Arch Pharm Res Vol 24, No 5, 371-376, 2001

Archives of Pharmacal Research
http://apr.psk.or.kr

# One-pot Synthesis of Cinnamylamines with Various Protecting Groups from Cinnamyl Ethers

**Young Hoon Jung and Ji Duck Kim**

*Organic & Medicinal Chemistry Laboratory, College of Pharmacy, Sungkyunkwan University, Suwon 440-746, Korea*

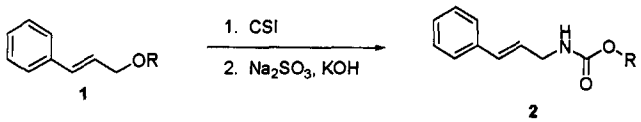
*(Received August 10, 2001)*

The reaction of various alkyl cinnamyl ethers with CSI afforded the corresponding cinnamylamines with various protecting groups, such as -NHMoc, -NH*i*Poc, -NHCbz, -NHPnz, -NHTroc and -NHAloc. In the case of cinnamyl *t*-butyl ether and cinnamyl *p*-methoxybenzyl ether, the corresponding cinnamyl carbamates were formed via a different reaction pathway from the above.

**Key words:** Cinnamylamines, Chlorosulfonyl isocyanate, Alkyl cinnamyl ethers, Carbamates, Protecting group

## INTRODUCTION

Carbamates have been widely used in peptide and protein synthesis as a protective group of the amines (Pennington and Dunn, 1994, Xiao *et al.*, 1997), and also used as biologically active compounds in the field of medicine and pharmaceutical industry (Atherton and Sheppard, 1989; Matassa *et al.*, 1990, Firestone *et al.*, 1984). Especially, carbamate moiety is frequently introduced for the derivatization of lead compound in medicinal chemistry (Leenders *et al.*, 2000, Lin *et al.*, 2000, Sun *et al.*, 2001). Representative protecting groups for this purpose are the Boc (*tert*-butoxycarbonyl), the Cbz (benzyloxycarbonyl), the Moc (methoxycarbonyl), the *i*Poc (isopropoxycarbonyl), the Pnz (*p*-nitrobenzyloxycarbonyl), the Moz (*p*-methoxybenzyloxycarbonyl), the Troc (2,2,2-trichloroethoxycarbonyl) and the Aloc (allyloxycarbonyl) group (Green and Wuts, 1999, Kocienski, 1994). Because of their important roles, continuous efforts have been made to obtain carbamates through simple and efficient methods. The conventional method for preparation of carbamates is the reaction of amines with the corresponding dialkyldicarbonate (Kn Iker and Braxmeier, 1996, Einhorn *et al.*, 1991, Saito *et al.*, 1989) or alkyl chloroformate (Yadav *et al.*, 1998, Atwell and Denny, 1984, Carson, 1981). An alternative method for the synthesis of them is the reaction of an isocyanate with the corresponding alcohol (Oertel, 1985, Bittner *et al.*, 2000). The others include the Hofmann rearrangement and its analogous reactions (Shono *et al.*, 1982, Matsumura *et al.*, 1997). In recent years, several effective synthetic methods have been developed through the modification of the above-mentioned methods (Chandrasekhar and Narsihmulu, 2000, Feroci *et al.*, 2000, Batey *et al.*, 1999; Inesi *et al.*, 1998, Ariza *et al.*, 1998, Otera *et al.*, 1995).




**Scheme 1.** One-pot synthesis of various cinnamyl carbamates from cinnamyl ethers

Recently we reported a novel synthetic method for *N*-allylcarbamates from cinnamyl alkyl ethers, using chlorosulfonyl isocyanate (CSI) (Kim *et al.*, 2001, Kim *et al.*, 2000, Jung and Kim, 2000). This synthetic method provides a simple and convenient alternative for the formation of the above-mentioned carbamates by varying the alkyl moiety of ethers. (Scheme 1)

## MATERIALS AND METHODS

Commercially available reagents were used without additional purification, unless otherwise stated. All anhydrous solvents were distilled over $CaH_2$ or $P_2O_5$ or Na/

