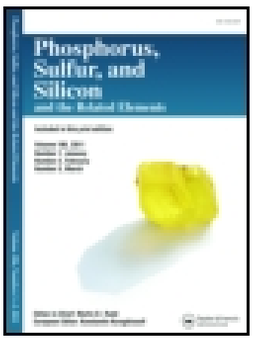

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ONE-POT CONVERSION OF CARBAMATES OF UNSATURATED β-AMINOESTERS INTO UNSATURATED β-LACTAMS BY USE OF TRIMETHYLSILYL IODIDE

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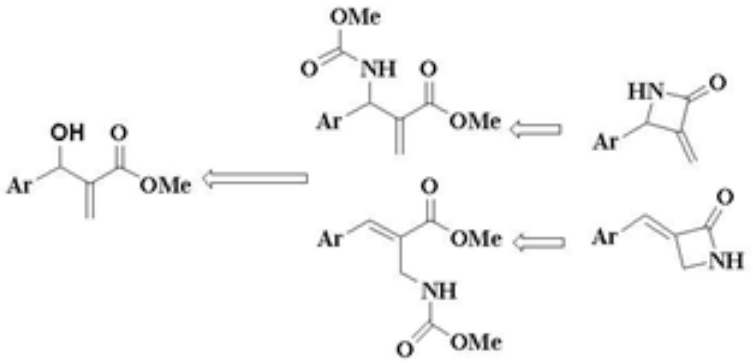
Abstract

Trimethylsilyl iodide (TMSI) is introduced as an efficient reagent for the one-pot and direct transformation of carbamates of unsaturated β-aminoesters into the corresponding α-methylene-β-lactams and α-arylidene-β-lactams. The mild reaction conditions, excellent yields and easy work-up procedures make it a useful alternative to previously applied procedures for the rapid synthesis of β-lactams from easily available Baylis-Hillman adducts.



Key words

Baylis-Hillman adducts, carbamates, unsaturated β-aminoesters, α-methylene-β-lactams, α-arylidene-β-lactams, trimethysilyl iodide

INTRODUCTION

2-Azetidinones, commonly known as β-lactams, are well-known heterocyclic compounds.[1] The activity of famous antibiotics such as penicillins, cephalosporins and carbapenems are attributed to the presence of the 2-azetidinone ring in these compounds.[2] Apart from clinical use, β-lactams can also serve as good synthons in the synthesis of many biologically active heterocycles. Several approaches have been developed for the synthesis of β-lactams including cyclization of β-aminoesters to α-methylene-β-lactams[3-6], Grignard reaction on azetidin-2,3-diones followed by dehydration using PPh_3/CCl_4 reagent[7], rhodium catalyzed olefin cross metathesis[8], thermal β-elimination of *trans*-3-allyl-3-sulfinyl-β-lactams[9], copper-catalyzed carbonylative coupling of cycloalkanes and amides[10], synthesis of optically active α-methylene β-lactams through lipase-catalyzed kinetic resolution[11], synthesis of optically active spiro-β-lactams by cycloadditions to α-alkylidene-β-lactams[12] and other miscellaneous approaches such as ring contraction and radical processes[1]. Recently Li and co-workers described the palladium-catalyzed direct oxidative carbonylation of *N*-allylamines palladium[13] and PPh_3-catalyzed umpolung cyclization of 2-propiolamidoacetates or α-propiolamido ketones[14]. Some of the reported methods exhibit disadvantages such as: 1) multi-step synthesis with the use of expensive or harmful reagents and 2) low yields. Thus, the development of simple, efficient and general methods for the synthesis of biologically active β-lactams, in one-step would be highly valuable and desirable. In continuation of our interest for the Baylis-Hillman adducts and their transformation into a variety of natural and unnatural compounds,[15-19] herein we wish to report our results on the direct transformation of carbamates of unsaturated β-aminoesters into the corresponding α-methylene-β-lactams and α-arylidene-β-lactams by use of trimethysilyl iodide.

