Lewis acid catalyzed *N*-acylation of carbamates and oxazolidinones

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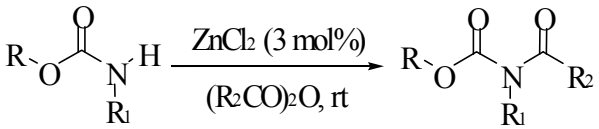
Abstract

The reaction of various carbamates and oxazolidinones with carboxylic acid anhydrides in presence of Lewis acid catalysis is described. The *N*-acylation was effectively promoted by catalytic amount of $ZnCl_2$ to produce the corresponding *N*-acyl products in good yields under solvent-free conditions. Carboxylic acids were also successfully used as acylating agents *via* mixed anhydride method.

Keywords: Acylation, carbamates, oxazolidinones, Lewis acid, zinc (II) chloride

Introduction

N-Acyl carbamates and oxazolidinones are important synthetic building blocks towards synthesis of bio-active molecules.[1, 2] Furthermore, *N*-acyl oxazolidinones have found extensive applications in the asymmetric synthesis as chiral auxiliaries.[3] The established methods to obtain these *N*-acyl compounds generally requires NH activation of amide and/or acyl donor, due to the less basic nature of nitrogen atom in carbamates and oxazolidinones compared to the amines. The methods include the reaction of carbamates and oxazolidinones with acid chlorides or anhydrides in basic reaction conditions using the bases such as trialkyl amines, pyridines etc.[2i, 4] and others.[5] The *N*-acylation of these less nucleophilic compounds has not received considerable attention under the acidic medium. To our knowledge, only few reports in the literature is described.[6] However, strong acidic conditions *viz.* conc. H_2SO_4 or HBr/AcOH as well as elevated temperatures are required to achieve such conversions. Recently, *N*-acylation of amides/oxazolidinones with acid anhydrides was demonstrated by the dual activation using $MgBr_2.OEt_2$.[7] Nevertheless, 2 equiv. of $MgBr_2.OEt_2$ and 3 equiv. of Et_3N were used for the reaction. Hence, the development of new methods using Lewis acids in catalytic amounts is of practical importance. In continuation of our interest in Lewis acid catalyzed transformations [8, 9] herein, we report a facile synthesis of *N*-acyl carbamates and oxazolidinones in the presence of Lewis acid catalyst (Scheme 1).



R= alkyl, aryl; R_1 = H, alkyl or
R=R_1 = -CH_2-CHBn-
R_2 = Me, Et, ^{n}Pr, ^{t}Bu, Ph

Scheme 1

Results and Discussion

In order to find the suitable conditions, the *N*-acetylation of benzyl carbamate **1a** with acetic anhydride was performed at room temperature in the presence of different Lewis acid catalysts under solvent-free conditions. All the catalysts used *i.e.* $ZnCl_2$, $FeCl_3$, $MoCl_5$, $B(C_6F_5)_3$ and I_2 were found to be effective towards the *N*-acylation of benzyl carbamate (entries 1 to 5, Table 1). No desired product was obtained when the reaction was carried out in the absence of catalyst even after 12 h (entry 6, Table 1). Although, most of these Lewis acid provided good to better yields, zinc(II) chloride, for obvious reasons (being cheapest, milder conditions and easy to handle) was chosen for further experiments.

Table 1. Catalytic activity of various Lewis acids for the *N*-acetylation of benzyl carbamate with acetic anhydride[a]

entry	Lewis acid (3 mol%)	time (min)	yield (%)[b]
1	$ZnCl_2$	5	95
2	$FeCl_3$	3	94
3	$MoCl_5$	5	92
4	$B(C_6F_5)_3$	10	92
5	I_2	15	85
6	-	720	-

[a]All the reactions were carried out at room temperature under solvent free conditions. [b]Isolated yields after column purification

As a first example, benzyl carbamate **1a** ($CbzNH_2$) was treated with acetic anhydride in presence of 3 mol% of $ZnCl_2$ under solvent-free conditions to afford the *N*-acetyl benzyl