*Correspondence to*: Young Hoon Jung, Sungkyunkwan University, Organic & Medicinal Chemistry Laboratory, College of Pharmacy, 300 Chonchon-Dong, Changan-Ku, Suwon 440-746, Kyonggi-Do, Korea
E-mail: yhjung@skku.ac.kr.

benzophenone prior to reaction. All reactions were performed under an inert atmosphere of nitrogen or argon. Melting points were measured on a Gallenkamp melting point apparatus and were not corrected. Nuclear magnetic resonance spectra ($^1$H and $^{13}$C NMR) were recorded on a Varian Unity Inova 500 MHz spectrometer for $CDCl_3$ solutions and chemical shifts are reported as parts per million (ppm) relative to, respectively, residual $CHCl_3$ $\delta_H$ (7.26 ppm) and $CDCl_3$ $\delta_C$ (77.0 ppm) as internal standards. Resonance patterns are reported with the notations s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). In addition, the notation br is used to indicate a broad signal. Coupling constants (*J*) are reported in hertz (Hz). IR spectra were recorded on a Nicolet 205 Infrared spectrophotometer and are reported as $cm^{-1}$. Thin layer chromatography was carried out using plates coated with Kieselgel $60F_{254}$ (Merck). For flash column chromatography, E. Merck Kieselgel 60 (230-400 mesh) was used. Elemental analyses were performed with an the EA 1110 analyzer, and high-resolution mass spectra (HRMS) were recorded on a JEOL, JMS-AX505WA spectrometer using the chemical ionization (CI) method.

**General procedure for preparation of cinnamyl alkyl ether**

**Method A**

To a solution of cinnamyl alcohol (5 mmol) in THF (28 ml) and DMF (7 ml) was added NaH (7.5 mmol, 60% in mineral oil) and alkyl halide (7.5 mmol). The reaction mixture was stirred at room temperature for 15h under $N_2$, quenched with $H_2O$ (20 ml), then extracted with EtOAc (20 ml). The organic layer was washed with $H_2O$ and brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (*n*-Hex : EtOAc) to afford cinnamyl alkyl ether.

**Method B**

To a solution of alcohol (5 mmol) in THF (28 ml) and DMF (7 ml) was added NaH (7.5 mmol, 60% in mineral oil) and cinnamyl bromide (7.5 mmol). The reaction mixture was stirred at room temperature for 15 h under $N_2$, quenched with $H_2O$ (20 ml), then extracted with EtOAc (20 ml). The organic layer was washed with $H_2O$ and brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (*n*-Hex : EtOAc) to afford cinnamyl alkyl ether.

**1-Allyloxy-3-phenylprop-2-ene (1f)**

$R_f$: 0.32 (EtOAc : hexane = 1 : 20); $^1$H NMR (500 MHz, $CDCl_3$) δ: 4.03 (d, 2H, *J*=6 Hz), 4.14 (d, 2H, *J*=6 Hz), 5.21 (dd, 1H, *J*=10.5 Hz, 1.5 Hz), 5.32 (dd, 1H, *J*=17 Hz, 1.5 Hz), 5.94 (ddt, 1H, *J*=17 Hz, 10.5 Hz, 6 Hz), 6.29 (dt, 1H, *J*=16 Hz, 6 Hz), 6.60 (d, 1H, *J*=16 Hz), 7.20-7.39 (m, 5H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ: 71.43, 71.82, 118.05, 127.23, 127.63, 128.44, 129.16, 129.24, 135.59, 137.40; IR (neat): 3340, 3045, 2887, 1671, 1436, 1335, 1096 $cm^{-1}$; HRMS (CI) calcd for $C_{12}H_{14}O$-H $(M-H)^+$ 173.0967. Found: 173.0962.