RESULTS AND DISCUSSION

We recently reported a mild and efficient one-pot easy conversion of Baylis-Hillman adducts into carbamates of unsaturated β-amino esters by use of the reaction with the Burgess reagent.[20] Treatment of Baylis-Hillman adducts **1** with the Burgess reagent in dry THF at 20°C gave sulfamate esters **2**. When heated to 95°C, these sulfamate esters undergo pyrolysis with elimination of SO_3 providing the corresponding carbamates **3a-g** in excellent yields. This reaction takes place via an S_N pathway and the alcohol moiety is displaced to form the urethane (Scheme 1).

When the sulfamate esters **2** were treated with sodium hydride, the corresponding sodium salt was obtained. However, when the sodium salt decomposed as a solid at 80°C and the reaction mixture was treated with water, a substitution with an allylic rearrangment (S_N') occurred to give the carbamates **4a-g**.

The ability to access β-aminoesters exclusively was exploited and its cyclization to α-methylene-β-lactams and α-arylidene-β-lactams, which are valuable precursors for the synthesis of substituted β-lactams, was investigated. A wide variety of methods are available to cyclize β-aminoesters into the corresponding β-lactams. Conventional bases such as isopropyl magnesium bromide,[21] *n*-butyllithium,[22] potassium *tert*-butoxide,[23] lithium hydroxide, potassium hydroxide[24] and bis[*N*,*N*-bis(trimethylsilyl)amino]tin(II),[25] were reported earlier to have been used in such cyclization reactios. Our interest in β-lactams stems from our work with trimethysilyl iodide (TMSI). In particular, we have found that TMSI which has been previously used as a versatile reagent for the mild dealkylation of carboxylic esters[26], alkyl ethers[27] and carbamates[28] serves as a new and useful source for cyclization of β-aminoesters into the β-lactams.

To explore the scope and versatility of this method and optimize the reaction conditions, the reaction of carbamate **3a** (1 mol%) and TMSI (3 mol%, generated in situ from TMSCl and NaI)[29] was used as a model system based on reported procedures.[26] When adduct **3a** is mixed with TMSI in an aprotic solvent, e.g. tetrachloromethane, and the solution is warmed to 50°C, the reaction proceeds smoothly and cleanly under mild conditions and after work-up the reaction, the product **5a** produced in 5 h and in 65% yield. We also verified the amounts of TMSI in preparation of **5a** and the best result was obtained using 5 mol% TMSI at 50°C in tetrachloromethane and the product **5a** was produced in 3 h and in 92% yield.

Using the optimized conditions for the reaction of the adducts **3a-g** and **4a-g** with TMSI, several α-methylene-β-lactams **5a-g** and α-arylidene-β-lactams **6a-g** were synthesized (Scheme 2). The results are summarized in Table 1. The structure of all products was established by spectroscopic methods (^{1}H NMR, IR) and elemental analyses. The reactions are clean and the products are obtained in high yields except for the reaction of derivatives with Ar = 4-MeOPh and Ar = 3-NO_2Ph (entries **c** and **g**, Table 1) because the ether and nitro substituents react with TMSI.

A proposed mechanism of this transformation is depicted in Scheme 3.[26-28] When the adduct **3c** as a simple model substrate is treated with 3 mol% TMSI in CCl_4 at 50°C, the corresponding silylated intermediate **7** and methyl iodide was produced in quantitative yields. When intermediate **7** is treated with excess TMSI for extended periods of time, the initially formed trimethylsilyl carboxylate moiety is slowly and efficiently converted into the acyl iodide **8** in high yield. To form the β-lactam cycle, the acyl moiety of intermediate **8** is attacked by exocyclic NH-group followed by the release of HI and produces the intermediate **9**. This

intermediate is converted directly into the product **5c** by addition of methanol and heating the reaction mixture. Methanol can cleave the O-Si bond of the trimethylsilyl carbamate to afford methyl trimethylsilyl ether (MeOTMS) and the carbamic acid **10** which spontaneously decarboxylates to produce the α-methylene-β-lactam **5c**.

