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Kinetic Studies of Intramolecular Additions of Alkyl Radicals onto Imines

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Abstract: *The approximate rate constants for 5-exo and 6-exo cyclizations of alkyl radicals onto imines have been kinetically determined to be $6.0x10^6$ s^{-1} and $6.7x10^5$ s^{-1} at 80 °C, respectively. Alkyl radical additions to imines were essentially irreversible and considerably slower than alkyl radical additions to hydrazones.* Copyright © 1996 Elsevier Science Ltd

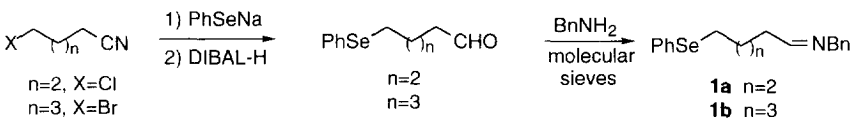
Radical cyclizations have attracted considerable interest in recent years, both synthetically[1] and mechanistically.[2] Although radical cyclizations of alkyl radicals onto C=C and C=O bonds[3] have been studied extensively, radical cyclizations to C=N bonds received relatively much less attention. Radical cyclizations of alkyl radicals onto C=N bonds of oxime ethers[4] and hydrazones[5] have been reported and their synthetic usefulness seems to be increasingly important.[6] Recently, radical cyclization of alkyl radicals onto imines has been reported by Bowman.[7] The rate constants for the cyclization of alkyl radicals onto *N,N*-diphenylhydrazones[8] and onto *N*-aziridinyl imines[9] were kinetically determined recently. The kinetic data showed that the cyclizations of alkyl radicals to C=N bonds of hydrazones were much faster than the cyclization of alkyl radicals to C=C and to C=O bonds, indicating that C=N bonds were much better radical acceptors than C=C and C=O bonds. However, neither unimolecular nor bimolecular rate constants for alkyl radical additions to imines have been reported. The only example for the rate constants of aryl radical additions to the imines was reported.[10]

Due to three different types of C=N bonds such as an imine, an oxime ether, and a hydrazone, we were initially interested in the dependence of the rate constants on the nature of C=N bonds. Specifically, we turned our attention to the following questions. (i) What are the effects of the electron density at iminyl carbons on radical cyclizations. (ii) Does the electron donating effect of the amino group in the hydrazone due to the resonance effect increase the cyclization rate ? Since the resonance effect in the oxime ether and the hydrazone would increase the electron density at the iminyl carbon, (i) and (ii) seem to be closely related.

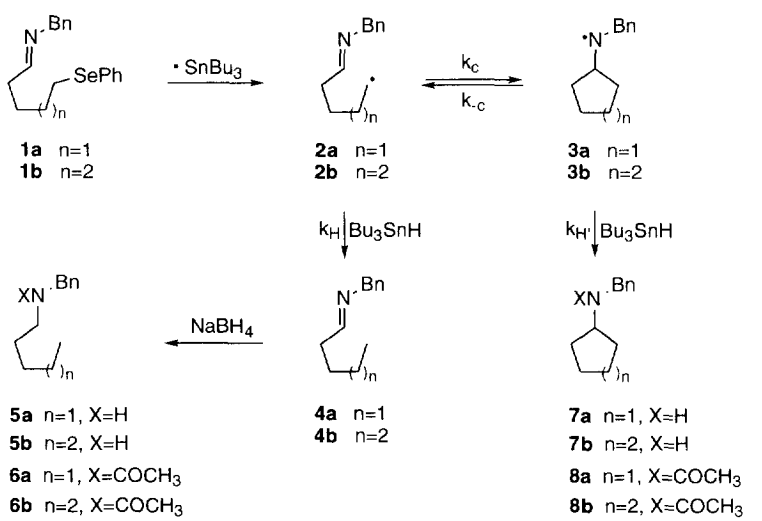
		$H_3CCH{=}N{-}CH_3$	$H_3CCH{=}N{-}OCH_3$	$H_3CCH{=}N{-}NMe_2$
C- Electron density	AM1-UHF	-4.075	-4.141	-4.177
	PM3-UHF	-4.092	-4.096	-4.127

