Pergamon

Tetrahedron 58 (2002) 4395–4402

TETRAHEDRON

Study of the stability of carbocations by chlorosulfonyl isocyanate reaction with ethers

Ji Duck Kim,[a] Gyoonhee Han,[b] Lak Shin Jeong,[c] Hyun-Ju Park,[a] Ok Pyo Zee[a] and Young Hoon Jung[a,*]

[a]*College of Pharmacy, Sungkyunkwan University, Suwon 440-746, South Korea*
[b]*Korea Research Institute of Bioscience and Biotechnology, Taejon 305-333, South Korea*
[c]*College of Pharmacy, Ewha Womans University, Seoul 120-750, South Korea*

Received 13 February 2002; accepted 12 April 2002

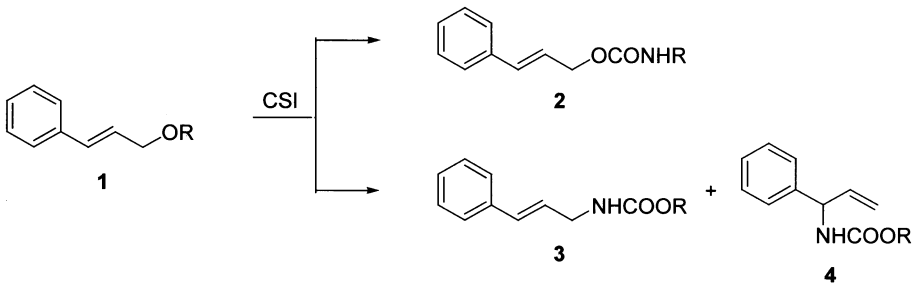
Abstract—The stability order of various alkyl, allyl, and benzyl carbocations was investigated using the novel technique for comparing the stability of carbocations in solution developed by using a simple CSI reaction with various ethers. The *p*-methoxycinnamyl carbocation was the most stable in our reaction system and the next stable carbocation was the *p*-methoxybenzyl carbocation. The stability of the other carbocations decreased with methacryl, *t*-butyl, cinnamyl, acryl, benzyl, 2° and allyl carbocations in that order.

1. Introduction

Of all the reaction intermediates, the carbocation is one of the organic reaction intermediate that has been extensively studied and perhaps is the most widely understood and used intermediate in organic synthesis.[1] Thus, various techniques for forming carbocations have been developed. In particular, in the gas phase, chemical ionization,[2] thermal ionization,[3] electron ionization,[4] photoionization,[5] etc.[6] have been developed and, in the solution phase, the ionization of alkyl halides[7] or alcohols[8] and their reactions with SbF_5[9] produce their corresponding carbocations. Many of the pioneering studies on the formation of benzylic carbocations have been carried out by Olah et al., under superacid conditions.[10]

Through the above techniques, the order of carbocation stability has been well studied using various parameters: thermochemistry (heat of formation, proton affinity, etc.)[11] and relative reaction rate (solvolysis, nucleophilic substitution, hydride transfer, etc.).[12] The chemistry of carbocation stability has been used in a number of syntheses[13] and applied to the development of novel synthetic methodologies.[14]

Recently, a novel synthetic method for *N*-allylcarbamate

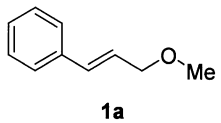
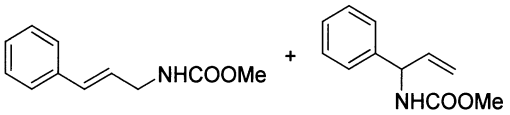
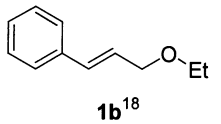
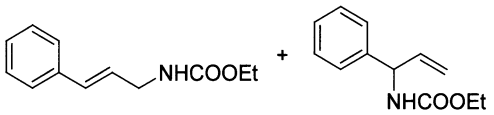
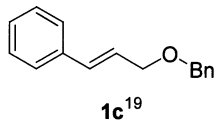
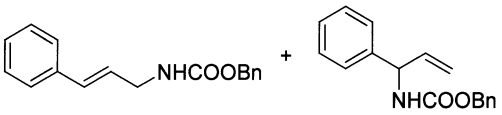
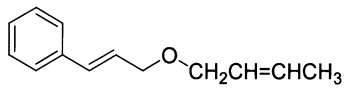
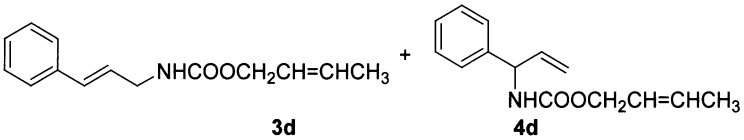
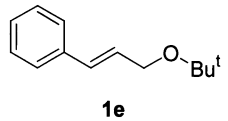
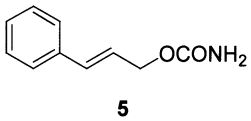


Scheme 1.

Keywords: chlorosulfonyl isocyanate; stability of carbocation; ether; carbamate.
* Corresponding author. Tel.: +82-31-290-7711; fax: +82-31-290-5403; e-mail: yhjung@skku.ac.kr

0040–4020/02/$ - see front matter
PII: S0040-4020(02)00413-1

Table 1. Conversions of cinnamyl ethers to the corresponding carbamate with CSI

	Ethers	Products	Yield (%)[a] ratio
1	 **1a**	 **3a** **4a**	87.5, 2.7:1
2	 **1b**[18]	 **3b** **4b**	83.5, 7.0:1
3	 **1c**[19]	 **3c** **4c**	89.8, 8.4:1
4	 **1d**	 **3d** **4d**	85.9, 7.4:1
5	 **1e**	 **5**	42.9

