Asian Journal of Chemistry; Vol. 23, No. 3 (2011), 1085-1087

ASIAN JOURNAL OF CHEMISTRY

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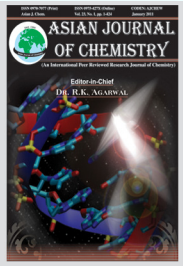

Synthesis of N-Acyl Carbamates and Oxazolidinones Using $HClO_4$-SiO_2 as Catalyst Under Solvent-Free Conditions

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(*Received*: 19 March 2010; *Accepted*: 2 November 2010) AJC-9240

Silica supported perchloric acid catalyzes efficiently the reaction of carbamates and oxazolidinones with anhydrides in the presence of silica sulfuric acid under solvent-free conditions. All the reactions were done at room temperature and the N-acyl carbamates and oxazolidinones were obtained with high yields and purity *via* an easy work-up procedure. This method is attractive and is in a close agreement with green chemistry.

Key Words: N-Acyl carbamates, N-Acyl oxazolidinones, Silica sulfuric acid, Solvent-free.

INTRODUCTION

N-Acyl carbamates and oxazolidinones are useful synthetic reagents in organic chemistry[1]. Particularly, N-acyl oxazolidinones have been found extensive applications in the asymmetric synthesis as chiral auxiliaries[2]. The most commonly used method involves the reaction of carbamates and oxazolidinones with acid chlorides or anhydrides in basic reaction conditions[3]. Recently, Lewis acids[4], such as H_2SO_4, HBr, $ZnCl_2$, $MgBr_2{\cdot}OEt_2$ have been shown to be effective for the synthesis of N-acyl carbamates and oxazolidinones. However, most of these procedures have significant drawbacks such as long reaction time, low yields, harsh reaction conditions, difficult work-up and use of environmentally toxic reagents or media. Hence, there is still a need to develop a practical and applicable method of the synthesis of N-acyl carbamates and oxazolidinones.

Homogeneous acidic catalysts such as H_2SO_4, HCl and BF_3 are commonly used for organic synthesis. However, the above-mentioned catalysts have several disadvantages because they are corrosive, toxic or volatile and generate large amounts of waste. Silica supported perchloric acid ($HClO_4$-SiO_2) has been used as an efficient heterogeneous catalyst for many organic transformations because of its low cost, ease of preparation, catalyst recycling and ease of handling[5]. In this paper, we report a simple and efficient synthesis of N-acyl carbamates and oxazolidinones by reaction of carbamates and oxazolidinones with anhydrides using this catalyst.

EXPERIMENTAL

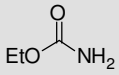
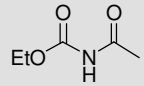
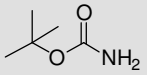
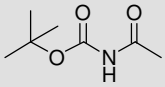
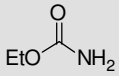
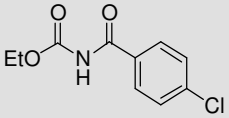
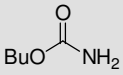
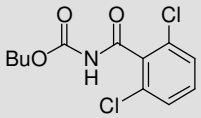
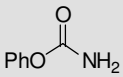
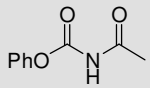
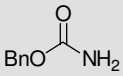
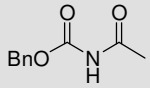
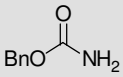
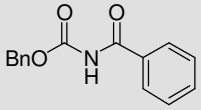
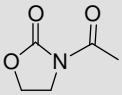
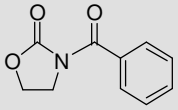
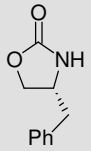
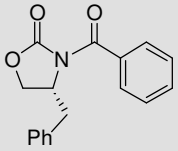
NMR spectra were determined on Bruker AV-400 spectrometer in DMSO-d_6 and were expressed in δ values relative to tetramethylsilane, coupling constants (*J*) were measured in Hz; elemental analysis were recorded on a Vario EL III elemental analyzer; melting points were determined on a meltng point, capillary tube apparatus and were uncorrected; commercially available reagents were used throughout without further purification unless otherwise stated.

General procedure for the preparation of 3: To a mixture of carbamte or oxazolidinone (1.0 mmol) and acid anhydride (1.2 mmol), $HClO_4$-SiO_2 (40 mg, 0.02 mmol) was added. The mixture was stirred at room temperature for the given time (Table-1). After completion of the reaction, $CHCl_3$ (20 mL) was added and the solid catalyst was removed by filtration. The solvent was evaporated and the crude product was puried by silica gel column chromatography using hexanes and ethyl acetate (3:1) as eluent.

Ethyl-4-chlorobenzoylcarbamate (3c): White powder, m.p. 105-106 ºC; IR (KBr, ν_{max}, cm^{-1}): 3251, 1758, 1742; ^1H NMR ($CDCl_3$, 400 MHz) δ: 8.10 (s, 1H), 7.82-7.49 (m, 4H), 4.26 (q, 2H, *J* = 7.6 Hz), 1.32 (t, 3H, *J* = 7.6 Hz); Anal. calcd. (%) for $C_{10}H_{10}NO_3Cl$: C 52.76, H 4.43; found (%): C 52.86, H 4.35.