Before we began our kinetic studies to determine rate constants for cyclization of alkyl radicals onto C=N bonds, we first calculated the electron densities of three different types of the iminyl carbon atoms using semi empirical calculation (MOPAC) and the results indicated that the electron density at the iminyl carbon of the hydrazone was higher than that of the imine as predicted. It is anticipated that the larger the electron density in an iminyl carbon is, the better the radical acceptor would be. We were, therefore, curious as to whether the cyclization rate would be dependent on the electron density at the iminyl carbon atom. We wish to report the results of our kinetic studies for the radical cyclizations of alkyl radicals onto imines.

Results and Discussion



Scheme 1

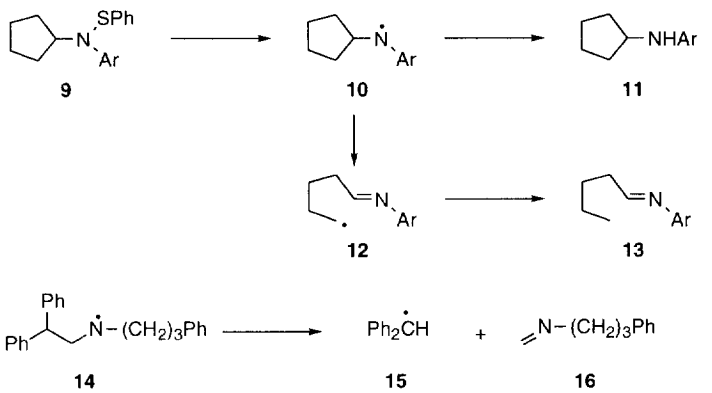


Scheme 2

In order to determine approximate rate constants for cyclizations of alkyl radicals onto imines, ω-benzeneselenenylimine **1a** and **1b** were chosen. The benzeneselenenyl group, which is readily abstracted by tributyltin radical, was chosen in place of halides for the present studies because of the lack of the

reactivity toward the amino and the imino group present in the intermediates or in the precursors. **1a** was prepared from 5-chloropentanenitrile by three step sequences using the standard procedures as shown in Scheme 1. Similarly, ω-benzeneselenenylimine **1b** was prepared from 6-bromohexanenitrile.

Rate constants (k_c) for cyclizations of alkyl radicals **2a** and **2b** to cyclized aminyl radicals **3a** and **3b** were determined by the tin hydride method. In this indirect method, the required alkyl radical **2** was generated by reaction of ω-benzeneselenenylimine **1** with Bu_3SnH/AIBN. The radical cyclization of **2** competed with the direct reduction of the alkyl radical, resulting from bimolecular hydrogen atom trapping by Bu_3SnH. The cyclized aminyl radical **3** also reacted with Bu_3SnH to afford the cyclized product **7**. Since the imino group in **4** is relatively unstable during workup, the imino group was reduced to the amino group with sodium borohydride in methanol. Furthermore, for the easy separation, a mixture of **5** and **7** was converted into the corresponding acetates **6** and **8** using acetyl chloride and triethylamine.



Concerning the reversibility of the cyclization step, alkyl radical additions to C=N bonds are energetically similar to alkyl radical additions to C=C bonds and would be irreversible, indicating that forward cyclizations would be much faster than ring opening reactions. According to the previous report by Bowman,[11] radical reaction of **9** with Bu_3SnH/AIBN afforded only **11** (54%) without the formation of **13**, suggesting that the ring opening reaction of **10** into **12** did not occur. However, β-elimination in **14** proceeded smoothly, yielding a mixture of **15** and **16**. Thus, the reversibility at the cyclization step depends on the nature of the starting radicals. In order to see whether the cyclization step would be irreversible or not, the rate equation was derived by assuming that the cyclization step would be reversible. Application of the steady state approximation to the kinetic analysis consistent with the mechanism shown in Scheme 1 leads to the approximate rate equation 1, where k_H and $k_{H'}$ are the second order rate constants for reactions of alkyl and aminyl radicals with Bu_3SnH, k_c and k_{-c} are the first order rate constants for cyclizations and ring opening reactions, and $[Bu_3SnH]_o$ represents the initial Bu_3SnH concentration. From eq 1, the ratio of rate constants (k_H/k_c) is found as the slope of a plot of **[6]**/**[8]** as a function of $[Bu_3SnH]_o$. Since k_H was previously known,[12] one can easily calculate k_c from its slope. Moreover, k_{-c} would be calculated from the intercept.