EXPERIMENTAL

Chemicals were purchased from Merck and Fluka. Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses were performed by use of a Heraeus CHNO-Rapid analyzer. IR spectra (ν_{max}/cm^{-1}) were determined on a Shimadzo FT-IR-8900 spectrometer. ^{1}H NMR spectra were recorded 500 MHz on a Bruker DRX-500 in $CDCl_3$ as solvent and with TMS as an internal standard. Preparative thin layer chromatography (TLC) was performed with Merck Kieselgel 60 H, F_{254}, Art No 7730. GC was carried out by using a Buck Scientific 910 (capillary column, MXT-5, 15 m). All solvents used were dried and distilled according to standard procedures. All reactions and manipulations were carried out under a nitrogen atmosphere and/or by using standard vacuum line techniques. The Supplemental Materials file contains sample ^{1}H and ^{13}C NMR spectra of products 6 (Figures S 1 -- S 14)

General procedure for the synthesis of α-methylene-β-lactams and α-arylidene-β-lactams by reaction of carbamates of unsaturated β-aminoesters with TMSI.[27]

To a stirred solution of TMSCl (6 mmol) and NaI (6 mmol) in CCl_4 (10 mL) was added carbamate **3** or **4** (1 mmol in 5 mL of CCl_4) dropwise within 5 min, and the resulting mixture was vigorously stirred for 3-12 h at 50°C (reaction monitored by TLC or GC). Work-up involved initial evaporation of the volatile component for removal of solvent and slight excess of TMSI, addition of degassed MeOH for the solvolysis of the silyl carbamates, evaporation of volatile

materials for removal of MeOH and decarboxylation. The mixture was then extracted with EtOAc (3×10 mL). The combined extract was washed with brine (2× 3 mL) and dried over Na_2SO_4 and then concentrated in *vacuo*. The crude product was purified by flash chromatography (EtOAc/hexane 1:1 as eluent) to afford the adducts **5a-g** and **6a-g** as solids. Some data of selected compounds are listed below.

3-Methylene-4-*p*-tolylazetidin-2-one (5b)

Pale yellow solid**;** M. p. 160-161°C; yield 87%; IR (neat): 3383, 3310 (NH), 1615 (CONH); Anal. Calcd. for $C_{11}H_{11}NO$ (Found: C, 76.26; H, 6.33; N, 7.97 requires C, 76.30; H, 6.36; N, 8.09%); ^{1}H NMR: δ = 2.32 (s, 3H), 5.59 (s, 1H), 5.92 (s, 1H), 6.16 (s, 1H), 6.37 (d, J = 1.51 Hz, br. NH), 7.21 (d, J = 7.43 Hz, 2H), 7.67 (d, J = 7.43 Hz, 2H) ppm.

4-(4-Hydroxyphenyl)-3-methyleneazetidin-2-one (5c)

Pale yellow solid**;** M. p. 162-163°C; yield 56%; IR (neat): 3441 (OH), 3402, 3324 (NH), 1613 (CONH); Anal. Calcd. for $C_{10}H_9NO_2$ (Found: C, 68.48; H, 5.03; N, 7.91 requires C, 68.57; H, 5.14; N, 8.00%); ^{1}H NMR: δ = 4.36 (s, br, OH), 5.14 (s, 1H), 5.78 (s, 1H), 5.92 (d, J = 1.50 Hz, br, NH), 6.34 (d, J = 1.50 Hz, 1H), 6.94 (d, J = 6.93 Hz, 2H), 7.77 (d, J = 6.93 Hz, 2H) ppm.