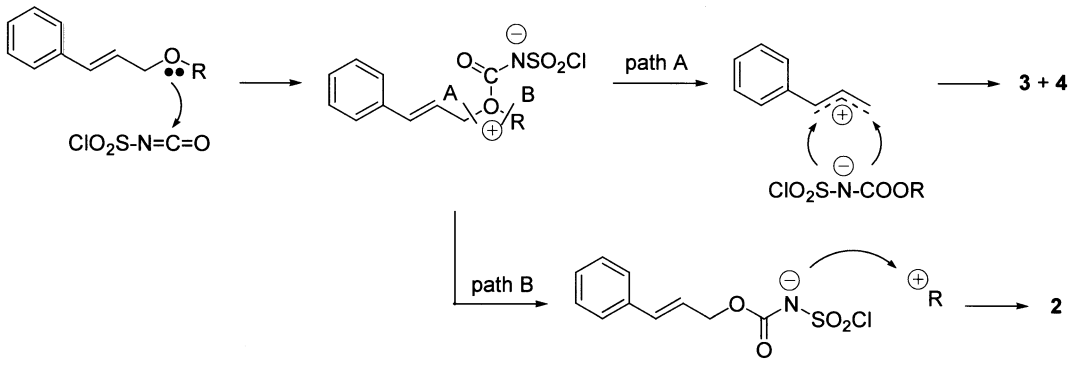
All the reactions were carried out in CH_2Cl_2 at 20°C.
[a] Isolated yield of pure material.

formation from various alkyl allyl ethers using chlorosulfonyl isocyanate (CSI) was reported.[15] The reaction mechanism involved an allyl carbocation intermediate[16] different from other CSI reactions with alkenes.[17] Herein we report the direct comparison of the stability of carbocations using the CSI reaction developed in this study.

2. Results and discussion

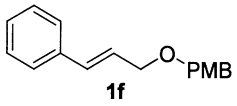
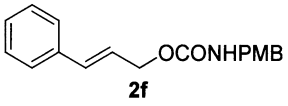
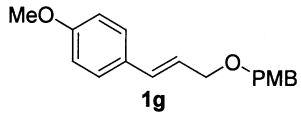
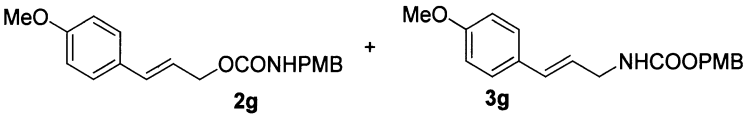
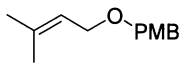
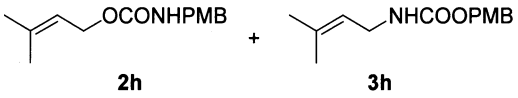
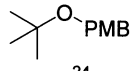
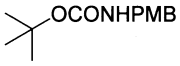
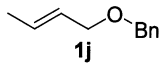
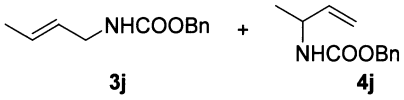
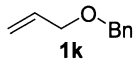
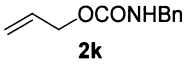
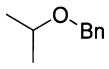
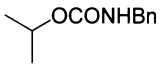
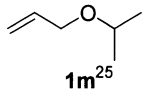
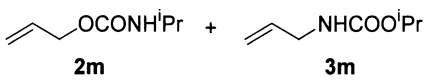
Our studies are based on the observation that various carbamates are formed from cinnamyl alkyl ethers using CSI in accord with the alkyl moiety of the cinnamyl alkyl ethers (Scheme 1). These results are summarized in Table 1.

The cinnamyl alkyl ethers were treated with CSI to produce the corresponding *N*-allylcarbamates as a mixture of regioisomers. The cinnamyl methyl ether (**1a**)[20] produced the terminal carbamate (**3a**)[21] and the internal carbamate (**4a**)[22] in a 2.7:1 ratio. As the size of the alkyl moiety of the ethers increased, the formation of the internal N-protected allylic amine decreased due to the steric hindrance with the phenyl ring (entries 1–4). However, for the cinnamyl *t*-butyl ether (**1e**),[23] the corresponding allyl carbamate was obtained as a single product (**5**) rather than the *N*-allylcarbamates (entry 5). These results suggest that the reaction pathways are determined by the stability of the carbocation obtained during the reaction process. Plausible reaction pathways are shown in Scheme 2. In path A, the stable allyl carbocation is formed by the cleavage of the C–O bond at A position followed by nitrogen anion attack to produce the *N*-allylcarbamates. However, when the formation of a more stable alkyl carbocation (R^+) rather than an allyl carbocation occurs, the



Scheme 2.

Table 2. Conversions of benzyl, allyl ethers to the corresponding carbamate with CSI

	Ethers	Products	Yield (%)[a] ratio
1	 **1f**	 **2f**	85.5
2	 **1g**	 **2g** + **3g**	45.7, 1:2.2[b]
3	 **1h**	 **2h** + **3h**	80.8, 1.2:1[b]
4	 **1i**[24]	 **2i**	32.7
5	 **1j**	 **3j** + **4j**	72.3, 1.1:1
6	 **1k**	 **2k**	70.1
7	 **1l**	 **2l**	60.2
8	 **1m**[25]	 **2m** + **3m**	46.1, 5.4:1[b]

All the reactions were carried out in CH_2Cl_2 at 20°C except for entries 1–3 (−78°C).
[a] Isolated yield of pure material.
[b] Isomer ratio determined from the ^1H NMR spectrum of the mixture after column chromatography.

reactions proceed through path B thus producing the corresponding allyl carbamates. Specifically, a cinnamyl carbocation is more stable than a benzylic carbocation and less stable than a 3° carbocation.

From these studies, a direct method was established for comparing the stability of various carbocations in the solution phase. This method was then applied to determine the stability order of other various carbocations.

