RSC Advances

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Journal:	*RSC Advances*
Manuscript ID:	RA-COM-05-2015-010127.R1
Article Type:	Communication
Date Submitted by the Author:	04-Jun-2015
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Chuthamat Duangkamol, Subin Jaita, Sirilak Wangngae, Wong Phakhodee, and Mookda Pattarawarapan*

A mechanochemical method for amidation of carboxylic acids and urethane-protected (Fmoc, Cbz, Boc) α-amino acids has been developed as a facile, efficient, and eco-friendly route toward amides and dipeptides.

Cite this: DOI: 10.1039/c0xx00000x

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COMMUNICATION

An efficient mechanochemical synthesis of amides and dipeptides using 2,4,6-trichloro-1,3,5-triazine and PPh_3

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

A rapid, facile, and efficient mechanochemical synthesis of amides from carboxylic acids has been developed through an *in-situ* acid activation with 2,4,6-trichloro-1,3,5-triazine and a catalytic amount of PPh_3. Under room temperature solvent-drop grinding of the reactants in the presence of inorganic base, a variety of carboxylic acids including aromatic acids, aliphatic acids, and *N*-protected α-amino acids undergo amidation to afford amides in moderate to excellent yields. The method is also compatible with Fmoc, Cbz, and Boc protecting groups which yields protected optically active dipeptides without detectable racemization.

Amide bond formation is one of the most important functional group transformations in organic synthesis since amides exhibit a wide range of applications, especially in pharmaceutical as well as agrochemical industries.[1] Thus, over the years, numerous methods toward the synthesis of this class of compounds have been increasingly introduced.[2] The most simple and straightforward route toward amides is through the direct reaction between carboxylic acids and amines.[3] However, the methods generally require expensive catalysts and/or harsh reaction conditions such as high temperature with relatively long reaction times. Alternatively, it is more preferable to convert carboxylic acids into more reactive species such as acyl halides, mixed anhydrides, or active esters before reacting with amines.[4]

Since the introduction of the "green chemistry" principles,[5] various synthetic processes have been adjusted or developed to be more environmentally benign mainly to minimize the use of toxic reagents and/or volatile organic solvents, while reduce the amount of wastes generated. Among the available green strategies, mechanochemical synthesis under neat or solvent-drop grinding in which a reaction is carried out in the absence or with a few drops of solvent is of great interest. In several cases, the method has proven to be highly effective in enhancing the reaction rate, product yield, and selectivity in comparing with the classical solution-based synthesis.[6] In addition, environmental pollution caused by solvents as well as the cost and energy requirement in solvent handling and disposal are minimized.

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† Electronic Supplementary Information (ESI) available: [Experimental procedure and spectroscopic data]. See DOI: 10.1039/b000000x/

In the synthesis of amides, although numerous reagent systems have been continuingly developed, there are only a few methods that enable amide bond formation with minimal use of solvents.[3b-f, 7] Apart from the studies by Lamaty[7f] and Juaristi[7k] where dipeptides and a tripeptide could be prepared from urethane-protected amino acid *N*-carboxyanhydrides under solvent-free ball-milling, most of the methods were carried out under high temperature microwave irradiation which limits their use to those simple and thermally stable substrates. Thus, there is still a high demand to explore environmentally benign yet efficient methods that would tolerate a wide range of functional groups under simple experimental setup and mild reaction conditions.

2,4,6-Trichloro-1,3,5-triazine (TCT) is an inexpensive and highly versatile reagent which has been used in various organic reactions.[8] In amide bond formation, it is generally applied in the presence of organic tertiary amine bases for activating carboxylic acids toward nucleophilic substitution.[8a] The acid activation step are typically carried out in organic solvents at low temperatures (0-5 ^{o}C). To the best of our knowledge, there is only one study that reported the use of silica-supported TCT in solvent-free amidation between carboxylic acids and ammonium salts of amines.[7i] However, difficult substrates such as those optically active protected α-amino acids were not evaluated.

Our previous study has shown that a combination of TCT with a catalytic amount of PPh_3 could effectively activate carboxylic acids toward $NaBH_4$ reduction.[9] This led us to further investigate the applicability of the method toward the amidation reaction. Herein, we wish to report a facile, efficient, low cost, and eco-friendly method toward amides and dipeptides through an *in-situ* activation of carboxylic acids or urethane-protected α-amino acids with the TCT-PPh_3 system in the presence of inorganic base under solvent-drop grinding.