**1-*p*-Methoxybenzyloxy-3-phenylprop-2-ene (1h)**

$R_f$: 0.39 (EtOAc : hexane = 1 : 6); $^1$H NMR (500 MHz, $CDCl_3$): δ 3.78 (s, 3H), 4.15 (d, 2H, *J*=6 Hz), 4.49 (s, 2H), 6.32 (dt, 1H, *J*=16 Hz, 6 Hz), 6.60 (d, 1H, *J*=16 Hz), 6.88 (dd, 2H, *J*=6.5 Hz, 2 Hz), 7.22-7.39 (m, 7H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 55.97, 71.19, 72.55, 114.56, 126.97, 127.20, 128.35, 129.26, 130.14, 131.10, 133.14, 137.50, 159.97; IR ($CH_2Cl_2$): 3027, 2923, 2866, 1607, 1485, 1347, 1254, 1074 $cm^{-1}$; mp: 38~40°C; Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.28; H, 7.20.

**General procedure for reaction of cinnamyl ether with chlorosulfonyl isocyanate (CSI)**

A suspension of $Na_2CO_3$ (6.75 mmol) in anhydrous $CH_2Cl_2$ (12 ml) was adjusted to 20°C or 78°C, then CSI (4.5 mmol) and cinnamyl ether (3 mmol) was added under $N_2$. The reaction mixture was stirred at 20°C or 78 °C, quenched with $H_2O$ (10 ml) when the reaction was completed (TLC monitoring), then extracted with EtOAc (10 ml × 2). The organic layer was added to an aqueous solution of $Na_2SO_3$ (25%) and KOH (10%), and the reaction mixture was stirred at room temperature for overnight. The organic layer was washed with $H_2O$ and brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (*n*-Hex : EtOAc) to afford N-protected amine.

***iso*-Propyl *N*-(3-phenylprop-2-enyl)carbamate (2b)**

$R_f$: 0.38 (EtOAc : hexane = 1 : 3); $^1$H NMR (500 MHz, $CDCl_3$): δ 1.18 (d, 6H, *J*=6.5 Hz), 3.88 (dd, 2H, *J*=6 Hz, 5 Hz), 4.81-4.90 (br, 1H), 4.88 (q, 1H, *J*=6.5 Hz), 6.13 (dt, 1H, *J*=16 Hz, 6 Hz), 6.44 (d, 1H, *J*=16 Hz), 7.17-7.29 (m, 5H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 22.89, 43.71, 68.92, 126.82, 127.07, 128.35, 129.28, 132.31, 137.31, 156.82; IR ($CH_2Cl_2$): 3312, 2982, 2923, 1686, 1544, 1451, 1378, 1265, 1143, 1112 $cm^{-1}$; mp: 55~56 °C; Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.12; H, 7.85; N, 6.46.

**Benzyl *N*-(3-phenylprop-2-enyl)carbamate (2c)**

$R_f$: 0.30 (EtOAc : hexane = 1 : 5); $^1$H NMR (500 MHz, $CDCl_3$): δ 3.99 (dd, 2H, *J*=6 Hz, 4.5 Hz), 4.88-4.97 (br, 1H), 5.15 (s, 2H), 6.17 (dt, 1H, *J*=16 Hz, 6 Hz), 6.53 (d, 1H, *J*=16 Hz), 7.23-7.39 (m, 10H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 43.88, 67.54, 126.52, 127.11, 128.41, 128.85, 129.10, 129.25, 129.29, 132.49, 137.25, 156.98; IR (KBr): 3319, 2973, 1710, 1686, 1543, 1451, 1261, 1248, 1138 $cm^{-1}$; mp: 62~63°C; Anal. Calcd for $C_{17}H_{17}NO_2$: C,

76.38; H, 6.41; N, 5.24. Found: C, 76.52; H, 6.46; N, 5.22.

**Benzyl *N*-(1-phenylallyl)carbamate (3c)**

$R_f$: 0.36 (EtOAc : hexane = 1 : 5); $^1$H NMR (500 MHz, $CDCl_3$): δ 5.12 (s, 2H), 5.15 (dd, 1H, *J*=5.5 Hz, 5 Hz), 5.24 (dd, 1H, *J*=9.5 Hz, 1.5 Hz), 5.25 (dd, 1H, *J*=18 Hz, 1.5 Hz), 5.33-5.40 (br, 1H), 6.01 (ddd, 1H, *J*=18 Hz, 9.5 Hz, 5.5 Hz), 7.21-7.38 (m, 10H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 57.81, 67.65, 116.54, 126.79, 127.74, 128.42, 128.87, 129.23, 129.46, 137.06, 138.27, 141.32, 156.25; IR ($CH_2Cl_2$): 3322, 3048, 2934, 1707, 1515, 1242, 1042 $cm^{-1}$; mp: 46~47°C; HRMS (CI) calcd for $C_{17}H_{17}NO_2$+H $(M+H)^+$ 268.1337. Found: 268.1343.