For a comparison of the stability of various carbocations, the alkyl, allyl, benzyl and *p*-methoxybenzyl (PMB) ethers were prepared according to the conventional methods and treated with CSI in dichloromethane solution to give the corresponding carbamates depending on the carbocation stability. These results are summarized in Table 2.

For entry 1, the fact that cinnamyl *N*-(*p*-methoxybenzyl)-carbamate (**2f**) was obtained as a single product means that the *p*-methoxybenzylic carbocation is more stable than the cinnamyl carbocation. With a similar analogy, the *p*-methoxycinnamyl carbocation is more stable than the *p*-methoxybenzylic carbocation (entry 2), which is similar in stability to the methacrylic carbocation (entry 3) and is more stable than the *t*-butyl carbocation (entry 4).[12e,26,27] The benzylic carbocation is less stable than the crotonylic carbocation (entry 5)[27] and more stable than the allylic and 2° carbocations. (entries 6 and 7).[27] Furthermore, in the case

Table 3. The CSI reactions with various solvents and temperature

	Ethers	Products	Solvent	*T* (°C)	Ratio[a]	Yield (%)[b]
1	**1g**	**2g+3g**	CH_2Cl_2	−78	1:2.2	45.7
2	**1g**	**2g+3g**	$CHCl_3$	−60	1:2.9	48.6
3	**1g**	**2g+3g**	CH_2Cl_2	20	1:4.1	67.7
4	**1g**	**2g+3g**	$CHCl_3$	20	1:4.3	68.4
5	**1g**	**2g+3g**	Et_2O	20	1:5.6	32.6
6	**1h**	**2h+3h**	CH_2Cl_2	−78	1.2:1	80.8
7	**1h**	**2h+3h**	$CHCl_3$	−60	1.9:1	84.5
8	**1h**	**2h+3h**	Et_2O	−78	1.7:1	81.6
9	**1h**	**2h+3h**	CH_2Cl_2	20	1.4:1	80.7
10	**1h**	**2h+3h**	$CHCl_3$	20	2.0:1	86.1
11	**1h**	**2h+3h**	Et_2O	20	1.8:1	87.9
12	**1i**	**2i**	CH_2Cl_2	20	–	32.7
13	**1i**	**2i**	$CHCl_3$	20	–	43.1
14	**1i**	**2i**	Et_2O	20	–	22.4
15	**1m**	**2m+3m**	CH_2Cl_2	20	5.4:1	46.1
16	**1m**	**2m+3m**	$CHCl_3$	20	8.4:1	48.8
17	**1m**	**2m+3m**	Et_2O	20	7.6:1	38.5

[a] Isomer ratio determined from the ^1H NMR spectrum of the mixture after column chromatography.
[b] Isolated yield of pure material.

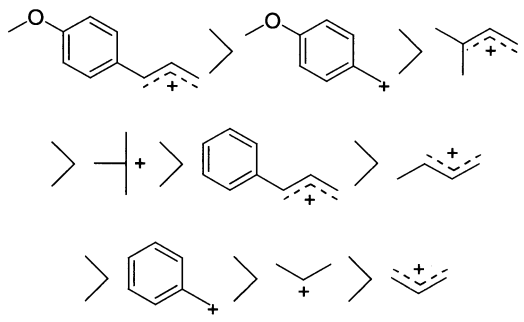


Figure 1.

of entry 8, we found that a 2° carbocation is more stable than an allylic carbocation.[3a,27]

However, for entries 2, 3, and 8, the mixture of **2** and **3** was formed and the chemical yield for entry 4 was very poor. Therefore, we investigated these reactions by varying the solvents and temperature to increase the ratio of the isomers and optimize the yield. Especially, we chose chloroform and ether (Et_2O), which might stabilize the carbocations rather than dichloromethane. These results are summarized in Table 3.

From Table 3, we found that chloroform and ether (Et_2O) provided an increased ratio of **2** and **3** compared to dichloromethane, and the ratio of the regioisomers was increased in accord with the temperature increase. The results of entries 6–11 provided information that the *p*-methoxybenzylic carbocation is more stable than the methacrylic carbocation. For the *p*-methoxybenzyl *t*-butyl ether (**1i**), the chemical yield was slightly increased in the chloroform solution.

From the results of Tables 1–3, the stability of the carbocations is as follows (Fig. 1).

The *p*-methoxycinnamyl carbocation is the most stable in our reaction system and the next stable carbocation is the *p*-methoxybenzyl carbocation. The stability of the other carbocations decreases with methacryl, *t*-butyl, cinnamyl, acryl, benzyl, 2° and allyl carbocations in that order.[28] For reference,[27] thermodynamic data in the gas phase for various carbocations suggests that the stability order of the carbocations is similar to that obtained under our reaction conditions except for the benzyl carbocation, which is more stable than the acryl carbocation.

3. Conclusion

In conclusion, a novel technique was developed to compare directly the stability of carbocations in the solution phase using a CSI reaction and to establish the stability order of the various carbocations. We are actively pursuing further investigation of the stability of the other interesting carbocations using CSI reactions.

4. Experimental

4.1. General

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/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 (^1H 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 $CHCl_3$ δ_H (7.26 ppm) and $CDCl_3$ δ_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.

4.2. General procedure for the preparation of ethers

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 alkyl halide (7.5 mmol). The reaction mixture was stirred at room temperature for 15 h, 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 ether.

4.2.1. 1-(But-2-enyloxy)-3-phenylprop-2-ene (1d). ^1H NMR (500 MHz, $CDCl_3$): δ 1.74(dd, 3H, *J*=6.5, 1.5 Hz), 3.98(dd, 2H, *J*=6.5, 1.5 Hz), 4.15(d, 2H, *J*=6 Hz), 5.65(dtq, 1H, *J*=13, 6.5, 1.5 Hz), 5.77(dtq, 1H, *J*=13, 6.5, 1.5 Hz), 6.31(dt, 1H, *J*=16, 6 Hz), 6.62(d, 1H, *J*=16 Hz), 7.23–7.41(m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.53, 71.22, 71.63, 126.93, 127.18, 128.19, 128.32, 129.24, 130.52, 133.03, 137.49; IR (neat): 3029, 2859, 1660, 1453, 1358, 1098 cm^{-1}; HRMS (CI) calcd for $C_{13}H_{16}O$–H $(M-H)^+$ 187.1123. Found: 187.1118.