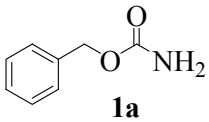
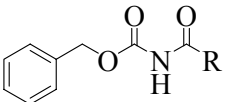
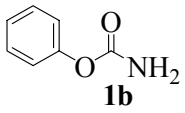
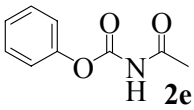
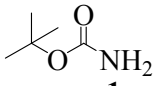
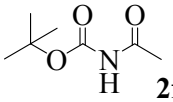
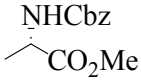
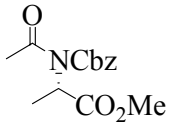
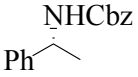
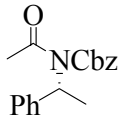
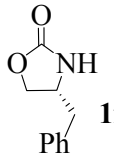
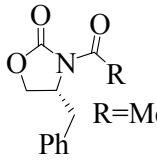
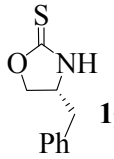
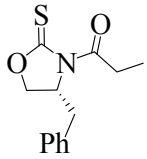
carbamate **2a** in 95% yield (entry 1, Table 2). Successful attempts were also taken to acylate **1a** with other acid anhydrides, propionic, pivalic and benzoic anhydrides under similar reaction conditions (entries 2 to 4, Table 2). Phenyl carbamate **1b**, furnished the corresponding *N*-acetyl product **2e** in 95% yield (entry 5, Table 2). However, *tert*-butyl carbamate **1c** ($BocNH_2$) failed to furnish the desired product **2f** (entry 6, Table 2). Certain secondary carbamates including amino-acid carbamate **1d** and amine carbamate **1e** were also studied for *N*-acetylation and was found to provide the acylated desired products **2g** and **2h** in 93% and 94% yields, respectively (entries 7 and 8, Table 2). Then after, we have further highlighted this Lewis acid catalyzed reaction by extending this method for *N*-acylation of oxazolidinones to produce important constructive products in asymmetric synthesis. Accordingly, oxazolidinone **1f** and 1,3-oxazolidine-2-thione **1g** were treated with different anhydrides in the presence of 3 mol% $ZnCl_2$ to obtain the corresponding *N*-acylated products **2i** to **2k** in good yields (entries 9 to 11, Table 2). The formation of corresponding acylated products **2g** to **2k** from **1d** to **1g** respectively was observed without any racemization (entries 7 to 11, Table 2).

Encouraged by the above results, we have further investigated the possibility of using carboxylic acids as acylating agents for the *N*-acylation of carbamates under the Lewis acid catalysis for the first time. Among the anhydrides studied, benzoic anhydride was found to be the least reactive (entry 4, Table 2). Therefore, we have decided to perform the *N*-acylation of carbamate with carboxylic acid in presence of benzoic anhydride by adopting the mixed anhydride method.[10] Consequently, the reaction of phenyl acetic acid **3a** with benzyl carbamate **1a** in presence of benzoic anhydride and 5 mol% $ZnCl_2$ in CH_2Cl_2 at room temperature for 1.5 h afforded the corresponding product **4a** in 85% yield (entry 1, Table 3). Phenyl carbamate **1b** was acylated to **4b** by using the same carboxylic acid **3a** under the similar conditions. Likewise, the other carboxylic acids **3b** and **3c** were also successfully participated in acylation reaction with carbamates **1a** and **1b** to give the corresponding acyl carbamates **4c** to **4e** (entries 3 to 5, Table 3. Attempts were also made to *N*-acylate the oxazolidinone **1f** with carboxylic acid **3a** *via* mixed anhydride method in presence of $ZnCl_2$ (3 mol%), but without success.[11]