***p*-Nitrobenzyl *N*-(3-phenylprop-2-enyl)carbamate (2d)**

$R_f$: 0.22 (EtOAc : hexane = 1 : 2); $^1$H NMR (500 MHz, $CDCl_3$): δ 4.01 (dd, 2H, *J*=6.5 Hz, 6 Hz), 4.92-5.00 (br, 1H), 5.23 (s, 2H), 6.20 (dt, 1H, *J*=16 Hz, 6.5 Hz), 6.54 (d, 1H, *J*=16 Hz), 7.24-7.52 (m, 5H), 7.53 (d, 2H, *J*=8 Hz), 8.23 (d, 2H, *J*=8 Hz); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 43.99, 65.95, 124.45, 126.02, 127.08, 128.55, 128.88, 129.32, 132.95, 137.05, 144.64, 148.38, 156.39; IR ($CH_2Cl_2$): 3318, 2978, 1699, 1606, 1523, 1453, 1348, 1323, 1249, 1109 $cm^{-1}$; mp: 91~92°C; HRMS (CI) calcd for $C_{17}H_{16}N_2O_4$+H $(M+H)^+$ 313.1188. Found: 313.1190.

**2,2,2-Trichloroethyl *N*-(3-phenylprop-2-enyl)carbamate (2e)**

$R_f$: 0.31 (EtOAc : hexane = 1 : 5); $^1$H NMR (500 MHz, $CDCl_3$): δ 4.04 (dd, 2H, *J*=6.5 Hz, 5 Hz), 4.77 (s, 2H), 5.10-5.17 (br, 1H), 6.21 (dt, 1H, *J*=16 Hz, 6.5 Hz), 6.56 (d, 1H, *J*=16 Hz), 7.24-7.38 (m, 5H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 44.04, 75.34, 125.66, 127.12, 128.56, 129.31, 129.76, 133.09, 137.04, 155.13; IR ($CH_2Cl_2$): 3339, 2943, 1711, 1527, 1455, 1278, 1238, 1147, 1072, 1036 $cm^{-1}$; mp: 74~76°C; HRMS (CI) calcd for $C_{12}H_{12}Cl_3NO_2$+H $(M+H)^+$ 308.0012. Found: 308.0018.

**Allyl *N*-(3-phenylprop-2-enyl)carbamate (2f)**

$R_f$: 0.23 (EtOAc : hexane = 1 : 10); $^1$H NMR (500 MHz, $CDCl_3$): δ 4.03 (dt, 2H, *J*=6 Hz, 5.5Hz), 4.65 (d, 2H, *J*=5.5 Hz), 4.86-4.93 (br, 1H), 5.28 (dd, 1H, *J*=10 Hz, 1.5 Hz), 5.37 (dd, 1H, *J*=15.5 Hz, 1.5 Hz), 5.98 (ddt, 1H, *J*=15.5 Hz, 10 Hz, 5.5 Hz), 6.25 (dt, 1H, *J*=16 Hz, 6 Hz), 6.57 (d, 1H, *J*=16 Hz), 7.27-7.42 (m, 5H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 43.83, 66.39, 118.47, 126.51, 127.09, 128.43, 129.29, 132.49, 133.57, 137.21, 156.82; IR ($CH_2Cl_2$): 3416, 3331, 3028, 2937, 1710, 1690, 1632, 1451, 1250, 1139 $cm^{-1}$; mp: 37~39°C; HRMS (CI) calcd for $C_{13}H_{15}NO_2$+H $(M+H)^+$ 218.1181. Found: 218.1174.