4.2.2. 1-*p*-Methoxybenzyloxy-3-phenylprop-2-ene (1f). ^1H 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, 6 Hz), 6.60(d, 1H, *J*=16 Hz), 6.88(dd, 2H, *J*=6.5, 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 (*n*-Hex); Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.28; H, 7.20.

4.2.3. 1-*p*-Methoxybenzyloxy-3-*p*-methoxyphenylprop-2-ene (1g). ^1H NMR (500 MHz, $CDCl_3$): δ 3.82(s, 3H), 3.83(s, 3H), 4.15(d, 2H, *J*=6 Hz), 4.51(s, 2H), 6.20(dt, 1H, *J*=16, 6 Hz), 6.57(d, 1H, *J*=16 Hz), 6.85–6.91(m, 4H), 7.27–7.35(m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ

55.98, 56.01, 71.39, 72.43, 114.52, 114.57, 124.60, 128.38, 130.15, 130.24, 131.14, 132.90, 159.90, 159.98; IR (CH_2Cl_2): 2938, 2845, 1668, 1582, 1513, 1464, 1303, 1250, 1179, 1031 cm^{-1}; mp: 46–47°C (*n*-Hex); Anal. Calcd for $C_{18}H_{20}NO_3$: C, 76.03; H, 7.09. Found: C, 76.21; H, 7.09.

4.2.4. 1-*p*-Methoxybenzyloxy-3-methylbut-2-ene (1h). ^1H NMR (500 MHz, $CDCl_3$): δ 1.67(s, 3H), 1.77(s, 3H), 3.80(s, 3H), 3.99(d, 2H, J=7 Hz), 4.45(s, 2H), 5.42(t, 1H, J=7 Hz), 6.88(dd, 2H, J=8, 1.5 Hz), 7.28(dd, 2H, J=8, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.76, 26.52, 55.93, 67.00, 72.42, 114.44, 121.93, 130.11, 131.40, 137.71, 159.84; IR (neat): 2925, 2864, 1607, 1511, 1447, 1371, 1249, 1061 cm^{-1}; HRMS (CI) Calcd for $C_{13}H_{18}O_2$+H $(M+H)^+$ 207.1485. Found: 207.1389.

4.2.5. 1-Benzyloxybut-2-ene (1j). ^1H NMR (500 MHz, $CDCl_3$): δ 1.77(dd, 3H, J=6.5, 1.5 Hz), 4.01(dd, 2H, J=6, 1.5 Hz), 4.55(s, 2H), 5.69(dtq, 1H, J=13, 6.5, 1.5 Hz), 5.78(dtq, 1H, J=13, 6.5, 1.5 Hz), 7.31–7.40(m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.58, 71.66, 72.65, 128.28, 128.32, 128.52, 130.40, 139.22; IR (neat): 2926, 2858, 1602, 1452, 1363, 1291, 1233, 1091 cm^{-1}; HRMS (CI) Calcd for $C_{11}H_{14}O$–H $(M-H)^+$ 161.0967. Found: 161.0963.

4.2.6. Benzyl *i*-propyl ether (1l). ^1H NMR (500 MHz, $CDCl_3$): δ 1.27(d, 6H, J=5.5 Hz), 3.73(q, 1H, J=5.5 Hz), 4.56(s, 2H), 7.25–7.41(m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.88, 70.78, 71.67, 128.09, 128.27, 129.07, 139.88; IR (neat): 2963, 2871, 1601, 1463, 1362, 1097 cm^{-1}; HRMS (CI) Calcd for $C_{10}H_{14}O$–H $(M-H)^+$ 149.0967. Found: 149.0959.

4.3. General procedure for the reaction of ether with CSI

A suspension of Na_2CO_3 (6.75 mmol) in anhydrous CH_2Cl_2 (12 ml) was adjusted to 20 or −78°C, then CSI (4.5 mmol) and ether (3 mmol) was added under N_2. The reaction mixture was stirred at 20 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 carbamate.

4.3.1. Ethyl *N*-(3-phenylprop-2-enyl)carbamate (3b). ^1H NMR (500 MHz, $CDCl_3$): δ 1.26 (t, 3H, J=7 Hz), 3.87(dd, 2H, J=6, 4.5 Hz), 4.15(q, 2H, J=7 Hz), 4.82–4.92(br, 1H), 6.17–6.23(dt, 1H, J=16, 6 Hz), 6.52(d, 1H, J=16 Hz), 7.22–7.37(m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.38, 43.74, 61.63, 126.78, 127.08, 128.36, 129.28, 132.26, 137.31, 157.31; IR (KBr): 3299, 2983, 2935, 1695, 1661, 1539, 1497, 1377, 1253, 1135 cm^{-1}; mp: 52–53°C (*n*-Hex); Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.04; H, 7.39; N, 6.69.

4.3.2. Ethyl *N*-(1-phenylallyl)carbamate (4b). ^1H NMR (500 MHz, $CDCl_3$): δ 1.24(t, 3H, J=7 Hz), 4.12(q, 2H, J=7 Hz), 5.01–5.10(br,1H), 5.24(dd, 1H, J=10, 1.5 Hz), 5.25(dd, 1H, J=17, 1.5 Hz), 5.33–5.37(br, 1H), 6.01(ddd, 1H, J=17, 10, 5 Hz), 7.22–7.37(m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.30, 57.64, 61.72, 116.37, 127.73, 128.34, 129.32, 138.45, 141.52, 156.54; IR (neat): 3321, 2979, 1702, 1517, 1347, 1252, 1058 cm^{-1}; HRMS (CI) Calcd for $C_{12}H_{15}NO_2$+H $(M+H)^+$ 206.1181. Found: 206.1185.

