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ARTICLE

Ureas as Safe Carbonyl Sources for the Synthesis of Carbamates with Deep Eutectic Solvents (DESs) as Efficient and Recyclable Solvent/Catalyst Systems

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A simple, efficient and eco-friendly one-pot synthesis of primary, *N*-mono- and *N*-disubstituted carbamates is developed from ureas. Corresponding carbamates were produced at 120 °C, within 18 h, and in the presence of the deep eutectic solvent as a recyclable catalytic system. The catalyst can be reused for several runs without any reduction in activity. To demonstrate the utility of this approach, a wide variety of alcohols and phenols were studied to find a vast range of carbamate derivatives in moderate to high yields.

Introduction

Carbamates and their derivatives are important chemicals that widely used in drug designing and medicinal chemistry (i.e., flupirtine, retigabine, albendazole and physostigmine are carbamate-based drugs),[1] agricultural chemistry (as herbicides, pesticides, bactericides, and antiviral agents),[2] cosmetics and the synthesis of organic and polymer compounds.[3] Some important carbamate derivatives with biological activities are depicted in Figure 1.[1-3] One of the most common applications of these structures in organic synthesis is the protection of amino groups as well as amino acids in the multi-step synthesis of multifunctional targets and structurally complicates natural products like peptides.[4]

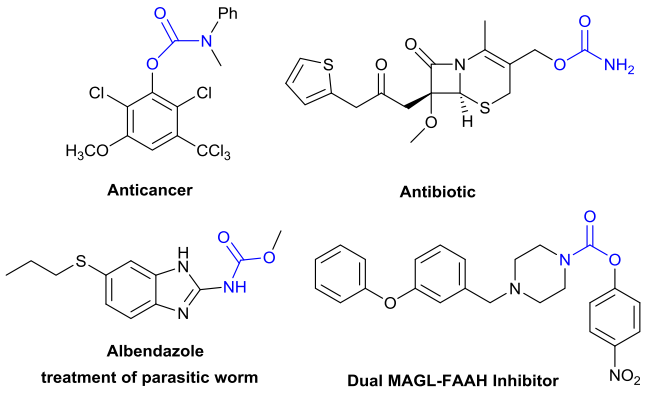

Figure 1. Some biologically active carbamates.

The classic and traditional approach for the synthesis of carbamates from amines and alcohols usually entails the use of toxic phosgene[5] or its derivatives in which corresponding carbamates such as methyl chloroformate,[6] ethyl chloroformate,[7] 1,1,1-trichloromethylformate (diphosgene)[8] and trichloroacetyl chloride[9] can be observed. One of the phosgene drawbacks is the production of large amounts of corrosive HCl as the by-product in the conversion.[10] Also, chloride impurities will be found in the final products and the purification of which is so difficult and a costly process.[5-10] In the view of environment protection and social safety, the development of non-phosgene processes is highly desired.[11] Therefore, to avoid the use of these extremely toxic, corrosive and hazardous reagents, many efforts have been carried out to develop alternatives.[12-16] For this purpose, several effective methods that apply the series of new reagents including isocyanates,[12] azides,[13] carbonates,[14] CO[15] and CO_2 [16] have been studied. Generally, the carbonylation with CO_2, CO and carbonates must be catalyzed by transitional metal complexes such as ones bearing Pd, Pt, Ru, Rh, Ir, Au, Al etc.[15, 16] Furthermore, these methodologies need to tolerate high temperatures and pressures, long reaction time, and high molar ratios of carbonylation agents.[15, 16] Furthermore, the mixture of CO and O_2 often involves the rigorous safety issues.[15] Although, the alternative reagents allow the synthesis of carbamates on a small scale, unfortunately, these methodologies are not suitable for the synthesis of large quantities of product and do not present desired performance.[15, 16]

In the past decades, scientists have emphasized on the use of nontoxic carbonylation agents for the synthesis of the broad range of organic compounds.[17] Urea and many of its derivatives are important classes of natural, low price and nontoxic carbonylation agents which have attracted much attention in recent years.[18] Up to now, only a few reports investigated the synthesis of carbamates through the