3-Methylene-4-(pyridin-4-yl)azetidin-2-one (5d)

Yellow solid**;** M. p. = 165-167°C; yield 78%; IR (neat): 3405, 3325 (NH), 1609 (CONH); Anal. Calcd. for $C_9H_8N_2O$ (Found: C, 67.41; H, 4.93; N, 17.41 requires C, 67.50; H, 5.00; N, 17.50%); ^{1}H NMR: δ = 5.17 (s, 1H), 5.59 (s, 1H), 5.98 (d, J = 1.51 Hz, 1H), 6.45 (d, J = 1.51 Hz, br, NH), 7.36 (d, 2H, J = 7.87 Hz), 8.57 (d, 2H, J = 7.87 Hz) ppm.

4-[4-(Dimethylamino)phenyl]-3-methyleneazetidin-2-one (5e)

Yellow solid**;** M. p. = 177-179°C; yield 78%; IR (neat): 3389, 3320 (NH), 1622 (CONH); Anal. Calcd. for $C_{12}H_{14}N_2O$ (Found: C, 71.13; H, 6.85; N, 13.77 requires C, 71.28; H, 6.73; N, 13.86%); ^{1}H NMR: δ = 3.12 (s, 6H) 5.21 (s, 1H), 5.51 (s, 1H), 5.93 (d, *J* = 1.51 Hz, br, NH), 6.26 (d, *J* = 1.51 Hz, 1H), 6.74 (d, *J* = 7.75 Hz, 2H), 7.77 (d, *J* = 7.75 Hz, 2H) ppm.

4-(4-Chlorophenyl)-3-methyleneazetidin-2-one (5f)

White solid**;** M. p. = 160-161°C; yield 87%; IR (neat): 3410, 3329 (NH), 1635 (CONH); Anal. Calcd. for $C_{10}H_8ClNO$ (Found: C, 61.91; H, 4.05; N, 7.17 requires C, 62.03; H, 4.13; N, 7.23%); ^{1}H NMR: δ = 5.27 (s, 1H), 5.62 (s, 1H), 6.12 (d, *J* = 1.50 Hz, br, NH), 6.33 (d, *J* = 1.50 Hz, 1H), 7.54 (d, *J* = 7.55 Hz, 2H), 7.85 (d, *J* = 7.55 Hz, 2H) ppm.

3-Methylene-4-(3-nitrophenyl)azetidin-2-one (5g)

Yellow solid**;** M. p. = 192-193°C; yield 42%; IR (neat): 3395, 3320 (NH), 1635 (CONH); Anal. Calcd. for $C_{10}H_8N_2O_3$ (Found: C, 58.73; H, 3.85; N, 13.70 requires C, 58.82; H, 3.92; N, 13.72%); ^{1}H NMR: δ = 5.37 (s, 1H), 5.73 (s, 1H), 6.25 (d, *J* = 1.53 Hz, br, NH), 6.73 (d, *J* = 1.53 Hz, 1H), 7.80 (t, *J* = 7.66 Hz, 1H), 8.27 (d, *J* = 7.68 Hz, 1H), 8.51 (d, *J* = 7.78, 1H), 8.74 (s, 1H) ppm.

3-Benzylideneazetidin-2-one (6a)

White solid**;** M. p. = 113-115°C; yield 94%; IR (neat): 3404, 3323 (NH), 1613 (CONH); Anal. Calcd. for $C_{10}H_9NO$ (Found: C, 75.40; H, 5.58; N, 8.71 requires C, 75.47; H, 5.66; N, 8.80%); ^{1}H NMR: δ = 4.19 (d, *J* = 1.52 Hz, 2H), 6.24 (t, *J* = 1.52**,** br, NH), 7.27-7.43 (m, 5H), 7.49 (t, *J* = 1.71 Hz, 1H)) ppm.

3-(4-Methylbenzylidene)azetidin-2-one (6b)

White solid**;** M. p. = 121-123°C; yield 88%; IR (neat): 3332, 3173 (NH), 1604 (CONH); Anal. Calcd. for $C_{11}H_{11}NO$ (Found: C, 76.20; H, 6.28; N, 8.00 requires C, 76.30; H, 6.36; N, 8.09%); ^{1}H NMR: δ = 2.61 (s, 3H), 4.29 (d, *J* = 1.51 Hz, 2H), 6.25 (t, *J* = 1.51**,** br, NH), 7.21 (d, *J* = 7.75 Hz, 2H), 7.67 (d, *J* = 7.75 Hz, 2H), 7.86 (t, *J* = 1.73 Hz, 1H) ppm.