4.3.3. Benzyl *N*-(3-phenylprop-2-enyl)carbamate (3c). ^1H NMR (500 MHz, $CDCl_3$): δ 3.99(dd, 2H, J=6, 4.5 Hz), 4.88–4.97(br, 1H), 5.15(s, 2H), 6.17(dt, 1H, J=16, 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, 2832, 1686, 1543, 1451, 1261, 1248, 1138 cm^{-1}; mp: 62–63°C (*n*-Hex); 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.

4.3.4. Benzyl *N*-(1-phenylallyl)carbamate (4c). ^1H NMR (500 MHz, $CDCl_3$): δ 5.12(s, 2H), 5.15(dd, 1H, J=5.5, 5 Hz), 5.24(dd, 1H, J=9.5, 1.5 Hz), 5.25(dd, 1H, J=18, 1.5 Hz), 5.33–5.40(br, 1H), 6.01(ddd, 1H, J=18, 9.5, 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, 3045, 2934, 1707, 1515, 1242, 1042 cm^{-1}; mp: 46–47°C (*n*-Hex); HRMS (CI) Calcd for $C_{17}H_{17}NO_2$+H $(M+H)^+$ 268.1337. Found: 268.1343.

4.3.5. But-2-enyl *N*-(3-phenylprop-2-enyl)carbamate (3d). ^1H NMR (500 MHz, $CDCl_3$): δ 1.72(d, 3H, J=6.5 Hz), 3.91–3.99(br, 2H), 4.52(d, 2H, J=5.5 Hz), 4.93–5.02(br, 1H), 5.61(dt, 1H, J=15, 5.5 Hz), 5.77(dq, 1H, J=15, 6.5 Hz), 6.18(dt, 1H, J=16, 6 Hz), 6.51(d, 1H, J=16 Hz), 7.22–7.36(m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.51, 43.79, 66.43, 126.41, 126.68, 127.09, 128.37, 129.28, 131.67, 132.30, 137.29, 157.09; IR (neat): 3340, 3034, 2937, 1706, 1524, 1383, 1250, 1121, 1066 cm^{-1}; HRMS (CI) Calcd for $C_{14}H_{17}NO_2$+H $(M+H)^+$ 232.1337. Found: 232.1335.

4.3.6. But-2-enyl *N*-(1-phenylallyl)carbamate (4d). ^1H NMR (500 MHz, $CDCl_3$): δ 1.72(d, 3H, J=6.5 Hz), 4.52(d, 2H, J=5.5 Hz), 4.95–5.05(br, 1H), 5.24(dd, 1H, J=10, 1.5 Hz), 5.25(dd, 1H, J=17, 1.5 Hz), 5.36–5.40(br, 1H), 5.59(dt, 1H, J=15, 5.5 Hz), 5.78(dq, 1H, J=15, 6.5 Hz), 6.00(ddd, 1H, J=17, 10, 5.5 Hz), 7.26–7.37(m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.49, 57.69, 66.53, 116.42, 126.29, 127.73, 128.36, 129.42, 131.85, 138.36, 141.42, 156.28; IR (CH_2Cl_2): 3319, 3038, 2939, 1703, 1518, 1321, 1247, 1096 cm^{-1}; mp: 53–55°C (*n*-Hex); HRMS (CI) Calcd for $C_{14}H_{17}NO_2$+H $(M+H)^+$ 232.1337. Found: 232.1331.

4.3.7. 3-Phenylprop-2-enyloxycarbonylamine (5). ^1H 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, 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: 118–120°C

(EtOAc/*n*-Hex); 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.

4.3.8. 3-Phenylprop-2-enyl *N*-(*p*-methoxybenzyl)carbamate (2f). ^{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, 6.5 Hz), 6.64(d, 1H, J=16 Hz), 6.87(dd, 2H, J=7, 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 cm^{-1}; mp: 104°C (EtOAc/*n*-Hex); 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.

4.3.9. 3-*p*-Methoxyphenylprop-2-enyl *N*-(*p*-methoxybenzyl)carbamate (2g) and *p*-methoxybenzyl *N*-(3-*p*-methoxybenzylprop-2-enyl)carbamate (3g). *3-p-Methoxyphenylprop-2-enyl N-(p-methoxybenzyl)carbamate* (**2g**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.79(s, 3H), 3.80(s, 3H), 4.31(d, 2H, J=6 Hz), 4.73(d, 2H, J=6 Hz), 4.97–5.03(br, 1H), 6.16(dt, 1H, J=16, 6 Hz), 6.61(d, 1H, J=16 Hz), 6.85–6.90(m, 4H), 7.20–7.34(m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 45.34, 55.99, 66.50, 114.50, 114.64, 122.91, 128.53, 129.59, 129.84, 131.05, 134.18, 157.01, 160.02, 160.24.

p-Methoxybenzyl N-(3-p-methoxybenzylprop-2-enyl)carbamate (**3g**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.80(s, 3H), 3.81(s, 3H), 3.94(dd, 2H, J=6 Hz, 5.5 Hz), 4.78–4.86(br, 1H), 5.06(s, 2H), 6.05(dt, 1H, J=16, 6 Hz), 6.45(d, 1H, J=16 Hz), 6.83–6.86(m, 4H), 7.20–7.34(m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 43.92, 55.96, 67.31, 114.71, 114.76, 124.25, 128.26, 129.39, 130.03, 130.68, 132.07, 157.01, 160.24, 160.29; IR (CH_2Cl_2): 3315, 2929, 1690, 1609, 1547, 1512, 1450, 1246, 1177, 1031 cm^{-1}; HRMS (CI) Calcd for $C_{19}H_{21}NO_4$+H $(M+H)^+$ 328.1549. Found: 328.1546.