Conclusions

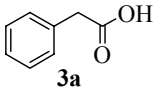
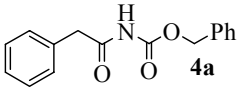
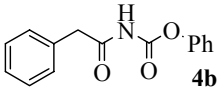
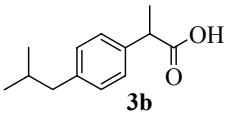
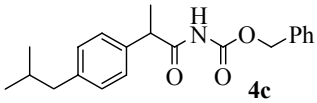
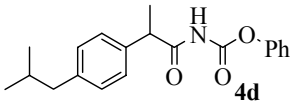
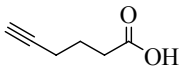
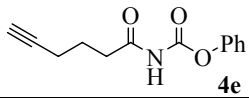
In summary, we have demonstrated a Lewis acid catalyzed method for the *N*-acylation of carbamates and oxazolidinones with acid anhydrides under solvent-free reaction conditions for the first time. The method was effectively extended to use the carboxylic acids as acylating agents. The simple procedure, mild reaction conditions and high yields of the products makes this methodology attractive for applications in organic synthesis.

Table 2. $ZnCl_2$-Catalyzed *N*-acylation of carbamates and oxazolidinones

entry	carbamate	anhydride	time (min)	product[a]
1	 **1a**	$(RCO)_2O$ R=Me	3	 R=Me **2a**
2	**1a**	R=Et	6	R=Et **2b**
3	**1a**	R=^{t}Bu	90	R=^{t}Bu **2c**
4	**1a**	R=Ph	300	R=Ph **2d**
5	 **1b**	$(MeCO)_2O$	4	 **2e**
6	 **1c**	$(MeCO)_2O$	5	 **2f**
7	 **1d**	$(MeCO)_2O$	7	 **2g**
8	 **1e**	$(MeCO)_2O$	10	 **2h**
9	 **1f**	$(RCO)_2O$ R=Me	15	 R=Me **2i**
10	**1f**	R=^{n}Pr	75	R=^{n}Pr **2j**
11	 **1g**	$(EtCO)_2O$	60	 **2k**

[a]All the products were characterized by ^{1}H NMR, mass and IR spectra. [b]Isolated yields. [c]CH_2Cl_2 was used as solvent. [d]Complex mixture was formed (based TLC).

Table 3. *N*-Acylation of carbamates using carbocylic acids[a]

entry	carboxylic acid	carbamate	time (h)	product[b]	yield (%)[c]
1	 **3a**	**1a**	1.5	 **4a**	85
2	**3a**	**1b**	1.5	 **4b**	80
3	 **3b**	**1a**	2	 **4c**	80
4	**3b**	**1b**	1.5	 **4d**	83
5	 **3c**	**1b**	2.5	 **4e**	78

[a]Reaction conditions: 5mol% $ZnCl_2$, 1.2 equiv $(PhCO)_2O$, CH_2Cl_2, rt. [b]All the products were characterized by ^1H NMR, mass and IR spectra. [c]Isolated yields.

Experimental Section

General Procedures. The chemicals such as carbamates, anhydrides, oxazolidinone, carboxylic acids and all the Lewis acid catalysts were purchased from Aldrich and used as received. Dichloromethane was distilled over calcium hydride. The optical rotations were recorded using a Jasco Dip 360 digital polarimeter. IR spectra were recorded on Perkin-Elmer 683 spectrometer. ^1H NMR (200 MHz and 300 MHz) and ^{13}C NMR (75 MHz) spectra of samples in $CDCl_3$ were recorded on Bruker Avance spectrometer. Chemical shifts were reported in ppm with respect to internal TMS. Coupling constants (*J*) are quoted in Hz. Mass spectra were obtained on an Agilent Technologies LC/MSD Trap SL.

General experimental procedure for *N*-acylation of carbamates and oxazolidinones with anhydrides (for products 2a to 2k)

To a mixture of carbamte or oxazolidinone (1.0 mmol) and anhydride (1.5 mmol), 3 mol% of anhydrous $ZnCl_2$ was added and the reaction stirred for the given time (see Table 2). The reaction mixture was diluted with dichloromethane (15 mL) and washed with water (10 mL) and brine (10 mL) solution. The organic layers were dried over Na_2SO_4 and evaporated *in vacuo*. The crude compound was purified by column chromatography (hexanes and ethyl acetate) to afford the corresponding *N*-acylated product.

