Thus, six structurally related HPAILs (Fig. 1) were prepared according to published procedure.^{12a} The obtained HPAILs were characterized and the results were compared with the literature data.

Initially, transamidation of acetamide with aniline was chosen as a model system to optimize the catalytic parameters (Table 1). Firstly, a control experiment was performed with conventional heating at 120 °C in the absence of any catalyst and additional solvent and, as expected, the complete lack of reactivity was observed even after a prolonged reaction time of 24 h (Table 1, entry 1). Whereas addition of 2 mol % amount of [MIMPS]₃PW₁₂O₄₀ to the reaction mixture resulted in the desired transformation product in 71% yield (Table 1, entry 2). The results revealed that the HPAILs

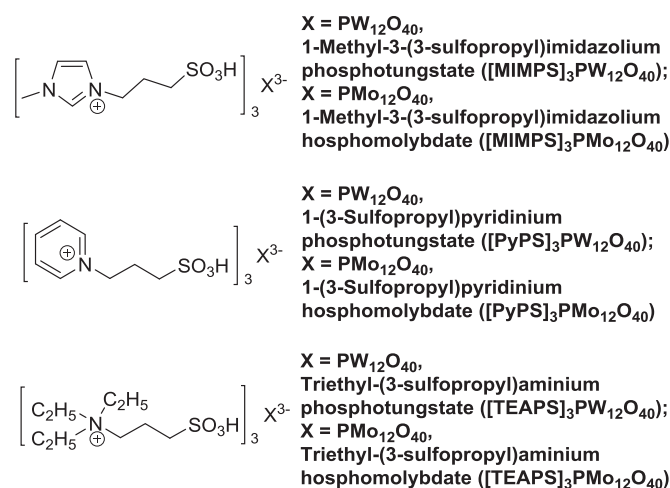


Fig. 1. *N*-Substituted imidazole, pyridine and triethylamine based HPAILs.

Table 1

Optimization of the reaction conditions for transamidation of acetamide with aniline^a

Entry	Catalyst	Temp (°C)	Time (min)	Yield ^b (%)
1 ^c	—	120	1440	0
2	[MIMPS] ₃ PW ₁₂ O ₄₀ , 2 mol %	120	1440	71
3	[MIMPS] ₃ PW ₁₂ O ₄₀ , 2 mol %	120	50	80
4	[MIMPS] ₃ PW ₁₂ O ₄₀ , 2 mol %	100	50	65
5	[MIMPS] ₃ PW ₁₂ O ₄₀ , 2 mol %	140	50	78
6	[MIMPS] ₃ PW ₁₂ O ₄₀ , 3 mol %	120	50	80
7	[MIMPS] ₃ PW ₁₂ O ₄₀ , 1 mol %	120	50	72
8 ^d	[MIMPS] ₃ PW ₁₂ O ₄₀ , 2 mol %	120	50	47
9 ^e	[MIMPS] ₃ PW ₁₂ O ₄₀ , 2 mol %	120	50	45
10 ^f	[MIMPS] ₃ PW ₁₂ O ₄₀ , 2 mol %	120	50	38
11 ^g	[MIMPS] ₃ PW ₁₂ O ₄₀ , 2 mol %	120	50	25
12 ^h	[MIMPS] ₃ PW ₁₂ O ₄₀ , 2 mol %	100	50	12
13 ⁱ	[MIMPS] ₃ PW ₁₂ O ₄₀ , 2 mol %	120	50	<5
14	[MIMPS] ₃ PMO ₁₂ O ₄₀ , 2 mol %	120	50	75
15	[PyPS] ₃ PW ₁₂ O ₄₀ , 2 mol %	120	50	83
16	[PyPS] ₃ PMO ₁₂ O ₄₀ , 2 mol %	120	50	78
17	[TEAPS] ₃ PW ₁₂ O ₄₀ , 2 mol %	120	50	72
18	[TEAPS] ₃ PMO ₁₂ O ₄₀ , 2 mol %	120	50	65
19	H ₃ PMO ₁₂ O ₄₀ , 2 mol %	120	50	75

^a Unless otherwise noted, all reactions were carried out with acetamide (2 mmol), aniline (2.6 mmol) and related catalyst under MW (700 W) and solvent-free conditions.

^b Isolated yields.

^c Conventional heating.

^d Toluene (1.0 mL) was used as solvent.

^e Xylene (1.0 mL) was used as solvent.

^f Mesitylene (1.0 mL) was used as solvent.

^g DMSO (1.0 mL) was used as solvent.

^h H₂O (1.0 mL) was used as solvent.

ⁱ *n*-C₅H₉OH (1.0 mL) was used as solvent.

should be absolutely necessary for the catalyzed transamidation. To our delight, it was shown that the rate and yield of the reaction both increased dramatically when MW-assisted heating at 120 °C was utilized in the catalyzed transamidation (Table 1, entry 3). In addition, lower or higher temperature (100 °C or 140 °C) was harmful to the transamidation product (Table 1, entries 4 and 5). Further, no improvement was observed in the presence of more amount of catalyst (Table 1, entry 6), but a decrease in the catalyst diminished the yield of the product considerably (Table 1, entry 7). In order to study the effect of the medium, reactions were carried

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