**Allyl *N*-(1-phenylallyl)carbamate (3f)**

$R_f$: 0.31 (EtOAc : hexane = 1 : 10); $^1$H NMR (500 MHz, $CDCl_3$): δ 4.63 (d, 2H, *J*=5.5 Hz), 5.21-5.27 (br, 1H), 5.26 (dd, 1H, *J*=10 Hz, 1.5 Hz), 5.27(dd, 1H, *J*=10.5 Hz, 1.5 Hz), 5.28 (dd, 1H, *J*=17 Hz, 1.5 Hz), 5.31 (dd, 1H, *J*=17 Hz, 1.5 Hz), 5.37-5.44 (br, 1H), 5.94 (ddt, 1H, *J*=17 Hz, 10 Hz, 5.5 Hz), 6.05 (ddd, 1H, *J*=17 Hz, 10.5 Hz, 6 Hz), 7.31-7.42 (m, 5H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 57.75, 66.45, 116.49, 118.17, 127.71, 128.40, 129.44, 133.46, 138.27, 141.34, 156.07; IR (neat): 3322, 3054, 2937, 1707, 1520, 1426, 1245, 1022 $cm^{-1}$; HRMS (CI) calcd for $C_{13}H_{15}NO_2$+H $(M+H)^+$ 218.1181. Found: 218.1187.

**3-Phenylprop-2-enyloxycarbonylamine (2g)**

$R_f$: 0.30 (EtOAc : hexane = 1 : 1); $^1$H NMR (500 MHz, $CDCl_3$): δ 4.73 (d, 2H, *J*=6.5 Hz), 4.73-4.78 (br, 2H), 6.30 (dt, 1H, *J*=16 Hz, 6.5 Hz), 6.60 (d, 1H, *J*=16 Hz), 7.25-7.40 (m, 5H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 66.39, 124.24, 127.31, 128.73, 129.30, 134.58, 136.85, 157.32; IR ($CH_2Cl_2$): 3398, 3250, 3187, 2925, 1670, 1561, 1411, 1316, 1050 $cm^{-1}$; mp: 112~116°C; Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.51; H, 6.63; N, 7.82.

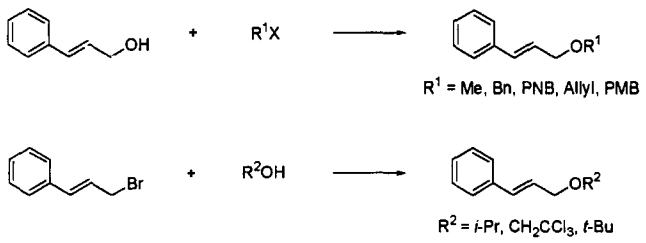
**3-Phenylprop-2-enyl *N*-(p-methoxybenzyl)carbamate (2h)**

$R_f$: 0.22 (EtOAc : hexane = 1 : 4); $^1$H NMR (500 MHz, $CDCl_3$): δ 3.79 (s, 3H), 4.33 (d, 2H, *J*=5.5 Hz), 4.76 (d, 2H, *J*=6.5 Hz), 4.97-5.03 (br, 1H), 6.30 (dt, 1H, *J*=16 Hz, 6.5 Hz), 6.64 (d, 1H, *J*=16 Hz), 6.87 (dd, 2H, *J*=7 Hz, 2 Hz), 7.22-7.40 (m, 7H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 45.13, 55.99, 66.23, 114.74, 124.62, 127.30, 128.67, 129.29, 129.65, 131.26, 134.33, 137.03, 156.98, 159.72; IR ($CH_2Cl_2$): 3332, 2917, 1718, 1692, 1543, 1513, 1437, 1274, 1251, 1033 $cm^{-1}$; mp: 104°C; Anal. calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.73; H, 6.41; N, 4.55.