Butyl-2,6-dichlorobenzoylcarbamate (3d): White powder, m.p. 110-112 ºC; IR (KBr, ν_{max}, cm^{-1}): 3259, 1770; ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.98 (s, 1H), 7.54-7.01 (m, 3H), 4.12 (t, 2H, *J* = 7.2 Hz), 1.65-1.56 (m, 2H), 1.33-1.26 (m, 2H), 0.97 (t, 3H, *J* = 7.2 Hz); Anal. calcd. (%) for $C_{12}H_{13}NO_3Cl_2$: C 52.76, H 4.43; found (%): C 52.86, H 4.35.

TABLE-1
PREPARATION OF N-ACYL CARBAMATES AND OXAZOLIDINONES CATALYZED BY $HClO_4$-SiO_2*

Entry	Carbamate	Anhydride	Product	Time (h)	m.p. (ºC)	Yield (%)**
a		$(MeCO)_2O$		5	76-77	85
b		$(MeCO)_2O$		3	77-78 (79-80)[6]	88
c		$(4\text{-}ClPhCO)_2O$		15	105-106	82
d		$(2,6\text{-}Cl_2PhCO)_2O$		20	110-112	91
e		$(MeCO)_2O$		3	119-121 (120-122)[3d]	90
f		$(MeCO)_2O$		3	106-107 (104-105)[3d]	89
g		$(PhCO)_2O$		60	109-110 (111-113)[3d]	85
h		$(MeCO)_2O$		5	59-60 (63-64)[7]	87
i		$(PhCO)_2O$		30	169-170 (167-168)[7]	90
j		$(MeCO)_2O$		45	110-111 (109)[2a]	76

*Reaction conditions: carbamate (1 mmol); anhydride (1 mmol); $HClO_4$-SiO_2 (0.02 mol); room temperature; neat. **Isolated yield.

RESULTS AND DISCUSSION

Initially, to optimize the amount of catalyst, the reaction of carbamate (**1**, 1 mmol) and acetic anhydride (**2**, 1.5 mmol) was studied under solvent-free conditions in the presence of $HClO_4$-SiO_2 at room temperature. The results are summarized in Table-2 and show that the reaction using 2 mol % $HClO_4$-SiO_2 proceeded in highest yield.

TABLE-2
AAMOUNTS OF CATALYST OPTIMIZATION FOR THE SYNTHESIS OF PHENYL ACETYLCARBAMATE*

Entry	$HClO_4$-SiO_2 (mol %)	Time (min)	Yield (%)**
1	0	60	16
2	1	5	76
3	2	3	90
4	3	3	90
5	4	2	89
6	5	2	88

*Reaction conditions: phenyl carbamate (1 mmol); acetic anhydride (1.5 mmol); room temperature; neat. **Isolated yield.

Based on the optimized reaction conditions, a variety of carbamates and oxazolidinones reacted smoothly with acid anhydrides in the presence of 2 mol % of $HClO_4$-SiO_2 at room temperature under solvent-free conditions to furnish the corresponding N-acyl carbamates and oxazolidinones in high yields. The reactions were rapid and in most cases N-acyl carbamates and oxazolidinones formation was complete in 1 h with excellent yields (Table-2). The structures of the products were established from their spectral properties (IR, ^1H NMR and elemental analysis).

The reusability of the catalyst was checked by separating $HClO_4$-SiO_2 from the reaction mixture by simple filtration, washing with $CHCl_3$ and drying in a vacuum oven at 60 ºC for 10 h prior to reuse in subsequent reactions. The recovered catalyst can be reused at least three additional times in subsequent reactions without significant loss in product yield (Table-3).

To emphasize the effect of catalyst the model reaction between phenyl carbamate and acetic anhydride was described and different acidic catalysts were subjected to the reaction.

TABLE-3
EFFECT OF REUSABILITY OF $HClO_4$-SiO_2 CATALYST ON PHENYL ACETYLCARBAMATE SYNTHESIS*

Run	Cycle	Yield (%)**
1	0	90
2	1	90
3	2	87
4	3	82

*Reaction conditions: phenyl carbamate (1 mmol); acetic anhydride (1.5 mmol); $HClO_4$-SiO_2 (0.02 mol); room temperature; neat. **Isolated yield.

All the reactions were run in the same conditions and similar amounts of catalysts (2 mol %) were used. As can be seen in Table-4, satisfactory results were obtained only with $HClO_4$-SiO_2 (entry 8).

TABLE-4
EFFECT OF ACIDIC CATALYST ON THE REACTION OF PHENYL CARBAMATE AND ACETIC ANHYDRIDE*

Entry	Catalyst	Time (min)	Yield (%)**
1	*p*-TsOH	60	62
2	H_2SO4	90	65
3	$NaHSO_4$	120	45
4	$NaHSO_3$	180	23
5	I_2	15	82
6	$ZnCl_2$	5	88
7	$MgBr_2{\cdot}OEt_2$	120	81
8	$HClO_4$-SiO_2	2	90

*Reaction conditions: phenyl carbamate (1 mmol); acetic anhydride (1.5 mmol); room temperature; neat. **Isolated yield.

Conclusion

In summary, it can be concluded that $HClO_4$-SiO_2 is an efficient catalyst in the reactions of carbamates and oxazolidinones with acid anhydrides to afford the N-acyl carbamates and oxazolidinones in good to excellent yields under solvent-free conditions in short reaction time. In contrast to the existing methods this method is general, simple, high yielding and environmentally friendly, avoiding the discharge of toxic volatile solvents and reagents.

ACKNOWLEDGEMENTS

The authors are pleased to acknowledge the financial support from Xinxiang Medical University.

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