3-(4-Hydroxybenzylidene)azetidin-2-one (6c)

White solid**;** M. p. = 143-145°C; yield 55%; IR (neat): 3434, (OH), 3308 (NH), 1657 (CONH); Anal. Calcd. for $C_{10}H_9NO_2$ (Found: C, 68.49; H, 5.02; N, 7.91 requires C, 68.57; H, 5.14; N, 8.00%); ^{1}H NMR: δ = 4.50 (d, *J* = 1.53 Hz, 2H), 5.08 (s, br, OH), 6.51 (t, *J* = 1.53 Hz**,** br, NH), 6.94 (d, *J* = 7.91 Hz, 2H), 7.77 d, *J* = 7.91 Hz, 2H), 7.96 (t, *J* = 1.72 Hz, 1H) ppm.

3-[(Pyridin-4-yl)methylene]azetidin-2-one (6d)

Pale yellow solid**;** M. p. = 132-134°C; yield 78%; IR (neat): 3424, 3314 (NH), 1643 (CONH); Anal. Calcd. for $C_9H_8N_2O$ (Found: C, 67.42; H, 4.93; N, 17.41 requires C, 67.50; H, 5.00; N, 17.50%); ^{1}H NMR: δ = 4.29 (d, *J* = 1.51 Hz, 2H), 6.25 (t, *J* = 1.51 Hz**,** br**,** NH), 7.36 (d, *J* = 8.38 Hz, 2H), 8.58 (d, *J* = 8.38 Hz, 2H), 8.63 (t, *J* = 1.70 Hz, 1H) ppm.

3-[4-(Dimethylamino)benzylidene]azetidin-2-one (6e)

Pale yellow solid**;** M. p. = 137-139°C; yield 78%; IR (neat): 3379, 3130 (NH), 1611 (CONH); Anal. Calcd. for $C_{12}H_{14}N_2O$ (Found: C, 71.22; H, 6.83; N, 13.81 requires C, 71.28; H, 6.93; N, 13.86%); ^{1}H NMR: δ = 3.11 (s, 6H), 4.24 (d, *J* = 1.50 Hz, 2H), 6.14 (t, *J* = 1.50 Hz**,** br, NH), 6.76 (d, *J* = 7.59 Hz, 2H), 7.78 d, *J* = 7.59 Hz, 2H), 7.95 (t, *J* = 1.71 Hz, 1H) ppm.

3-(4-Chlorobenzylidene)azetidin-2-one (6f): yellow solid**;** M. p. = 146-148°C; yield 95%; IR (neat): 3337, 3148 (NH), 1606 (CONH); Anal. Calcd. for $C_{10}H_8ClNO$ (Found: C, 61.92; H, 4.04; N, 7.11 requires C, 62.04; H, 4.13; N, 7.23%); ^{1}H NMR: δ = 4.29 (d, *J* = 1.52 Hz, 2H),

6.28 (t, *J* = 1.50 Hz, br, NH), 7.54 (d, *J* = 7.95 Hz, 2H), 7.85 d, *J* = 7.95 Hz, 2H), 7.98 (t, *J* = 1.75 Hz, 1H) ppm.

3-(3-Nitrobenzylidene)azetidin-2-one (6g): yellow solid**;** M. p. = 168-170°C; yield 42%; IR: 3338, 3158 (NH), 1699 (CONH), 1309 (NO_2); Anal. Calcd. for $C_{10}H_8N_2O_3$ (Found: C, 58.72; H, 3.84; N, 13.63 requires C, 58.82; H, 3.92; N, 13.72%); ^{1}H NMR: δ = 4.41 (d, *J* = 1.51 Hz, 2H), 6.81 (t, *J* = 1.50 Hz, br, NH), 7.77 (s, 1H, 7.81 (t, *J* = 7.66 Hz, 1H), 8.27 (d, *J* = 7.68 Hz, 1H), 8.51 (d, *J* = 7.64, 1H), 8.74 (s, 1H) ppm.