## RESULTS AND DISCUSSION

Our studies are based on the observation that various carbamates are formed from cinnamyl alkyl ethers using CSI in accord with the alkyl moiety of the cinnamyl alkyl ethers. The ethers as starting materials were prepared using Williamson's ether synthesis, namely, nucleophilic substitution of cinnamyl alcohol with alkyl halides (R= Me, Bn, PNB, allyl and PMB) or same reaction of alkyl alcohols (R=*iso*-propyl, 2,2,2-trichloroethyl and *tert*-butyl) with cinnamyl bromide. (Scheme 2)

Our previous report (entry 1) showed that the CSI reaction of cinnamyl methyl ether (**1a**) (Verlhac and Pereyre, 1990) produced the methyl carbamates **2a** (Takagi and Yamamoto, 1989) and **3a** (Kresze and M nsterer, 1983) as a 2.7:1 mixture of regioisomers. In the cases of benzyl cinnamyl ether (**1c**) (Charette *et al.*, 2000), the results were similar to that obtained in the




**Scheme 2.** Synthesis of various alkyl cinnamyl ethers

methyl case to afford benzyl carbamate, except for the decrease of the internal benzyl carbamate due to the steric hindrance of the benzyl group (entry 3). However, in the case of *iso*-propyl ether (Salehi *et al.*, 1998) (entry 2), *iso*-propyl carbamate was obtained as a sole product. With these studies, we modify the alkyl moiety of ethers to obtain the corresponding carbamates using CSI reaction. The results are summarized in Table I.

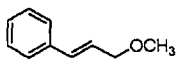
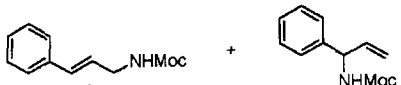
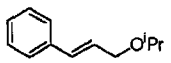
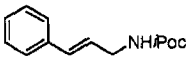
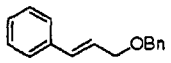
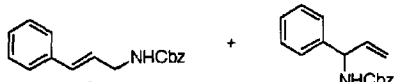
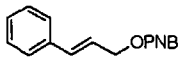
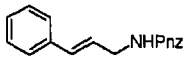
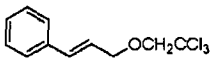
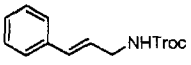
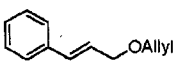
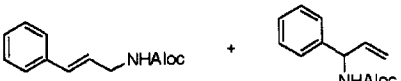
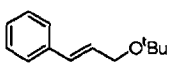
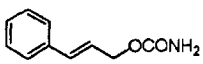
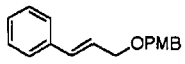
From the result of the Table I, *p*-nitrobenzyloxycarbonyl (Pnz), 2,2,2-trichloroethyloxycarbony (Troc) and allyloxycarbonyl (Aloc) protected amines were produced in high yields from the corresponding ether using CSI reactions. In order to obtain *t*-butoxycarbony (Boc) protected amine, cinnamyl *t*-butyl ether (Tiecco *et al.*, 1998) was treated with CSI. However, rather than obtaining *t*-butyl carbamate, we unexpectedly obtained the cinnamyl carbamate (entry 7). With the *p*-methoxybenzyl ethers, the results were quite similar to that obtained in the *t*-butyl case, except for the increase in the chemical yield (entry 8).

In conclusion, we developed the one-pot synthetic method for cinnamylamines with various protecting groups, such as -NHMoc, -NH*i*Poc, -NHCbz, -NHPnz, -NHTroc and -NHAloc, from the corresponding ethers using CSI reaction.

## ACKNOWLEDGEMENTS

The authors wish to acknowledge the financial support of the Korea Research Foundation made in the program

**Table I.** Conversions of cinnamyl ethers to the corresponding carbamates with CSI[a]

| | Ethers | Protected Amines | Yield (%) ratio |
|---|---|---|---|
| 1 |  **1a** |  **2a** + **3a** | 87.5 2.7 : 1 |
| 2 |  **1b** |  **2b** | 76.5 |
| 3 |  **1c** |  **2c** + **3c** | 89.8 8.4 : 1 |
| 4 |  **1d** |  **2d** | 84.1 |
| 5 |  **1e** |  **2e** | 73.7 |
| 6 |  **1f** |  **2f** + **3f** | 95.7 4.1 : 1 |
| 7 |  **1g** |  **2g** ( Coc-NH$_2$ ) | 42.9 |
| 8 |  **1h** |  **2h** ( Coc-NH-PMB ) | 85.5 |

[a]All the reactions were carried out at 20°C expect for entry 8 (-78°C) and isolated yield of pure material.

year of 1998.