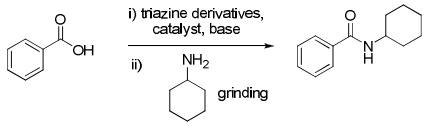
Initially, the reaction conditions for the amidation were optimized using benzoic acid and cyclohexylamine as the model substrates. The reaction was carried out by grinding the reactants and reagents together at room temperature using mortar and pestle. Since benzoic acid, TCT and PPh_3 are all solids, a few drops of dichloromethane (*ca.* 1.5 μL/mg of the solids) were used as a lubricant during grinding to facilitate homogeneous mixing. Types of inorganic base were varied, while other triazine derivatives which have been applied in carboxylic acid activation including 2,4-dichloro-6-methoxy-1,3,5-triazine (DMCT)[10] and 2-chloro-4,6-dimethoxy-1,3,5-triazine (CDMT)[11] were also evaluated. For the ease of comparison, the acid activation time was kept at 10 min, while the reaction time after adding the amine was fixed at 20 min for all the tested conditions.

According to Table 1, using 1:0.1 equiv. of TCT and PPh_3 in the presence of Na_2CO_3 gave *N*-cyclohexylbenzamide in 80%

yield (entry 1). When replacing Na_2CO_3 with K_2CO_3 or Cs_2CO_3 (entries 2-3), the product was quantitatively obtained, possibly due to the higher solubility of these bases in the molten mixture. The reaction was less effective when using other less reactive chlorotriazine derivatives (entries 4-5).

Since *N*-methylmorpholine (NMM) is commonly used as a base and/or a catalyst in combination with TCT and other chlorotriazine derivatives,[8a, 8e, 8g, 12] it was also applied under our solvent-drop grinding conditions (entries 6-7). Nevertheless relatively lower yields of the product were obtained possibly due to decomposition of the presumed reactive morpholiniumtriazine intermediate.[13] In a control experiment where the reaction was carried out in the presence of K_2CO_3 without a catalyst (entry 8), the reaction was incomplete and the product was obtained in only 39% yield. This result strongly confirmed the catalytic role of PPh_3 in the amidation reaction.

Table 1 Optimization for mechanosynthesis of *N*-cyclohexylbenzamide[a]



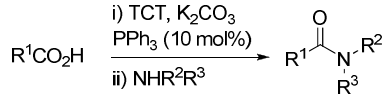
entry	trizine derivative	catalyst (mol%)	base	% yield
1	TCT	PPh_3(10)	Na_2CO_3	80
2	TCT	PPh_3(10)	K_2CO_3	99
3	TCT	PPh_3(10)	Cs_2CO_3	99
4	DMCT	PPh_3(10)	K_2CO_3	42
5	CDMT	PPh_3(10)	K_2CO_3	36
6	TCT	NMM (10)	K_2CO_3	61
7	TCT	-	NMM	43
8	TCT	-	K_2CO_3	39

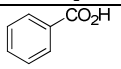
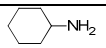
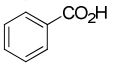
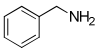
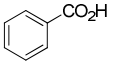
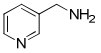
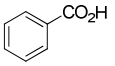
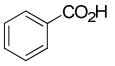
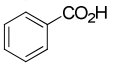
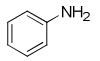
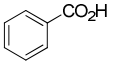
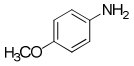
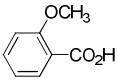
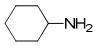
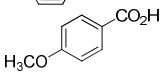
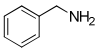
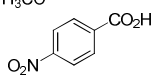
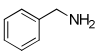
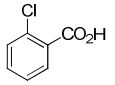
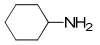
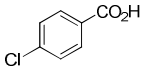
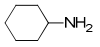
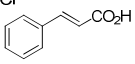
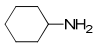
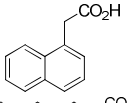
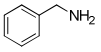
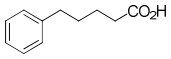
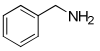
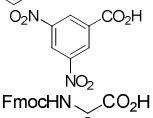
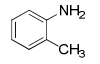
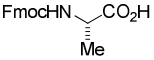
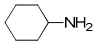
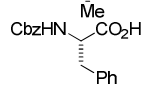
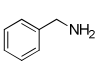
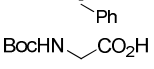
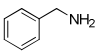
[a]A mixture of triazine derivative (0.27 mmol), catalyst, and benzoic acid (0.27 mmol) was ground together using mortar and pestle in the presence of base (0.54 mmol) for 10 min. Cyclohexylamine (0.30 mmol) was then added, followed by grinding for 20 min.