$$\frac{[6]}{[8]} = \frac{k_H}{k_c}[Bu_3SnH]_0 + \frac{k_H k_{-c}}{k_H' k_c} \quad (1)$$

Table 1. Product Yields from Radical Cyclization of **1a** with Bu_3SnH at 80 °C in Benzene[a]

$[1a]_0$	$[Bu_3SnH]_0$	[**6a**][b]	[**8a**][b]
0.032M	0.16M	14.3%	85.7%
0.032M	0.24M	21.4%	78.6%
0.032M	0.32M	25.0%	75.0%
0.032M	0.40M	30.6%	69.4%
0.032M	0.48M	33.6%	66.4%
0.032M	0.56M	37.5%	62.5%

[a]Total yields of products were 78-83%. [b] Products were acetylated and compositions were determined by HPLC.

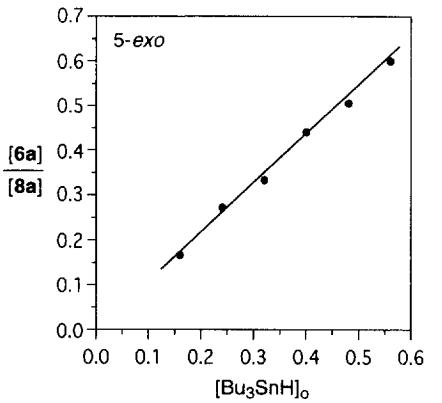


Figure 1

Approximate Rate Constant for 5-*exo* Cyclization. Radical reaction of **1a** (0.032M) with an excess amount of Bu_3SnH (0.16M-0.56M) using a catalytic amount of AIBN as a radical initiator in benzene at 80 °C for 1 h was performed under pseudo-first-order conditions at several different Bu_3SnH concentrations and two experiments were performed at each Bu_3SnH concentration. The reaction mixture was treated with sodium borohydride in methanol to reduce the imino group into the amino group. After usual workup, the residue was acetylated with acetyl chloride and triethylamine in dichloromethane. After removal of an excess amount of Bu_3SnH by a short silica gel column chromatography, the resulting solution was analyzed by HPLC and products were identified by comparison with authentic samples (**6a** and **8a**). Authentic samples were independently prepared, their response factors were determined, and the ratio of the product yields of **6a** and **8a** were finally calibrated. The isolated yields of product **6a** and **8a** were generally high (78%-83%) and the cyclized product **8a** was obtained as a major product. Furthermore, it is noteworthy that we were unable to detect the formation of N-benzylpiperidine resulting from 6-*endo* cyclization under the present conditions, although a small amount of 6-*endo* cyclization product was previously isolated with the similar substrate under relatively diluted cyclization conditions by Bowman.[11] The experimental results are summarized in Table 1 and depicted graphically in Figure 1. A plot of Bu_3SnH *vs* the ratio of **[6a]/[8a]** gave a straight line with a slope of $k_H/k_c = 1.06$, in which the slope indicates a relative rate of hydrogen atom abstraction to 1,5-*exo* cyclization. Since the rate constant for hydrogen atom transfer to n-butyl radical was known to be 6.4×10^6 $M^{-1}s^{-1}$ at 80°C,[12] the rate constant for 5-*exo* cyclization (k_c) could be calculated to be 6.0×10^6 s^{-1} from eq 1. The intercept in Figure 1 was close to zero (0.004), which clearly indicates that ring opening reaction of aminyl radical **3** is much slower than the cyclization. Thus, the cyclization of **2** is essentially irreversible.