CONCLUSION

In summary, for the first time we showed that TMSI was an effective reagent for the direct transformation of carbamates of unsaturated β-aminoesters into the corresponding α-methylene-β-lactams and α-arylidene-β-lactams. The mild reaction conditions, excellent yields and easy work-up procedures make it a useful alternative to previously applied procedures for the rapid synthesis of β-lactams from easily available Baylis-Hillman adducts.

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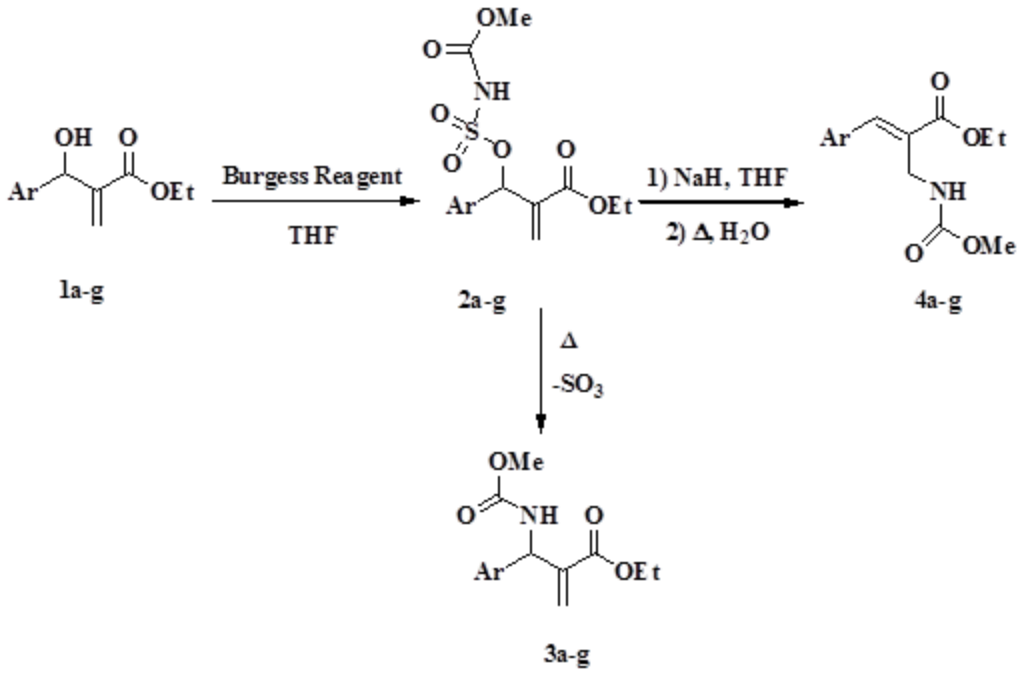
Table 1. Conversation of carbamates of unsaturated β-aminoesters into the corresponding α-methylene-β-lactams and α-arylidene-β-lactams.

Entry	Ar	β-lactam 5[a]		β-lactam 6[a]	
		Time (h)	Yield[b] (%)	Time (h)	Yield[b] (%)
a	C_6H_5	3	92[c]	3	94
b	4-Me-C_6H_4	7	87	7	88
c	4-MeO-C_6H_4	10	56	12	55
d	4-Pyridyl	7	78	7	78
e	4-$(Me)_2$N-C_6H_4	6	78	6	78
f	4-Cl-C_6H_4	3	94	3	95
g	3-NO_2-C_6H_4	12	42	12	42