## REFERENCES


Ariza, X., Urpi, F., Viladomat, C., and Vilarrasa, J., One-Pot Conversion of Azides to Boc-Protected Amines with Trimethylphosphine and Boc-ON. *Tetrahedron Lett.*, 39, 9101-9102 (1998).

Atherton, E. and Sheppard, R. C., In Solid Phase Peptide Synthesis, A Practical Approach. Oxford-IRL. Press, New York. (1989).

Atwell, G. J. and Denny, W. A., Monoprotection of α,ω-Alkanediamines with the *N*-Benzyloxycarbonyl Group. *Synthesis*, 1032-1033 (1984).

Batey, R. A., Yoshina-Ishii, C., Taylor, S. D., and Santhakumar, V., A New Protocol for the Formation of Carbamates and Thiocarbamates using carbamoyl Imidazolium Salts. *Tetrahedron Lett.*, 40, 2669-2672 (1999).

Bittner, S., Temtsin, G., and Sasson, Y., Synthesis of *N*-Quinonyl Carbamates via 2-Chloro-3-isocyanato-1,4-naphthoquinone. *Synthesis*, 1084-1086 (2000).

Carson, J. F., *N*-2,2,2-Trichloroethoxycarbonyl-L-amino Acids. *Synthesis*, 268-270 (1981).

Chandrasekhar, S. and Narsihmulu, C., Direct conversion of azides to carbamates and sulfonamides using Fe/$NH_4Cl$: effect of sonication. *Tetrahedron Lett.*, 41, 7969-7972 (2000).

Charette, A. B., Marcoux, J. -F., Molinaro, C., Beauchemin, A., Brochu, C., and Isabel, E., Preparation Solid-State Structure, and Synthetic Applications of Isolable and Storable Haloalkylzinc Reagent. *J. Am. Chem. Soc.*, 122, 4508-4509 (2000).

Einhorn, J., Einhorn, C., and Luche, J. -L., A Mild and Efficient Sonochemical *tert*-Butoxycarbonylation of Amines from Their Salts. *Synlett*, 37-38 (1991).

Feroci, M., Inesi, A., and Rossi, L., The reaction of amines with an electrogenerated base. Improved synthesis of arylcarbamic esters. *Tetrahedron Lett.*, 41, 963-966 (2000).

Firestone, R. A., Pisano, J. M., Falck, J. R., McPhaul, M. M., and Krieger, M. Selective Delivery of Cytotoxic Compounds to Cells by the LDL Pathway. *J. Med. Chem.*, 27, 1037-1043 (1984).

Green, T. W. and Wuts, P. G. M., Protecting Groups in Organic Synthesis (3rd). John Wiley & Sons Inc., New York. (1999).

Inesi, A., Mucciante, V., and Rossi, L., A Convenient Method for the Synthesis of Carbamate Esters from Amines and Tetraethylammonium Hydrogen Carbonate. *J. Org. Chem.*, 63, 1337-1338 (1998).

Jung, Y. H. and Kim, J. D., A Novel Synthetic Methods for -Amino Acids from Allyl Ethers *via* *N*-Allylcarbamates. *Arch. Pharm. Res.*, 23, 574-578 (2000).

Kim, J. D., Lee, M. H., Lee, M. J., and Jung, Y. H., Synthesis of *N*-protected Allylic Amines from Allyl Ethers *Tetrahedron*, 57, 8257-8266 (2001).

Kim, J. D., Lee, M. H., Lee, M. J., and Jung, Y. H., Novel Synthetic Method for N-Allylcarbamates from Allyl ethers using Chlorosulfonyl isocyanate. *Tetrahedron Lett.*, 41, 5073-5076 (2000).

Knölker, H. J. and Braxmeier, T., Synthesis of Carbamates by DMAP-Catalyzed Reaction of Amines with Di-*tert*-butyldicarbonate and Alcohols. *Tetrahedron Lett.*, 37, 5861-5864 (1996).

Kocienski, P. J., Protecting Groups. Thieme, Stuttgart. (1994).