Table 2. Product Yields from Radical Cyclization of **1b** with Bu_3SnH at 80 °C in Benzene[a]

$[\mathbf{1b}]_o$	$[Bu_3SnH]_o$	[**6b**][b]	[**8b**][b]
0.025M	0.19M	61.5%	38.5%
0.025M	0.25M	68.5%	31.5%
0.025M	0.31M	73.6%	26.4%
0.025M	0.35M	76.5%	23.5%
0.025M	0.41M	78.4%	21.6%

[a]Total yields of products were 77-81%. [b] Products were acetylated and compositions were determined by HPLC.

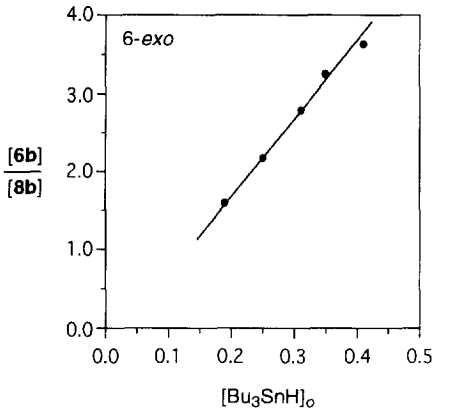


Figure 2

Approximate Rate Constant for 6-*exo* Cyclization. In order to determine the approximate rate constant for the 6-*exo* cyclization of an alkyl radical to an imine, ω-benzeneselenylbenzylimine **1b** (0.025M) was treated with an excess amount of Bu_3SnH (0.19M-0.41M) and a catalytic amount of AIBN in benzene at 80 °C for 1 h. The reaction mixture was treated with sodium borohydride in methanol prior to acetylation to reduce the imino group. The ratio of products were determined by HPLC analysis and by comparison with independently prepared authentic samples. **6b** was obtained as a major product and the total isolated yields of product **6b** and **8b** were 77-81%. The experimental results are shown in Table 2 and depicted graphically in Figure 2. A plot of Bu_3SnH *vs* the ratio of **[6b]**/**[8b]** gave a straight line with a slope of $k_H/k_c = 9.52$, in which the slope indicates the relative rate of hydrogen atom abstraction over 6-*exo* cyclization. With the use of 6.4×10^6 $M^{-1}s^{-1}$ at 80°C for k_H,[12] the rate constant for 6-*exo* cyclization could be calculated to be 6.7×10^5 s^{-1} from eq 1.

Conclusions

The kinetic analysis for intramolecular additions of alkyl radicals onto the imines provide several important experimental results. First, alkyl radical additions to C=N bonds are much faster than alkyl radical additions to C=C bonds ($k_{5\text{-}exo} = 2.5 \times 10^5$ s^{-1}, $k_{6\text{-}exo} = 5 \times 10^3$ s^{-1})[1d] indicating that C=N bonds are much better radical acceptors than C=C bonds. Furthermore, 5-*exo* cyclization is faster than 6-*exo* cyclization. Second, intramolecular additions of alkyl radicals to imines are essentially irreversible. Third, as predicted from data of the electron density at the iminyl carbon atom, alkyl radical additions to hydrazones ($k_{5\text{-}exo} > 2.5 \times 10^8$ s^{-1}, $k_{6\text{-}exo} = 4.7 \times 10^6$ s^{-1})[9] are much faster than alkyl radical additions to imines. The present result suggests that cyclization rates might be dependent on the electron densities at iminyl carbon atoms, although further studies are needed to clarify the relation between the cyclization rate and the electron density at the carbon atom of the radical acceptor.

Experimentals

General. ^{1}H NMR (200 MHz) and ^{13}C NMR (50.3 MHz) spectra were recorded in $CDCl_3$ on a Bruker Fourier Transform AC 200 spectrometers. IR spectra were recorded on a Bomem MB-100 Fourier Transform spectrophotometer. Analytical reversed-phase HPLC work was done using the Hitachi L-6200, L-4250, 655A-52, D-2500 system with Microsorb-MV 100A spherical silica-based 5μm amino (4.6mm x 25cm) column (3/97 IPA/Hexane isocratic solvent system with a flow rate of 0.5 mL/min) and using UV detection 250 nm. High-resolution mass spectra were obtained on a Jeol JMS-SX-102. Flash column chromatography was performed on silica gel (using E. Merck 230 - 400 mesh ASTM silica gel). Bu_3SnH was purchased from Aldrich Chemical Co., Inc., Milwaukee, WI.