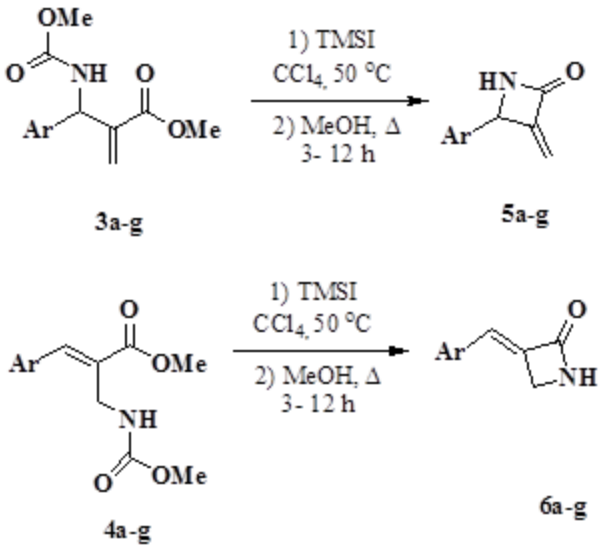
[a]All compounds have been fully characterized spectroscopy by ^{1}H NMR, IR, and elemental analyses.

[b]Yields are based on isolated products.

[c]Analysed by comparison of its spectroscopic data (^{1}H NMR, IR) with those of an authentic sample (Ref. 30).

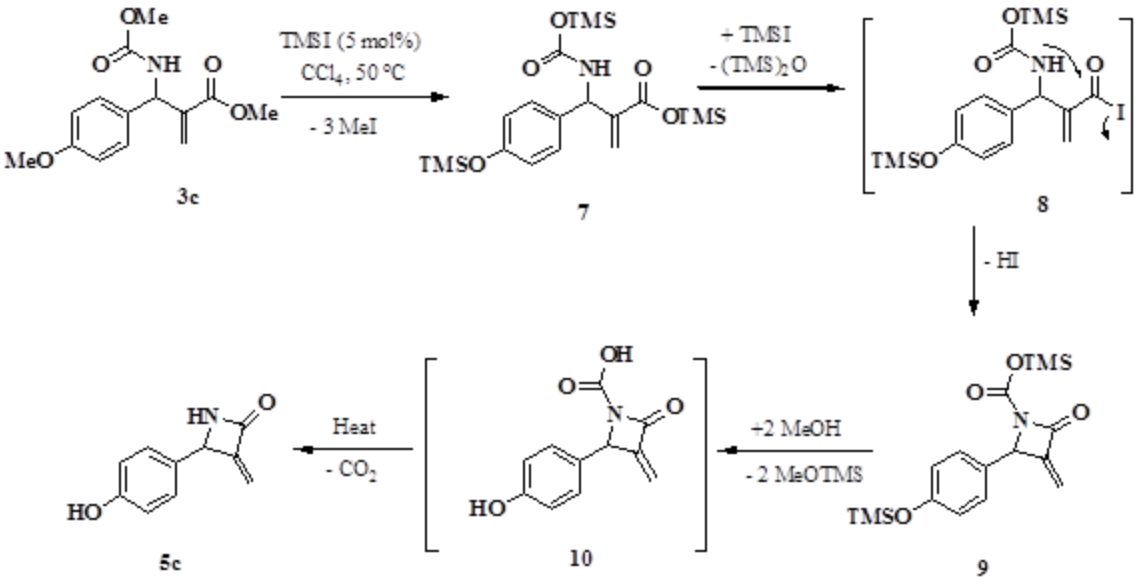


Scheme 1. Conversation of Baylis-Hillman adducts into the corresponding carbamates of unsaturated β-aminoesters.



Ar = C_6H_5, 4-Pyridyl, 4-ClC_6H_4, 3-$NO_2C_6H_4$, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-$NMe_2C_6H_4$

Scheme 2. Synthesis of α-methylene-β-lactams and α-arylidene-β-lactams by reaction of carbamates of unsaturated β-amino ester with TMSI.



Scheme 3. A proposed mechanism for the formation of β-lactams.