To evaluate substrate compatibility of the developed conditions, the best reaction condition (Table 1, entry 2) was applied in the reactions between a series of carboxylic acids and a variety of amines as shown in Table 2. It was observed that, under grinding, most carboxylic acids were completely activated within 10 min, while the amide bond formation typically required 20 min for completion. Benzoic acid reacted smoothly with primary and secondary aliphatic amines (entries 1-3, 5), although the reaction with sterically hindered isopropyl amine gave lower yield of the corresponding product (entry 4). Coupling of benzoic acid with the poor nucleophilic aromatic amines including aniline and *p*-methoxyaniline was also less effective (entries 6-7).

Electronic effect of substituents on the aromatic ring of acids has some influence on the reaction rate. While the electron-rich aromatic acids (entries 8-9) were converted into the respective amides in excellent yields regardless of the presence of the –OMe group at the ortho position, the electron-poor 4-nitrobenzoic acid gave somewhat lower product yield (entry 10). The reaction also proceeded well with aromatic acids containing halogen substituents (entries 11-12). *α,β*-Unsaturated cinnamic acid, and aliphatic acids including 1-naphthyl acetic acid and 5-phenylvaleric acid reacted smoothly with the applied amines to give the corresponding amide products in excellent yields (entries 13-15). However, the reaction between the electron poor 3,5-dinitrobenzoic acid and the steric 2-methylaniline gave moderate yield of the product (entry 16).

Table 2 Mechanochemical amidation promoted by TCT-PPh_3.[a]



entry	R^1CO_2H	NHR^2R^3	% yield[Ref]
1			99[14]
2			99[15]
3			90[16]
4			59[17]
5			99[18]
6			60[19]
7			77[20]
8			92[21]
9			99[22]
10			83[23]
11			93[24]
12			99[25]
13			95[26]
14			92[27]
15			90[28]
16			51[29]
17			78
18			84[30]
19			89[7d]

[a]Unless otherwise specified, a mixture of TCT (0.27 mmol), PPh_3 (0.027 mmol), carboxylic acid (0.27 mmol), and K_2CO_3 (0.54 mmol) was ground together for 10-15 min at ambient temperature before adding amine (0.30 mmol), followed by grinding for 20 min.

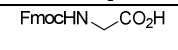
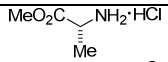
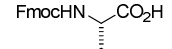
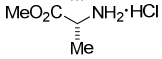
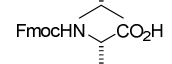
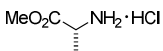
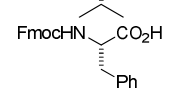
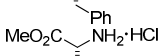
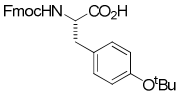
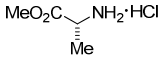
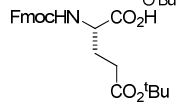
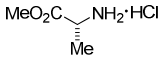
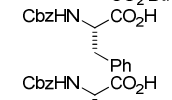
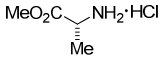
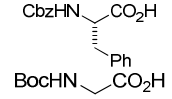
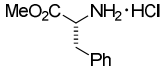
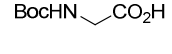
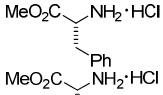
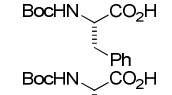
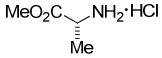
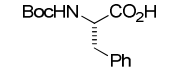
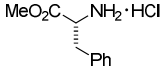
Amidation of urethane protected α-amino acids containing 9-fluorenylmethyloxycarbonyl (Fmoc), benzyloxycarbonyl (Cbz), and tert-butyloxycarbonyl (Boc) groups (entries 17-19) was found to proceed without protecting group removal and no

significant racemization was observed based on chiral HPLC analysis of the optically active products.