Kresze, G. and Münsterer H., Bis(methoxycarbonyl)sulfur Diimide, a Convenient Reagent for the Allylic Amination of Alkenes. *J. Org. Chem.*, 48, 3561-3564 (1983).

Leenders, R. G. G. and Scheeren, H. W., A Novel β-D-glycosyl carbamate forming reaction. *Tetrahedron Lett.*, 41, 9173-9175 (2000).

Lin, G., Liao, W. C., and Chiou, S. Y., Quantitative Structure-Activity Relationships for the Pre-Steady-State Inhibition of Cholesterol Esterase by 4-Nitrophenyl-*N*-substituted Carbamates. *Bioorg. Med. Chem.*, 8, 2601-2607 (2000).

Matassa, V. G., Maduskuie, T. P., Shapiro, H. S., Hesp, B., Snyder, D. W., Aharony, D., Krell, R. D., and Keith, R. A., Evolution of a Series of Peptidoleukotriene Antagonists: Synthesis and Structure/Activity Relationships of 1,3,5-Substituted Indoles and Indazoles. *J. Med. Chem.*, 33, 1781-1790 (1990).

Matsumura, Y., Maki, T., and Satoh, Y., Electrochemically Induced Hofmann Rearrangement. *Tetrahedron Lett.*, 38, 8879-8882 (1997).

Oertel, G., Polyurethane Handbook. Hanser Publishers, Munich. (1985).

Otera, J., Fujita, Y., and Sato, T., Distannoxane-Catalyzed Conversion of Chiral Alcohol to N-[1-(1-Naphthyl)-ethyl]carbamate. *Synlett*, 433-434 (1995).

Pennington, M. W. and Dunn, B. M., In Methods in Molecular Biology, Vol 35, Peptide Synthesis Protocols. Humana Press, Totowa. NJ, pp 91-94 (1994).

Saito, S., Nakajima, H., Inaba, M. and Moriwake, T., One-Pot Transformation of Azido-Group to N-(t-Butoxycarbonyl)amino Group. *Tetrahedron Lett.*, 30, 837-838 (1989).

Salehi, P., Iranpoor, N., and Behbahani, F. K., Selective and Efficient Alcoholyses of Allylic, Secondary- and Tertiary Benzylic Alcohols in the Presence of Iron (III). *Tetrahedron*, 54, 943-948 (1998).

Shono, T., Matsumura, Y., Yamane, S., and Kashimura, S., The Hofmann Rearrangement Induced by Electroorganic Method. *Chemistry Lett.*, 565-568 (1982).

Sun, X., Zeckner, D. J., Current, W. L., Boyer, R., McMillian, C., Yumibe, N., and Chen, S. H., *N*-Acyloxymethyl Carbamate Linked Prodrugs of Pseudomycins Are Novel Antifungal Agents. *Bioorg. Med. Chem. Lett.*, 11, 1875-1879 (2001).

Takagi, M. and Yamamoto, K., Palladium(0)-Catalyzed

Amination of Allylic Acetate with Methyl Carbamate. *Chemistry Lett.*, 2123-2124 (1989).

Tiecco, M., Testaferri, L., Temperini, A., Bagnoli, L., Marini, F., and Santi, C., Electrophilic Azido Selenenylation of Alkenes. A Simple Synthtic Route to Racemic Taxol Side Chain. *Synthtic. Commun.*, 28, 2167-2179 (1998).

Verlhac, J. -B., and Pereyre, M., Organotin Homoenolate Equivalents-Acess to β-Acyl- and β-Aryl- Propionaldehydes through Heterosubstituted Allyltins and Vinyltins. *Tetrahedron,* 46, 6399-6412 (1990).

Xiao, X. -Y., Ngu, K., Chao, C., and Patel, D. V., Selective Solid Phase Synthesis of Ureas and Hydantoins from Common Phenyl Carbamate Intermediates. *J. Org. Chem.*, 62, 6968-6973 (1997).

Yadav, J. S., Reddy, G. S., Reddy, M. M., and Meshram, H. M., Zinc Promoted Simple and Convenient Synthesis of Carbamates: An Easy Access for Amino Group Protection. *Tetrahedron Lett.*, 39, 3259-3262 (1998).