5-Benzeneselenenylpentanal. By use of the known procedure,[13] 5-benzeneselenenylpentanenitrile was prepared from 5-chloropentanenitrile. 5-Benzeneselenenylpentanenitrile (1.89 g, 7.9 mmol) in CH_2Cl_2 (15 mL) in an apparatus protected from oxygen and moisture was cooled to -78°C, and diisobutylaluminum hydride in toluene (1.0 M, 10.3 mL, 10.3 mmol) was added dropwise over 15 min. When the addition was complete, the temperature was allowed to rise to 25°C and remain there for 2h. The reaction mixture was poured into a saturated aqueous ammonium chloride (30 mL) and the mixture was stirred vigorously for 50 min, after which CH_2Cl_2 (20 mL) and 5% HCl solution (5 mL) were added, and stirring was continued for an additional 3 h. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (40 mL x 2). The combined organic solutions were washed with saturated NaCl solution, dried over $MgSO_4$, and concentrated *in vacuo* to give an oil. The crude residue was purified by passing through a short column of silica gel to give 5-benzeneselenenylpentanal (1.53 g, 80%) as a colorless oil : IR (NaCl) 2932, 1721, 1578, 1477, 1437, 1071, 1022, 737, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.70 (s, 1H), 7.40-7.48 (m, 2H), 7.19-7.24 (m, 3H), 2.89 (t, 2H), 2.40 (t, 2H), 1.74-1.66 (m, 4H); ^{13}C NMR ($CDCl_3$) 201.9, 132.5, 130.0, 129.0, 126.7, 43.1, 29.4, 27.2, 22.0 ppm.

6-Benzeneselenenylhexanal was prepared from 6-benzeneselenenylhexanenitrile (1.89 g, 7.9 mmol) using the similar procedure described for 5-benzeneselenenylpentanal. The product was obtained as a colorless oil (1.61 g, 78%) : IR (NaCl) 2930, 1722, 1579, 1477, 1437, 1071, 1022, 737, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.73 (s, 1H), 7.42-7.48 (m, 2H), 7.21-7.24 (m, 3H), 2.88 (t, 2H), 2.39 (t, 2H), 1.73-1.58 (m, 4H), 1.46-1.41 (m, 2H); ^{13}C NMR ($CDCl_3$) 202.3, 132.4, 130.3, 128.9, 126.6, 43.6, 29.7, 29.0, 27.4, 21.4 ppm.

ω-Benzeneselenenylbenzylimine 1a. To a flask containing dry molecular sieves (4A, particle size 2-3 μl) in dry benzene (5 mL) at room temperature under a nitrogen atmosphere was added 5-benzeneselenenylpentanal (672 mg, 2.79 mmol) in dry benzene (4 mL) and benzylamine (299 mg, 2.79 mmol). The mixture was stirred for 1h, filtered off, and concentrated *in vacuo*. ω-Benzeneselenenylbenzylimine **1a** (894 mg, 97%) was isolated as colorless oil. : IR (NaCl) 2927, 1667, 1578, 1494, 1472, 1452, 1436, 1072, 1023, 735, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.74 (br s, 1H), 7.49-7.43 (m, 2H), 7.35-7.21 (m, 8H), 4.53 (s, 2H), 2.91 (t, 2H), 2.35-2.26 (m, 2H), 1.79-1.65 (m, 4H); ^{13}C NMR ($CDCl_3$) 165.5, 139.2, 132.5, 129.0, 128.4, 127.9, 126.9, 126.7, 65.0, 35.3, 29.7, 27.5, 26.0 ppm. HRMS(EI) m/z (M^+); calcd for $C_{18}H_{21}NSe$: 331.0839. Found: 331.0835.