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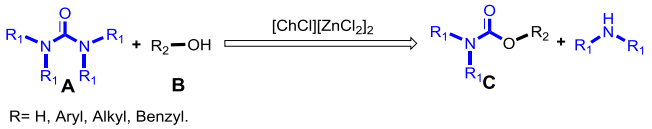
treatment of ureas with alcohols.[19] Unfortunately, in most cases, the reactions proceed at the relatively high temperatures, low reactivity of phenols and in the presence of unrecoverable catalysts. However, an eco-friendly, mild, better yielding and practical approach are still under attention to constructing this synthetic, pharmaceutical and industrial important scaffolds.[19]

The most common pollutants in the industrial and laboratory scale processes are due to the usage of volatile organic solvents, especially halogenated solvents.[20] From the economic and environmental point of view, according to the advantages of deep eutectic solvents (DESs) such as being non-hazardous, non-toxic, stable, non-flammable, and inexpensive nature, they are very good and effective alternatives for organic solvents.[21] DESs have been known as preferable alternative solvents/catalysts for organic synthesis that led to a spectacular resurgence of interest.[22]

In recent years, as part of our ongoing research program searching for the new, green and applicable synthesis of carbamates,[23] we have reported numerous highly active and selective methods. In this effort, we develop a green, eco-friendly, mild, and highly efficient method for the one-pot synthesis of primary, *N*-mono- and *N*-disubstituted carbamates using ureas as safe carbonyl source with choline chloride:Zinc (II) chloride ([ChCl][$ZnCl_2$]$_2$) as a recoverable catalyst and solvent (Scheme 1).



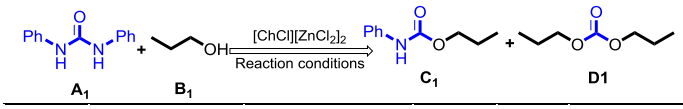
Scheme 1. Primary, *N*-mono- and *N*-disubstituted carbamates synthesis (C) via ureas.

Results and discussion

We initiated our studies by investigating various reaction conditions for the synthesis of primary, *N*-mono- and *N*-disubstituted carbamates. Then, we postulated that the main difficulty in this methodology is the low reactivity of urea. On the other hand, it was envisioned that under more efficient reaction conditions, one-pot synthesis of desired products starting from *N,N'*-diarylurea would be beneficial. Therefore, *N, N'*-diphenylurea (**A1**) and 1-propanol (**B1**) in the presence of [ChCl][$ZnCl_2$]$_2$, were chosen as the model substrates for the optimization of reaction conditions. Various reaction parameters including the reaction time, temperature and molar ratios of reagents were investigated to improve the amount of the desired carbamate in the model reaction and results are summarized in Table 1.

According to these data, the presence of [ChCl][$ZnCl_2$]$_2$ is necessary for the reaction progress and the best result obtained when the molar ratio of urea:alcohol (2:1) was applied in this reaction (Table 1 entries 1, 2). Decreasing the amount of urea content than alcohol resulted in an increased carbonate production as a side product. As a result, the corresponding carbamate is prepared in lower yields (Table 1 entries 3, 4). Furthermore, increasing the amount of urea content compared to alcohol did not increase yields (Table 1 entries 5, 6). Next, we examined the effect of changing the amounts of [ChCl][$ZnCl_2$]$_2$ as the catalyst. Finally, It was found that the reaction of **A1** (2 mmol) and **B1** (1 mmol) in the presence of 3.0 cm^3 of [ChCl][$ZnCl_2$]$_2$ gave the highest yield of 1-propyl phenylcarbamate, at 120 ^oC within 18 h (Table 1 entry 2).

Table 1. Optimization of reaction parameters for the synthesis of 1-propyl phenylcarbamate(**C**1).



Entry	Molar ratio A_1:B_1	[ChCl][$ZnCl_2$]$_2$ [cm^3]	Temp [^oC]	Tim [h]	Yield (%)[a] C1	Yield (%)[a] D1
1	2 : 1	--	120	18	0	0
2	2 : 1	3	120	18	83	trace
3	1 : 1	3	120	18	51	21
4	1.5 : 1	3	120	18	70	14
5	2.5 : 1	3	120	18	82	trace
6	3 : 1	3	120	18	83	trace
7	2 : 1	1	120	18	53	trace
8	2 : 1	2	120	18	66	trace
9	2 : 1	4	120	18	74	11
10	2 : 1	5	120	18	71	13
11	2 : 1	3	80	18	43	trace
12	2 : 1	3	100	18	58	trace
13	2 : 1	3	140	18	62	16
14	2 : 1	3	160	18	51	23
15	2 : 1	3	120	6	58	trace
16	2 : 1	3	120	12	72	trace
17	2 : 1	3	120	24	7	11
18	2 : 1	3	120	30	65	17

[a] Isolated yield.