Benzyl propionylcarbamate (2b). White powder, m.p. 119-121 ^{o}C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.60 (br s,1H), 7.39-7.34 (m, 5H), 5.18 (s, 2H), 2.79 (q, *J* = 7.4 Hz, 2H), 1.16 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.7, 151.9, 135.2, 128.84, 128.80, 128.4, 67.9, 29.7, 8.4; IR(KBr): ν 3261, 3187, 1756, 1696, 1526, 1195, 1048 cm^{-1}; EIMS: *m/z* 230.0 (M+Na).

Benzyl pivaloylcarbamate (2c). White solid, m.p. 103-105 ^{o}C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.70 (br s, 1H), 7.44-7.32 (m, 5H), 5.20 (s, 2H), 1.23 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ175.8, 151.0, 135.2, 128.74,128.72, 67.8, 40.3, 27.0; IR (KBr): ν 3296, 2964, 1772, 1687, 1515, 1209, 1165, 700 cm^{-1}; HRMS-ESI Calcd for $C_{13}H_{17}NO_3Na$: 258.1109; Found: 258.1106.

Phenyl acetylcarbamate (2e). White powder, m.p. 120-122 ^{o}C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.10 (br s, 1H), 7.46 -7.35 (m, 2H), 7.33 - 7.22 (m, 1H), 7.20-7.12 (m, 2H), 2.49 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.1,150.9, 149.9, 129.7, 126.5, 121.6, 24.3; IR (KBr): ν 3257, 3197, 1769, 1704, 1531, 1483, 1220, 1117, 729 cm^{-1}; HRMS-ESI Calcd for $C_9H_9NO_3Na$: 202.0475; Found: 202.0480.

(*S*)-Methyl 2-(*N*-(benzyloxycarbonyl) acetamido) propa-noate (2g). Colorless liquid; $[\alpha]_D^{25}$= -14.6 (*c* 1 in $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.40-7.34 (m, 5H), 5.38- 5.13 (m, 3H), 3.53 (s, 3H), 2.54 (s, 3H), 1.48 (s, 2H), 1.45 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ172.3, 171.2, 153.6, 134.6, 128.9, 128.8, 128.7, 69.0. 52.3, 51.9, 26.6, 15.5 ; IR (neat): ν 3457, 2949, 1745, 1703, 1435, 1385, 1252, 698 cm^{-1}; HRMS-ESI Calcd for $C_{14}H_{17}NO_5Na$: 302.1011; Found: 302.1004.

(*R*)-Benzyl acetyl(1-phenylethyl)carbamate (2h). Colorless liquid; $[\alpha]_D^{25}$= -55.5 (*c* 1.5 $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.44-7.12 (m, 8H), 7.10-6.95 (m, 2H), 6.18-5.97 (q, *J* = 6.6 Hz, 1H), 5.10-4.97 (dd, *J = 6.4* Hz, *J = 13.6* Hz, 2H), 2.53 (s, 3H), 1.65 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.1, 154.8, 141.3, 134.7, 128.6, 128.5, 128.3, 126.8, 126.5, 68.5, 51.6, 27.0, 17.2.; IR (KBr): υ 3032, 2944, 1734, 1695, 1239, 697 cm^{-1}; HRMS-ESI Calcd for $C_{18}H_{19}NO_3Na$: 320.1262; Found: 320.1275. **2a,**[12] **2d,**[12] **2i,**[13] **2j**[14] **and 2k**[15]**:** IR, ^{1}H, ^{13}C NMR and mass spectral data of these known compounds were identical with the reported data

General experimental procedure for *N*-acylation of carbamates with carboxylic acids (for products 4a to 4e)

To a stirred solution of 5 mol% anhydrous $ZnCl_2$ in anhydrous dichloromethane (10 mL), carboxylic acid (1.2 mmol) was added followed by the addition of benzoic anhydride (1.2 mmol) under a nitrogen atmosphere at room temperature. After 10 min, a solution of carbamate in CH_2Cl_2 was added and the resulting reaction mixture was stirred for the given time (see Table 3). The reaction mixture was diluted with dichloromethane (20 mL) and washed with water (10 mL) then brine (10 mL) and the organic layers were dried over Na_2SO_4, and evaporated *in vacuo*. The crude compound was purified by column chromatography (hexanes and ethyl acetate) to afford the corresponding *N*-acylated product.