ω-Benzeneselenenylbenzylimine 1b was prepared in 96% yield by the method described for **1a**.; IR (NaCl) 2928, 1662, 1579, 1494, 1477, 1453, 1073, 1024, 736, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.75 (br s, 1H), 7.45-7.48 (m, 2H), 7.34-7.21 (m, 8H), 4.54 (s, 2H), 2.89 (t, 2H), 2.31-2.25 (t, 2H), 1.77-1.66 (m, 2H), 1.61-1.42 (m, 4H); ^{13}C NMR ($CDCl_3$) 165.8, 139.3, 132.4, 130.4, 128.9, 128.4, 127.9, 126.9, 126.6, 65.0, 35.7, 29.6, 29.4, 27.7, 25.4 ppm. HRMS(EI) m/z (M^+); calcd for $C_{19}H_{23}NSe$: 345.0996. Found: 345.0990.

Kinetic experiments. For a typical experiment, weighed amounts of ω-benzeneselenenylbenzylimine **1a** (660 mg, 2.0 mmol) and benzene(5 mL) were placed in a 10 mL volumetric flask. The mixture was degassed with nitrogen, and degassed benzene was added by syringe to the mark. To 10 mL test tubes were added 0.5 mL of the stock solution of **1a**, and the appropriate amount of Bu_3SnH (0.40-1.40 mmol), a catalytic amount of AIBN and enough degassed benzene to fill the tube to the 2.5 mL mark. The tubes were degassed by the freeze-thaw method and placed in a constant temperature bath at 80°C(±1°C). After 1h, the tubes were cooled and the benzene was removed under reduced pressure. To detect the quenched imine **4a** effectively, products were reducted by $NaBH_4$(12 mg) in methanol(2 mL). Methanol was removed and the residue was acetylated with acetyl chloride(20 μl) and triethylamine(45 μl) in CH_2Cl_2 (2 mL) for 8 h. The solvent was removed under reduced pressure and the crude product was filtered through a short column of silica gel. Products compositions were determined by HPLC analysis by comparison with independently prepared authentic samples. Compound **6a**, **6b**[14] and **8b**[15] were previously known. **6a** was prepared by N-alkylation of N-benzyl acetamide with 1-bromopentane and potassium hydride in THF and **6b** was prepared by acetylation of benzyl n-hexylamine with acetyl chloride and triethylamine.

N-Benzyl-N-pentylacetamide (6a). IR (NaCl) 2940, 1645, 1435, 1364, 1248, 1029, 983, 730, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34-7.14 (m, 5H), 4.57(4.49) (s, 2H), 3.32(3.14) (t, 2H), 2.15(2.07) (s, 3H), 1.54-1.43 (m, 2H), 1.37-1.18 (m, 4H), 0.89-0.80 (m, 3H); ^{13}C NMR ($CDCl_3$) 170.7, 170.4, 137.8, 137.0, 128.8, 128.4, 127.9, 127.4, 127.1, 126.1, 51.8, 47.9, 47.8, 46.0, 29.0, 28.9, 28.0, 27.1, 22.4, 22.3, 21.8, 21.4, 13.9, 13.8 ppm. Analytical HPLC retention time, 13.78 min.

N-Benzyl-N-hexylacetamide (6b). IR (NaCl) 2935, 1645, 1495, 1439, 1364, 1245, 1029, 981, 730, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.32-7.12 (m, 5H), 4.56(4.48) (s, 2H), 3.32(3.14) (t, 2H), 2.13(2.06) (s, 3H), 1.52-1.46 (m, 2H), 1.20-1.32 (m, 6H), 0.87-0.81 (m, 3H); ^{13}C NMR ($CDCl_3$) 170.7, 170.3, 137.7, 136.9, 128.7, 128.3, 127.8, 127.3, 127.0, 126.0, 51.8, 47.9, 47.8, 46.0, 31.4, 31.3, 28.2, 27.4, 26.5, 26.3, 22.4, 22.3, 21.7, 21.3, 13.9, 13.8 ppm. Analytical HPLC retention time, 13.60 min.