In the next step of our investigation, the catalytic activities of a wide range of commonly available DESs were checked out in the model reaction under the optimized conditions and the results are summarized in Table 2.

Based on the results presented in Table 2, when choline chloride and metal chlorides based DESs including $AlCl_3$, $LaCl_3$, $MnCl_2$ and $CaCl_2$ were used as catalyst no catalytic activity was observed. Also, the usage of DESs such as [ChCl][$ZnCl_2$], [ChCl][$FeCl_3$]$_2$, [ChCl][$SnCl_2$]$_2$, [ChCl][$NiCl_2$]$_2$ [ChCl][$CuCl_2$]$_2$, [ChCl][$CoCl_2$]$_2$, [ChCl][$CrCl_3$]$_2$, [ChCl][$ZnCl_2$][$SnCl_2$], [ChCl]$_2$[$Zn(NO_3)_2$], [(BMIM)Cl][$TiCl_4$] (BMIM = 1-butyl-3-methylimidazolium) and [BTMAC][$ZnCl_2$]$_2$ (BTMAC = Benzyltrimethylammonium chloride) as catalyst, was led to the synthesis of desired products in lower yields. Unfortunately, during the usage of [ChCl][$ZnCl_2$]$_3$ as catalyst, a large quantity of dipropyl carbonate as the side product has been formed and detected. These results indicate the low selectivity of catalyst for the formation of desired carbamates in the model reaction.

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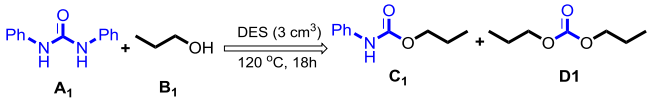
Table 2. Results of 1-propyl phenylcarbamate (**C1**) from 1-propanol (**B1**) and *N, N′*-diphenylurea (**A1**) over different DESs.[a]