Inspired by these results, we further investigate the applicability of this protocol in the synthesis of protected dipeptides. All reactions were carried out with 20 min activation of the *N*-protected α-amino acid, followed by 20 min reaction with α-amino methyl ester hydrochloride without further optimization. As shown in Table 3, the peptide coupling proceeded relatively well to provide urethane-protected dipeptides in good yields. According to ^{1}H NMR, the product from each reaction was also obtained as a single diasteromer. This data further confirmed that the amidation proceeded without racemization.

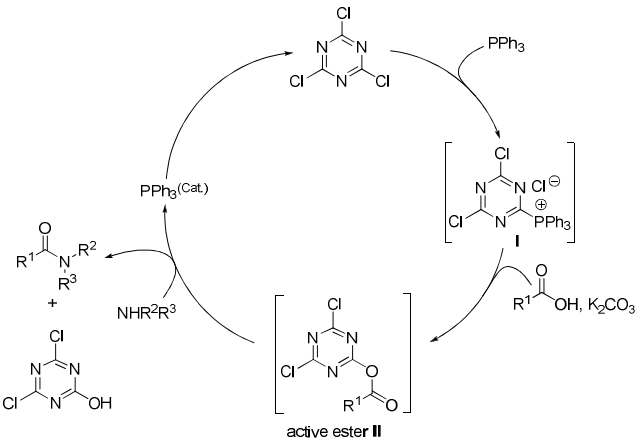
It is noted that while the reported solvent-free ball-milling method toward dipeptides required amino acid *N*-carboxyanhydrides as the substrates which were limited to those containing Boc group,[7f, 7k] our protocol shows high degree of functional group compatibility, while the commercially available *N*-protected α-amino acids (Fmoc, Cbz, or Boc) can be used directly without requirement for further modification. To ensure the reproducibility of the method, the synthesis of *N*-phenylbenzamide was also carried out in triplicate and the product was obtained in 60%, 62%, and 59% yields with %RSD of 2.53% indicating high degree of repeatability.[31]

Table 3 Mechanosynthesis of protected dipeptides[a]

entry	R^1CO_2H	NHR^2R^3	% yield[Ref]
1			81[32]
2			76[33]
3			79[34]
4			85[35]
5			92[36]
6			79[36]
7			83[11b]
8			71[37]
9			88[38]
10			77[7f]
11			77[39]

[a]A mixture of TCT (0.27 mmol), PPh_3 (0.027 mmol), *N*-protected α-amino acid (0.27 mmol) and K_2CO_3 (0.81 mmol) was ground together for 20 min. α-Amino methyl ester hydrochloride (0.30 mmol) was then added, followed by grinding for 20 min.

The mechanism for the TCT-PPh_3 mediated amidation was proposed as depicted in Scheme 1. Adding PPh_3 to TCT resulted in TCT activation, presumably through the formation of triazinylphosphonium salt **I**. Displacement of the phosphonium group with a carboxylate ion provides an acyloxytriazine **II** while PPh_3 is regenerated into the catalytic cycle. Subsequent nucleophilic substitution of the active ester **II** with an amine furnish the amide bond formation with concomitant release of the hydroxyl derivative of TCT.



Scheme 1 Proposed mechanism for amidation mediated by TCT-PPh_3 system.

In summary, a mechanochemical method for amidation of carboxylic acids was developed through an *in-situ* activation of carboxylic acids with TCT-PPh_3 system in the presence of inorganic base. The protocol offers several advantages including the use of low-cost, readily available, and easy to handle reagents. The reaction conditions are mild yet effective allowing rapid synthesis of optically active dipeptides with a range of protecting groups (Fmoc, Cbz, Boc) without detectable racemization. The simplicity of the process with significant reduction of volatile organic solvent makes this method an excellent green alternative to the traditional solution-based methodologies.

Acknowledgements

Financial supports from the Thailand Research Fund through the Royal Golden Jubilee Ph.D. Program (Grant No. PHD/0206/2556) to S.W. and the Center of Excellence for Innovation in Chemistry (PERCH-CIC) are gratefully acknowledged.

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