4.3.10. 3-Methylbut-2-enyl *N*-(*p*-methoxybenzyl)carbamate (2h) and *p*-methoxybenzyl *N*-(3-methylbut-2-enyl)-carbamate (3h). *3-Methylbut-2-enyl N-(p-methoxybenzyl)carbamate* (**2h**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.72(s, 3H), 1.76(s, 3H), 3.79(s, 3H), 4.30(d, 2H, J=5.5 Hz), 4.59(d, 2H, J=7 Hz), 4.93–4.98(br, 1H), 5.34(t, 1H, J=7 Hz), 6.86(dd, 2H, J=8, 1.5 Hz), 7.22(dd, 2H, J=8, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.72, 26.48, 45.28, 55.97, 62.50, 114.70, 119.84, 129.47, 131.38, 157.33, 159.66.

p-Methoxybenzyl N-(3-methlbut-2-enyl)carbamate (**3h**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.66(s, 3H), 1.71(s, 3H), 3.77(d, 2H, J=5.5 Hz), 3.81(s, 3H), 4.60–4.64(br, 1H), 5.03(s, 2H), 5.18(t, 1H, J=5.5 Hz), 6.88(dd, 2H, J=7.5, 1.5 Hz), 7.30(dd, 2H, J=7.5, 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.52, 26.30, 39.64, 55.99, 67.12, 114.58, 121.22, 129.58, 130.67, 157.31, 160.20; IR (CH_2Cl_2): 3334, 2963, 2932, 1700, 1613, 1515, 1465, 1301, 1245, 1178, 1134, 1036 cm^{-1}; HRMS (CI) Calcd for $C_{14}H_{19}NO_3$+H $(M+H)^+$ 250.1443. Found: 250.1443.

4.3.11. *t*-Butyl *N*-(p-methoxybenzyl)carbamate (2i). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.47(s, 9H), 3.80(s, 3H), 4.25(d, 2H, J=5 Hz), 4.75–4.83(br, 1H), 6.86(dd, 2H, J=8, 2 Hz), 7.21(dd, 2H, J=8, 2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 29.13, 44.87, 55.99, 80.03, 114.68, 129.57, 131.71, 156.55, 159.59; IR (neat): 3332, 3051, 2937, 1705, 1543, 1255, 1130, 1019 cm^{-1}; HRMS (CI) Calcd for $C_{13}H_{19}NO_3$+H $(M+H)^+$ 238.1443. Found: 238.1436.

4.3.12. Benzyl *N*-(but-2-enyl)carbamate (3j) and benzyl *N*-(1-methylallyl)carbamate (4j). *Benzyl N-(but-2-enyl)-carbamate* (**3j**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.68(d, 3H, J=6.5 Hz), 3.70–3.79(br, 2H), 4.76–4.85(br, 1H), 5.09(s, 2H), 5.48(dq, 1H, J=15, 6,5 Hz), 5.61(dt, 1H, J=15, 6.5 Hz), 7.30–7.40(m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.35, 43.71, 67.39, 127.85, 128.81, 129.23, 140.41, 156.92.

Benzyl N-(1-methylallyl)carbamate (**4j**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.24(d, 3H, J=6.5 Hz), 4.28–4.36(br, 1H), 4.70–4.78(br, 1H), 5.11(s, 2H), 5.12(dd, 1H, J=10 Hz, 1.5 Hz), 5.15(dd, 1H, J=17, 1.5 Hz), 5.84(ddd, 1H, J=17, 10, 5.5 Hz), 7.30–7.40(m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.35, 49.39, 67.36, 114.69, 127.85, 128.81, 129.23, 137.26, 140.41, 156.30; IR (neat): 3410, 3331, 3033, 2971, 2937, 1769, 1729, 1691, 1531, 1454, 1334, 1293, 1241, 1134, 1053 cm^{-1}; HRMS (CI) Calcd for $C_{12}H_{15}NO_2$+H $(M+H)^+$ 206.1181. Found: 206.1178.

4.3.13. Allyl *N*-benzylcarbamate (2k). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.39(d, 2H, J=5.5 Hz), 4.60(d, 2H, J=5.5 Hz), 5.02–5.08(br, 1H), 5.23(dd, 1H, J=10.5, 1.5 Hz), 5.32(dd, 1H, J=17, 1.5 Hz), 5.94(ddt, 1H, J=17, 10.5, 5.5 Hz), 7.27–7.36(m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 45.73, 66.35, 118.36, 128.13, 128.22, 129.33, 133.67, 139.34, 157.15; IR (neat): 3334, 3052, 2933, 1707, 1529, 1252, 1136, 1013 cm^{-1}; HRMS (CI) Calcd for $C_{11}H_{13}NO_2$+H $(M+H)^+$ 192.1024. Found: 192.1031.

4.3.14. *i*-Propyl *N*-benzylcarbamate (2l). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.24(d, 6H, J=6 Hz), 4.37(d, 2H, J=5.5 Hz), 4.96(q, 1H, J=6 Hz), 4.91–5.00(br, 1H), 7.27–7.36(m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.90, 45.62, 68.91, 128.06, 128.15, 129.31, 139.54, 157.12; IR (neat): 3334, 2959, 1701, 1526, 1363, 1257, 1129 cm^{-1}; HRMS (CI) Calcd for $C_{11}H_{15}NO_2$+H $(M+H)^+$ 194.1181. Found: 194.1187.