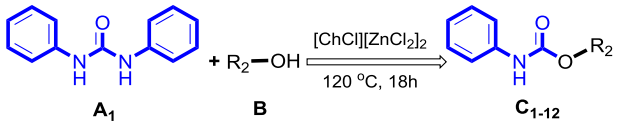


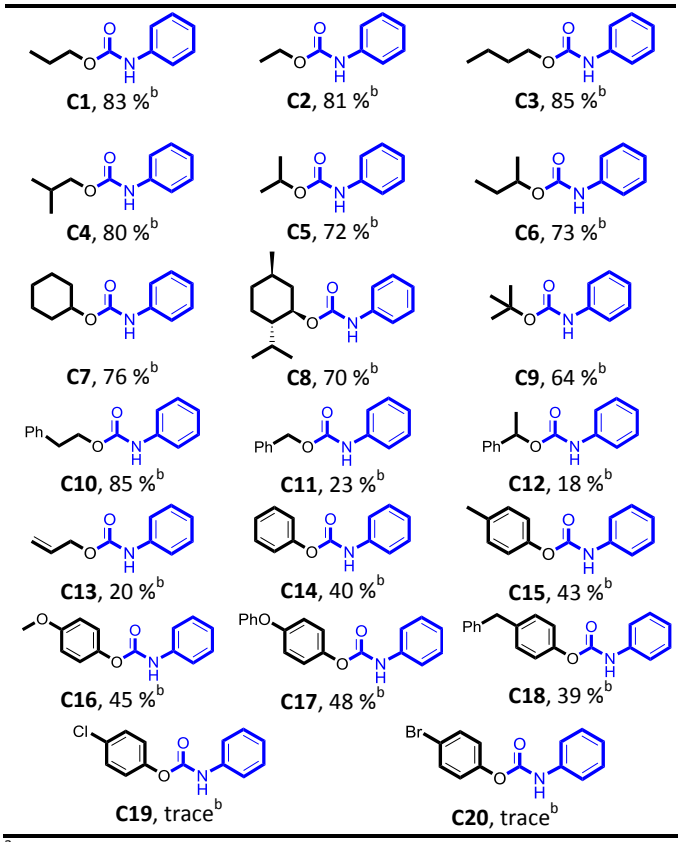
Entry	DES	Yield (%)[b]	
		C1	D1
1	$[ChCl][ZnCl_2]$	62	trace
2	$[ChCl][ZnCl_2]_2$	83	trace
3	$[ChCl][ZnCl_2]_3$	74	14
4	$[ChCl][FeCl_3]_2$	43	trace
5	$[ChCl][SnCl_2]_2$	56	trace
6	$[ChCl][AlCl_3]_2$	0	0
7	$[ChCl][NiCl_2]_2$	39	trace
8	$[ChCl][CuCl_2]_2$	38	trace
9	$[ChCl][CoCl_2]_2$	41	trace
10	$[ChCl][LaCl_3]_2$	0	0
11	$[ChCl][CrCl_3]_2$	54	trace
12	$[ChCl][MnCl_2]_2$	0	0
13	$[ChCl][CaCl_2]_2$	0	0
14	$[ChCl][ZnCl_2][SnCl_2]$	72	trace
15	$[ChCl]_2[Zn(NO_3)_2]$	68	trace
16	[(BMIM)Cl][$TiCl_4$]	47	trace
17	[(BMIM)Cl][$AlCl_3$]	0	0
18	$[BTMAC][ZnCl_2]_2$	70	trace

[a] Reaction conditions: 1-propanol (1 mmol), *N, N′*-diphenylurea (2 mmol), DES (3 cm^3), 120 °C, 18 h.
[b] Isolated yield.

Having determined the optimal reaction conditions, the scopes of proposed one-pot methodology for the synthesis of *N*-monosubstituted carbamates with varies alcohol and phenol derivatives were investigated. Experimentally, it was found that primary and secondary alcohols present good to excellent yields of carbamates (Table 3, entries **C1-8** and **C10**). It was noticed that reaction with tertiary alcohols lead to the formation of the desired carbamate in lower yields (Table 3, entry **C9**). The steric hindrance seems to be the main reason and causes low product yields. Interestingly, in the case of L-(-)-menthol, the reaction can produce the corresponding L-(-)-menthyl phenylcarbamate without any epimerization (Table 3, entry **C8**). Unfortunately, the reaction of allyl alcohol, benzyl alcohols and phenol under the same conditions afforded the corresponding carbamates in low yields, even with increasing the reaction time and temperature (Table 3, entries **C11-24**). In addition, phenol nucleophiles containing an electron donating group provided desired carbamates in low yields (Table 3, entries **C15-18**). Moreover, when phenols containing an electron withdrawing group were used as the nucleophile, the amounts of wanted products were so insignificant and the purification of which using experimental methods like column chromatography and thin-layer chromatography were unsuccessful (Table 3, entries **C19-20**). These results showed that along with the steric hindrance, the nucleophilicity of alcohols plays a serious role in the efficiency of the reaction.

Table 3. Synthesis of *N*-monosubstituted carbamates (**C1–20**) from alcohols or phenols by *N, N′*-diphenylurea in the presence of $[ChCl][ZnCl_2]_2$.[a]





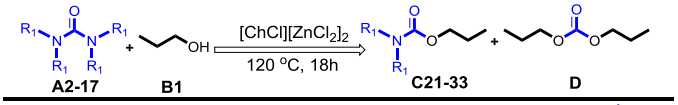
[a] Reaction conditions: alcohols or phenols (1 mmol), *N, N′*-diphenylurea (2 mmol), $[ChCl][ZnCl_2]_2$ (3 cm^3), 120 °C, 18 h.
[b] Isolated yield.