Benzyl 2-phenylacetylcarbamate (4a). White solid, m.p. 128-130 ^{o}C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.10 (br s, 1H), 7.38-7.17 (m, 10H), 5.16 (s, 2H), 4.05 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.5, 151.7, 135.0, 133.6, 133.5, 129.5, 128.8, 128.6, 127.5, 127.4, 68.1, 42.9; IR

(KBr): υ 3255, 3172, 1758, 1693, 1523, 1220, 702 cm^{-1}; HRMS-ESI Calcd for $C_{16}H_{15}NO_3Na$: 292.0949; Found: 292.0955.

Phenyl 2-phenylacetylcarbamate (4b). Semi solid; ^1H NMR (200 MHz, $CDCl_3$): δ 7.70 (br s, 1H), 7.42-7.14 (m, 8H), 7.07 (d, *J* = 7.3 Hz, 2H), 4.07 (s, 2H).; ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.1, 150.2, 150.0, 133.3, 129.8 (2C), 128.9, 127.6, 126.6, 121.5, 42.9.; IR (KBr): υ 3256, 2925, 1760, 1533, 1486, 1186, 804 cm^{-1}; HRMS-ESI Calcd for $C_{15}H_{13}NO_3Na$: 278.0793; Found: 278.0798.

Benzyl 2-(4-isobutylphenyl)propanoylcarbamate (4c). Light yellowish solid, m.p. 124-126 ^oC; ^1H NMR (200 MHz, $CDCl_3$): δ 7.36 (br s, 1H), 7.37-7.06 (m, 9H), 5.12 (s, 2H), 4.30-4.12 (q, *J* = 6.6 Hz, 1H), 2.45 (d, *J* = 7.3 Hz, 2H), 1.97-1.74 (m, 1H), 1.48 (d, *J* = 6.6 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 6H).; ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.1, 151.0, 141.2, 137.2, 135.1, 129.8, 128.8, 128.5, 128.4, 127.7, 67.9, 45.9, 45.2, 30.3, 22.5, 18.8.; IR (KBr): υ 3256, 2925, 1750, 1541, 1517, 1238. 697 cm^{-1}; HRMS-ESI Calcd for $C_{21}H_{25}NO_3Na$: 362.1732; Found: 362.1724.

Phenyl 2-(4-isobutylphenyl)propanoylcarbamate (4d). White powder, m.p. 80-82 ^oC; ^1H NMR (200 MHz, $CDCl_3$): δ 8.20-8.08 (m, 2H), 8.00 (br s, 1H), 7.71 -7.55 (m, 1H), 7.56-7.31 (m, 2H), 7.30-7.19 (m, 2H), 7.18-7.05 (m, 2H), 3.76 (q, *J* = *6.8* Hz,1H), 2.46 (d, *J* = 7.0 Hz, 2H), 1.96-1.74 (m, 1H), 1.54 (dd, *J* = 7.0, 2.3 Hz, 3H), 0.91 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.8, 149.9, 149.7, 141.3, 137.1, 129.8, 129.7, 127.8, 127.4, 126.4, 121.5, 45.7, 45.2, 30.3, 22.6, 19.0; IR(KBr): ν 3263, 2955, 1762, 1704, 1456, 1287 cm^{-1}; HRMS-ESI Calcd for $C_{20}H_{24}NO_3$: 326.1749; Found: 326.1756.

Phenyl hex-5-ynoylcarbamate (4e). White solid, m.p. 74-76 ^oC; ^1H NMR (200 MHz, $CDCl_3$): δ 7.80 (br s, 1H), 7.52-7.09 (m, 5H), 2.98 (t, *J* = 7.3 Hz, 2H), 2.38-2.26 (m, 2H), 2.02-1.84 (m, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.0, 150.4, 150.0, 129.8, 126.6, 121.6, 83.5, 69.4, 35.0, 22.9, 17.9.; IR (KBr): υ 3426, 3271, 2924, 1758, 1525, 1146, 658 cm^{-1}.; HRMS-ESI Calcd for $C_{13}H_{13}NO_3Na$: 254.0793; Found: 254.0796.

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