4.3.15. Allyl *N*-*i*-propylcarbamate (2m) and *i*-propyl *N*-allylcarbamate (3m). *Allyl N-i-propylcarbamate* (**2m**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.16(d, 6H, J=6.5 Hz), 3.82(q, 1H, J=6.5 Hz), 4.50–4.60(br, 3H), 5.20(dd, 1H, J=10.5, 1.5 Hz), 5.30(dd, 1H, J=17, 1.5 Hz), 5.92(ddt, 1H, J=17, 10.5, 5.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.59, 43.64, 65.82, 110.03, 133.75, 156.11.

i-Propyl N-allylcarbamate (**3m**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.23(d, 6H, J=6 Hz), 3.74–3.82(br, 2H), 4.62–4.70(br, 1H), 4.93(q, 1H, J=6 Hz), 5.14(dd, 1H, J=10, 1.5 Hz), 5.18(dd, 1H, J=15.5, 1.5 Hz), 5.65(ddt, 1H, J=15.5, 10, 5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.81, 43.97, 68.68, 116.41, 135.46, 156.89; IR (neat): 3337, 3328, 2964, 1704, 1700, 1529, 1354, 1260, 1248, 1135, 1089 cm^{-1}; HRMS (CI) Calcd for $C_7H_{13}NO_2$+H $(M+H)^+$ 144.1014. Found: 144.1022.

Acknowledgements

The authors wish to acknowledge the financial support of the Korea Research Foundation made in the program year of 1998.