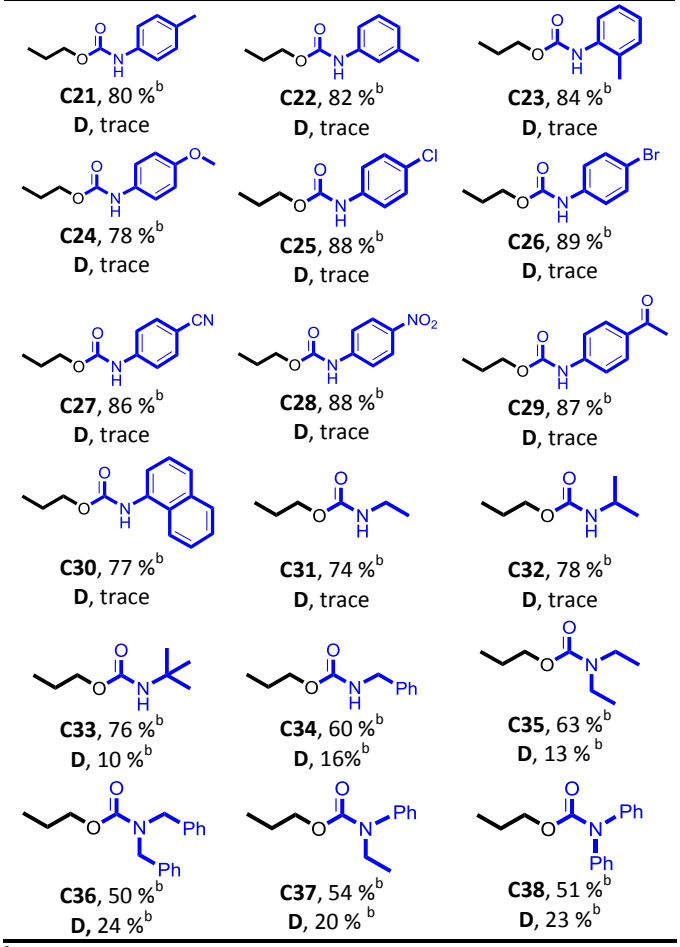
In the next step, we explored the scope and limitations of carbamates synthesis by employing various ureas. Therefore, a range of commercially available *N, N′*-disubstituted ureas and *N, N′*-tetrasubstituted ureas including aromatic and aliphatic substitutes were applied in reaction and the results are summarized in Table 4.

Under optimized conditions, *N, N′*-diphenyl ureas with both electron donating and electron withdrawing substituents underwent the conversion efficiently. However, *N, N′*-diphenyl ureas bearing electron-withdrawing groups had slightly higher yields than those with electron-donating moieties (Table 3, entries **C21-29**). Importantly, good to excellent yields were obtained when *N, N′*-dialkylureas were treated with primary, secondary and tertiary aliphatic substrates (Table 3, entries **C31-34**). However, *N, N′*-tetrasubstituted ureas such as 1,1,3,3-tetraethylurea, 1,1,3,3-tetrabenzylurea, 1,3-dibenzyl-1,3-diethylurea, 1,1,3,3-tetraphenylurea and also 1,3-dibenzylurea

gave desired carbamates in moderate yields (Table 3, entries **C35-38**). In these cases, due to the more activity of *N, N'*-tetrasubstituted ureas rather than *N, N'*-disubstituted ureas in this reaction conditions, the amount of carbonate side product was increased.

Table 4. Synthesis of *N*-mono- and *N*-disubstituted carbamates (**C21–38**) from 1-propanol by various ureas in the presence of $[ChCl][ZnCl_2]_2$.[a]

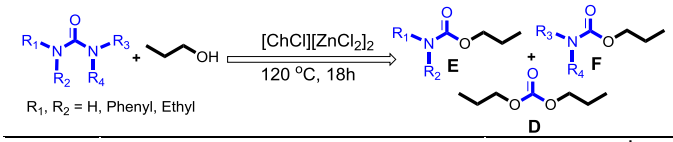




[a] Reaction conditions: 1-propanol (1 mmol), ureas (2 mmol), $[ChCl][ZnCl_2]_2$ (3 cm^3), 120 °C, 18 h.
[b] Isolated yield.