N-Benzyl-N-cyclopentylacetamide (8a). A solution of cyclopentanone(421 mg, 5 mmol) and benzylamine (536 mg, 5 mmol) in CH_2Cl_2 (5 mL) was treated with $MgSO_4$ (1 g) at room temperature for 4 h. The mixture was filtered, washed with CH_2Cl_2 and concentrated to dryness. The crude product was dissolved in methanol(10 mL) and treated with $NaBH_4$ (76 mg, 2 mmol) at 0°C for 30min. The methanol solution was poured into water (40mL) and extracted with CH_2Cl_2 (30 mL x 2). After drying ($MgSO_4$) and removal of the solvent *in vacuo*, the crude oily product was acetylated with triethylamine(658 mg, 6.5 mmol) and acetyl chloride(471 mg, 6 mmol) in CH_2Cl_2 (12 mL) for 2 h. After usual workup, the crude product was purified by silica gel column chromatography to give **8a** (511 mg, 57%) as a colorless oil. IR (NaCl) 2954, 1642, 1430, 1354, 1214, 1030, 979, 731, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35-7.11 (m, 5H), 4.95-4.81(4.25-4.11) (m, 1H), 4.50(4.43) (s, 2H), 2.23(1.96) (s, 3H), 1.85-1.76 (m, 2H), 1.75-1.28 (m, 4H); ^{13}C NMR ($CDCl_3$) 171.5, 170.7, 139.1, 138.2, 128.5, 128.0, 126.9, 126.2, 125.4, 59.8, 55.5, 47.8, 44.7, 29.9, 29.0, 23.6, 23.5, 22.6, 22.1 ppm. HRMS(EI) m/z (M^+); calcd for $C_{14}H_{19}NO$: 217.1467. Found: 217.1452. Analytical HPLC retention time, 17.48 min.

N-Benzyl-N-cyclohexylacetamide (8b). N-Cyclohexyl-N-benzylacetamide **8b** was similarly prepared by the procedure used for **8a**. IR (NaCl) 2930, 1640, 1427, 1358, 1321, 1244, 1007, 978, 732, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34-7.13 (m, 5H), 4.52(4.44) (s, 2H), 4.61-4.43(3.70-3.52) (m, 1H), 2.19(1.96) (s, 3H), 1.81-1.50 (m, 5H), 1.48-1.12 (m, 4H), 1.11-0.97 (m, 1H); ^{13}C NMR ($CDCl_3$) 171.1, 170.5, 139.5, 138.4, 128.4, 128.0, 126.7, 126.2, 125.5, 58.4, 53.2, 47.3, 44.3, 31.8, 30.5, 25.7, 25.5, 25.3, 25.0, 22.3, 21.8 ppm. Analytical HPLC retention time, 15.04 min.