References

1. (a) Surya Prakash, G. K.; Schleyer, P. v. R. *Stable Carbocation Chemistry*; Wiley: New York, 1997. (b) Vogel, P. *Carbocation Chemistry*; Elsevier: Amsterdam, 1985. (c) Laube, T. *Chem. Rev.* **1998**, *98*, 1277.
2. (a) Dymerski, P. P.; Prinstein, R. M.; Bente III, P. F.; McLafferty, F. W. *J. Am. Chem. Soc.* **1976**, *98*, 6834. (b) Safron, S. A.; King, G. A.; Horvat, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 6333. (c) Meot-Ner, M. *J. Am. Chem. Soc.* **1978**, *100*, 4694. (d) Bohme, D. K.; Mackay, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 978.
3. (a) Aue, D. H.; Davidson, W. R.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 6700. (b) Darbeau, R.; Delaney, M. S.; Ramelow, U.; James, K. R. *Org. Lett.* **1999**, *1*, 761.
4. (a) Schultz, J. C.; Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 3917. (b) Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 3290. (c) Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4067.
5. (a) Eland, J. H. D. *Int. J. Mass Spectr. Ion. Phys.* **1972**, *8*, 143. (b) Eland, J. H. D. *Photo-electro Spectroscopy*; Butterworths: London, 1974. (c) Bock, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 613. (d) Cozens, F.; Bogdanova, R.; Régimbald, M.; Gaecia, H.; Marti, V.; Scaiano, J. C. *J. Phys. Chem. B* **1997**, *101*, 6921.
6. (a) Fontijn, A. *Pure Appl. Chem.* **1974**, *39*, 287. (b) Safron, S. A.; King, G. A.; Horvat, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 6333. (c) Barber, M.; Bordoli, R. S.; Sedgwick, R. D.; Tyler, A. N. *J. Chem. Soc., Chem. Commun.* **1981**, 325. (d) McNeal, C. J.; Macfarlane, R. D. *J. Am. Chem. Soc.* **1981**, *103*, 1609.
7. (a) Arnett, E. M.; Petro, C. *J. Am. Chem. Soc.* **1978**, *100*, 5402. (b) Arnett, E. M.; Hofelich, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 2889. (c) Mayr, H.; Förner, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 6032.
8. (a) Okazaki, T.; Terakawa, E.; Kitagawa, T.; Takeuchi, K. *J. Org. Chem.* **2000**, *65*, 1680. (b) Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5466. (c) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667. (d) Williams, S. G.; Norrington, F. E. *J. Am. Chem. Soc.* **1976**, *98*, 508.
9. (a) Raber, D. J.; Bingham, R. C.; Harris, J. M.; Fry, J. L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 5977. (b) Takeuchi, K.; Takasuka, M.; Shiba, E.; Kinoshita, T.; Okazaki, T.; Abboud, J.-L. M.; Notario, R.; Castano, O. *J. Am. Chem. Soc.* **2000**, *122*, 7351. (c) Wolf, J. F.; Abboud, J. L. M.; Taft, R. W. *J. Org. Chem.* **1977**, *42*, 3316.
10. (a) Laube, T.; Olah, G. A.; Bau, R. *J. Am. Chem. Soc.* **1997**, *119*, 3087. (b) Olah, G. A.; Cornisarow, M. B.; Kim, C. J. *J. Am. Chem. Soc.* **1969**, *91*, 1458. (c) Christe, K. O.; Zhang, X.; Bau, R.; Hegge, J.; Olah, G. A.; Surya Prakash, G. K.; Sheehy, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 481.
11. (a) Dóbé, S.; Bérces, T.; Turányi, T.; Márta, F.; Grussdorf, J.; Temps, F.; Wagner, H. G. *J. Phys. Chem.* **1996**, *100*, 19864. (b) Aschi, M.; Cacace, F.; Petris, G.; Pepi, F. *J. Phys. Chem.* **1996**, *100*, 16522. (c) Lias, S. G.; Shold, D. M.; Ausloos, P. *J. Am. Chem. Soc.* **1980**, *102*, 2540. (d) Tanaka, T.; McKay, G. I.; Bohme, D. K. *Can. J. Chem.* **1978**, *56*, 193. (e) Lau, Y. K.; Nishizawa, K.; Tse, A.; Brown, R. S.; Kebarle, P. *J. Am. Chem. Soc.* **1981**, *103*, 6291. (f) Baer, T. *J. Am. Chem. Soc.* **1980**, *102*, 2482.
12. (a) Pirinccioglu, N.; Thibblin, A. *J. Am. Chem. Soc.* **1998**, *120*, 6512. (b) Abboud, J.-L. M.; Herreros, M.; Notario, R.; Lomas, J. S.; Mareda, J.; Müller, P.; Rossier, J.-C. *J. Org. Chem.* **1999**, *64*, 6401. (c) Takeuchi, K.; Takasuka, M.; Shiba, E.; Kinoshita, T.; Okazaki, T.; Abboud, J.-L. M.; Notario, N.; Castaño, O. *J. Am. Chem. Soc.* **2000**, *122*, 7351. (d) Ritchie, C. D.; Hofelich, T. C. *J. Am. Chem. Soc.* **1980**, *102*, 7039. (e) Sharma, R. B.; Sharma, D. K. S.; Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc.* **1985**, *107*, 3747. (f) Peterson, P. E.; Brockington, R.; Vidrine, D. W. *J. Am. Chem. Soc.* **1976**, *98*, 2660.
13. (a) Peng, Z.-H.; Woerpel, K. A. *Org. Lett.* **2001**, *3*, 675. (b) Johnson, W. S.; Brinkmeyer, R. S.; Kapoor, V. M.; Yarnell, T. M. *J. Am. Chem. Soc.* **1977**, *99*, 8341. (c) Johnson, W. S.; Dumas, D. J.; Berner, D. *J. Am. Chem. Soc.* **1982**, *104*, 3510. (d) Röper, S.; Frackenpohl, J.; Schrake, O.; Wartchow, R.; Hoffmann, H. M. R. *Org. Lett.* **2000**, *2*, 1661. (e) Sepiol, J. J.; Wilamowski, J. *Tetrahedron Lett.* **2001**, *42*, 5287. (f) Akiyama, T.; Ishida, Y.; Kagoshima, H. *Tetrahedron Lett.* **1999**, *40*, 4219. (g) van Tamelen, E. E.; Hwu, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 2490.
14. (a) Machiguchi, T.; Hasegawa, T.; Ishiwata, A.; Terashima, S.; Yamabe, S.; Minato, T. *J. Am. Chem. Soc.* **2001**, *121*, 4771. (b) Ishikawa, T.; Okano, M.; Aikawa, T.; Saito, S. *J. Org. Chem.* **2001**, *66*, 4635. (c) Krasutsky, P. A.; Kolomitsyn, I. V.; Kiprof, P.; Carlson, R. M.; Fokin, A. A. *J. Org. Chem.* **2000**, *65*, 3926. (d) Tian, F.; Battiste, M. A.; Dolbier Jr., W. R. *Org. Lett.* **1999**, *1*, 193. (e) Kita, Y.; Furukawa, A.; Futamura, J.; Higuchi, K.; Ueda, K.; Fujioka, H. *Tetrahedron* **2001**, *57*, 815.
15. (a) Kim, J. D.; Lee, M. H.; Han, G.; Park, H.; Zee, O. P.; Jung, Y. H. *Tetrahedron* **2001**, *57*, 8257. (b) Kim, J. D.; Lee, M. H.; Lee, M. J.; Jung, Y. H. *Tetrahedron Lett.* **2000**, *41*, 5073. (c) Jung, Y. H.; Kim, J. D. *Arch. Pharm. Res.* **2001**, *24*, 371. (d) Jung, Y. H.; Kim, J. D. *Arch. Pharm. Res.* **2000**, *23*, 574.
16. (a) Roberson, C. W.; Woerpel, K. A. *J. Org. Chem.* **1999**, *64*, 1434. (b) Dhar, D. N.; Daniel, J.; Shukla, D. *Chem. Lett.* **1992**, 1575. (c) Hall, R. H.; Jordaan, A.; Villiers, O. G. *J. Chem. Soc., Perkin Trans. 1* **1975**, 626. (d) Lorincz, T.; Erden, I.; Näder, R.; Meijere, A. D. *Synth. Commun.* **1986**, *16*, 123.
17. (a) Dhar, D. N.; Murthy, K. S. K. *Synthesis* **1985**, 47. (b) Szabo, W. A. *Aldrichim. Acta* **1977**, *10*, 116. (c) Rasmussen, J. K.; Hassner, A. *Chem. Rev.* **1976**, *76*, 389. (d) Lysek, R.; Kaluza, Z.; Furman, B.; Chmielewski, M. *Tetrahedron* **1998**, *54*, 14065. (e) Kobayashi, Y.; Ito, Y.; Terashima, S. *Tetrahedron* **1992**, *48*, 55. (f) Cossio, F. P.; Roa, G.; Lecea, B.; Ugalde, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 12306 (g) Clau, K.; Grimm, D.; Prossel, G. *Liebigs Ann. Chem.* **1974**, *4*, 539. (h) Effenberger, F.; Fischer, P.; Prossel, G.; Kiefer, G. *Chem. Ber.* **1971**, *104*, 1987.
18. Cheik-Rouhou, F.; Le Bigot, T.; El Gharbi, R. *Synth. Commun.* **1986**, *16*, 1739.
19. Charette, A. B.; Marcoux, J.-F.; Molinaro, C.; Beauchemin, A.; Brochu, C.; Isabel, E. *J. Am. Chem. Soc.* **2000**, *122*, 4508.
20. Verlhac, J.-B.; Pereyre, M. *Tetrahedron* **1990**, *46*, 6399.
21. Takagi, M.; Yamamoto, K. *Chemistry Lett.* **1989**, 2123.
22. Kresze, G.; Münsterer, H. *J. Org. Chem.* **1983**, *48*, 3561.

23. Tiecco, N.; Testaferri, L.; Temperini, A.; Bagnoli, L.; Marini, F.; Santi, C. *Synth. Commun.* **1998**, *28*, 2167.
24. Okada, M.; Kitagawa, O.; Fujita, M.; Taguchi, T. *Tetrahedron* **1996**, *52*, 8135.
25. Fellous, R.; Rabine, J.-P.; Lizzani-Cuvelier, L.; Luft, R. *Bull. Soc. Chim. Fr.* **1974**, 923.
26. Kebarle, P. *Int. J. Mass Spectr.* **2000**, *200*, 313.
27. Lossing, F. P.; Holmes, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 6917.
28. Presented at the 221st ACS National Meeting, San Diego, CA, April, 2001.