Subsequently, the chemo selectivity of this approach was also studied by the reaction of 1-propanol and different ureas. Chemo selective formation of the of the propyl carbamate was carried out by the reaction of 1-propanol with urea (Table 5, entry **1**), 1-phenylurea (Table 5, entry **2**), 1,1-diphenylurea (Table 5, entry **3**),1-ethylurea (Table 5, entry **4**) and 1,1-diethylurea (Table 5, entry **4**) in good yields with no formation of carbonate and *N*-mono- and *N*-disubstituted carbamates by products. However, using 1-ethyl-3-phenylurea undergoes the produces unequal amount of 1-propyl phenylcarbamate and 1-propyl propylcarbamate along with a remarkable amount of dipropyl carbonate were obtained. Although using 1,1-diethyl-3,3-diphenylurea and 1-ethyl-3-phenylurea gave the carbonate product in more yield, other results were the same. The steric hindrance of applied ureas as well as the leaving strength of amines, probably resulted in this observations.

Table 5. Investigation of the reaction between 1-propanol and various substituted of ureas.[a]

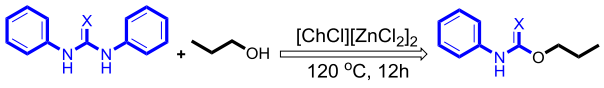


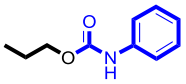
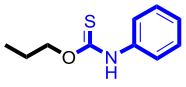
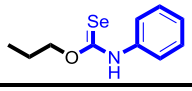
Entry	R				Yield (%)[b]
	R_1	R_2	R_3	R_4	
1	H	H	H	H	E=F=58, D=0
2	Phenyl	H	H	H	E=0, F=74, D=0
3	Phenyl	Phenyl	H	H	E=0, F=80, D=0
4	Ethyl	H	H	H	E=0, F=69, D=0
5	Ethyl	Ethyl	H	H	E=0, F=73, D=0
6	Phenyl	H	Ethyl	H	E=17, F= 57, D=12
7	Phenyl	Phenyl	Ethyl	Ethyl	E=9, F= 55, D= 17

[a] Reaction conditions: 1-propanol (1 mmol), *N, N'*-diphenylurea (2 mmol), DES (3 cm^3), 120 °C, 18 h.
[b] Isolated yield.

Next, we decided to apply the reaction in the synthesis of thiocarbamate and selenocarbamate. For this purpose, the reaction of 1-pentanol with 1,3-diphenylthiourea or 1,3-diphenylselenourea have been tested under the optimized conditions and the results are summarized in Table 6. Unfortunately, these tests were unsuccessful for the synthesis of desired products and starting materials were only observed. These results show that the $[ChCl][ZnCl_2]_2$ is unable to activate thiocarbonyl and selenocarbonyl groups.

Table 6. Investigation of the reaction between 1-propanol and *N, N*- diphenyl substituted of ureas, thioureas and selenoureas.[a]



Entry	X	Product structure	Yield (%)[b]
1	O		83
2	S		0
3	Se		0

[a] Reaction conditions: 1-propanol (1 mmol), *N, N'*-diphenylurea, thiourea or selenourea (2 mmol), DES (3 cm^3), 120 °C, 18 h.
[b] Isolated yield.

The recyclability and reusability are important features of catalysts which especially signify both economic and environmental viewpoints in the industrial and chemical processes. Therefore, the recyclability of $[ChCl][ZnCl_2]_2$ as a deep eutectic solvent and the catalytic system was investigated in the model reaction. After the completion of the reaction, all products and remaining precursors were extracted with diethyl ether (3 × 10 mL). Then, DES was separated from the ethereal solution, dried by evaporation at 70 °C under vacuum condition for 30 min and reused in the model reaction for the next runs. As illustrated in Figure 2, the efficiency of DES was found to be notable even after five cycles with the lowest decrease in the activity of which.

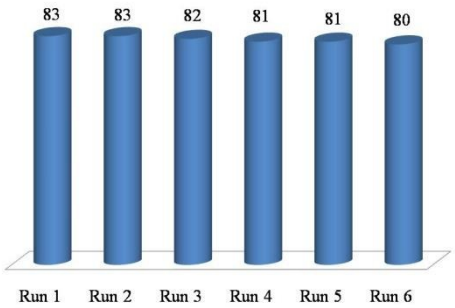


Figure 2. Reuse of $[ChCl][ZnCl_2]_2$ catalyst in the synthesis of 1-propyl phenylcarbamate.