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References

1. For reviews, see: (a) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon Press: New York, 1986. (b) Curran, D. P. *Synthesis* **1988**, 417, 489. (c) Jasperse, C. P.; Curran, D. P. *Chem. Rev.* **1991**, *91*, 2137. (d) Curran, D. P. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1992; vol. 4, pp 715, 779.
2. (a) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073. (b) Beckwith, A. L. J.; Ingold, K. U. In Rearrangements in Ground and Excited States; DeMayo, P., Eds.; Academic: New York, 1980; Vol. 1, pp 188. (c) Newcomb, M. *Tetrahedron* **1993**, 49, 1151.
3. (a) Beckwith, A. L. J.; Kazlauskas, R.; Syner-Lyons, M. R. *J. Org. Chem.* **1983**, *48*, 4718. (b) Dowd, P.; Choi, S. C. *J. Am. Chem. Soc.* **1987**, *109*, 3493. (c) Dowd, P.; Choi, S. C. *J. Am. Chem. Soc.* **1987**, *109*, 6548. (d) Beckwith, A. L. J.; Hay, B. P. *J. Am. Chem. Soc.* **1989**, *111*, 230. (e) Beckwith, A. L. J.; Hay, B. P. *J. Am. Chem. Soc.* **1989**, *111*, 2674. (f) Walton, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1991**, *113*, 5791. (g) Dowd, P.; Zhang, W. *J. Am. Chem. Soc.* **1991**, *113*, 9875. (h) Beckwith, A. L. J.; Raner, K. D. *J. Org. Chem.* **1992**, *57*, 4954. (i) Dowd, P.; Zhang, W. *J. Org. Chem.* **1992**, *57*, 7163.
4. (a) Corey, E. J.; Pyne, S. G. *Tetrahedron Lett.* **1983**, *24*, 2821. (b) Hart, D. J.; Seely, F. L. *J. Am. Chem. Soc.* **1988**, *110*, 1631. (c) Bartlett, P.A.; Mclaren, K.L.; Ting, P.C. *J. Am. Chem. Soc.* **1988**, *110*, 1663. (d) Parker, K.A.; Spero, D. M.; Epp, J.V. *J. Org. Chem.* **1988**, *53*, 4628. (e) Enholm, E. J.; Burroff, J. A.; Jaramillo, L. M. *Tetrahedron Lett.* **1990**, *31*, 3727. (f) Barton, D.H.R.; Dalko, P.I.; Greco, S. D. *Tetrahedron Lett.* **1991**, *32*, 4713. (g) Marco-Contelles, J.; Pozuelo, C.; Jimeno, M. L.; Martinez, L.; Martinez-Grau, A. *J. Org. Chem.* **1992**, *57*, 2625. (h) Hart, D. J.; Ramanarayanan, K.; Pook, L. M.; Seely, F. L. *Tetrahedron Lett.* **1993**, *34*, 7819. (i) Naito, T.; Tajiri, K.; Harimoto, T.; Ninomiya, I.; Kiguchi, T. *Tetrahedron Lett.* **1994**, *35*, 2205.
5. (a) Kim, S.; Kee, I. S.; Lee, S. *J. Am. Chem. Soc.* **1991**, *113*, 9882. (b) Kim, S.; Kee, I. S. *Tetahedron Lett.* **1993**, *34*, 4213. (c) Sturino, C. F.; Fallis, A. G. *J. Am. Chem. Soc.* **1994**, *116*, 7447.
6. (a) Hatem, J.; Henriet-Bernard, C.; Grimaldi, J.; Maurin, R. *Tetrahedron Lett.* **1992**, *33*, 1057. (b) Kiguchi, T.; Tajiri, K.; Ninomiya, I.; Naito, T.; Hiramatsu, H. *Tetrahedron Lett.* **1995**, *36*, 253. (c) Kim, S.; Lee, I. Y.; Yoon, J. Y.; Oh, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 5138.
7. (a) Bowman, W. R.; Stephenson, P. T.; Terrett, N. K.; Young, A. R. *Tetrahedron Lett.* **1994**, *35*, 6369. (b) Bowman, W. R.; Stephenson, P. T.; Young, A. R. *Tetrahedron Lett.* **1995**, *36*, 5623.
8. Sturino, C. F.; Fallis, A. G. *J. Org. Chem.* **1994**, *59*, 6514.
9. Kim, S.; Cheong, J. H.; Yoon, K.S. *Tetrahedron Lett.* **1995**, *36*, 6069.
10. (a) Tomaszewski, M. J.; Warkentin, J. *J. Chem. Soc., Chem. Comm.* **1993**, 966. (b) Tomaszewski, M. J.; Warkentin, J. *Tetrahedron Lett.* **1992**, *33*, 2123.
11. Bowman, W. R.; Clark, D. N.; Marmon, R. J. *Tetrahedron* **1994**, *50*, 1275.
12. Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739.
13. Dowd, P.; Kennedy, P. *Synth. Commun.* **1981**, *11*, 935.
14. *Chem. Abstr.* **1986**, *107*,115328h.
15. Ishibashi, H.; Nakamura, N.; Ito, K.; Kitayama, S.; Ikeda, M. *Heterocycles* **1990**, *31*, 1781.

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