Conclusions

In summary, we reported a green, efficient, inexpensive and operationally simple process for the one-pot synthesis of *N*-mono- and *N*-disubstituted carbamates. Remarkably, the current method has many important highlights such as (i) usage of ureas as an inexpensive and natural carbonyl source; (ii) application of $[ChCl][ZnCl_2]_2$ as recoverable catalyst and solvent system that proved to be a safe and eco-friendly reaction medium and (iii) convenient and very simple separation and purification process. In view of the potential applicability of carbamates in drug design and the synthesis of natural and bioactive molecules, it is significant that this phosgene-free methodology can be widely used for carbamate-based marketed drugs and opens the new avenue for further research in this area.

Experimental

General experimental:

All chemicals were purchased from the Merck, Flucka and Aldrich Chemical Companies in high purity. The products were characterized by comparison of their spectral and physical data such as NMR, FT-IR, MS, CHNS and melting point with the literature. ^1H and ^{13}C NMR spectra were recorded with Bruker Avance DPX 250MHz instruments with Me_4Si or solvent resonance as the internal standard. Fourier transform infrared (FTIR) spectra were obtained using a Shimadzu FT-IR 8300 spectrophotometer. Determination of the purity of the substrate and monitoring of the reactions was accomplished by thin-layer chromatography (TLC) on a silica-gel polygram SILG/UV 254 plates.

Preparation of $[ChCl][ZnCl]_2$ as deep eutectic solvent:[24]

For the preparation of this deep eutectic solvent, a mixture of choline chloride (10 mmol, 1.39 g) and zinc(II) chloride (20 mmol, 2.72 g) was heated to 100 °C until a clear colorless liquid appeared, then allowed to cool at room temperature and used without further purification.

General procedure for the preparation of primary, *N*-mono- and *N*-disubstituted carbamates derivatives (C1-33):

Alcohol or phenol (1.0 mmol) was treated with ureas (2.0 mmol) in the presence of $[ChCl][ZnCl_2]_2$ (3 cm^3) at 120 °C under solvent-free magnetic stirring for 18 h. The progress of the reaction was monitored by TLC. After the completion of the reaction, the mixture was cooled down to room temperature. The reaction mixture was separated from DES by multiple dilutions using diethyl ether (3 × 10 mL). Then, all starting materials were washed with H_2O (2 × 15 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to afford final products. Finally, obtained crude was purified by recrystallization from the CH_2Cl_2 or chromatograph using ethyl acetate /petroleum ether (1/9). The purity and identity of the product were confirmed by FT-IR, ^1H NMR, ^{13}C NMR, and MS. The recovered catalyst was activated by heating under reduced vacuum at 70 °C for 30 min and reused for next cycles.

Acknowledgments

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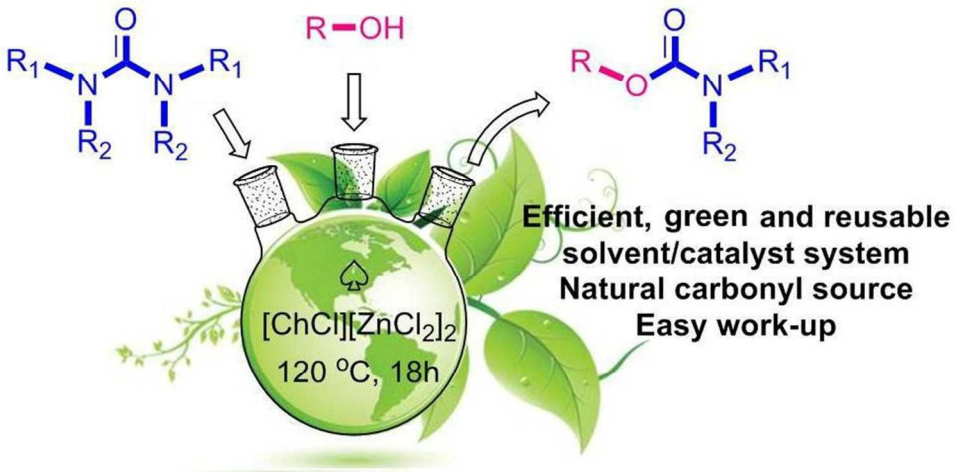

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