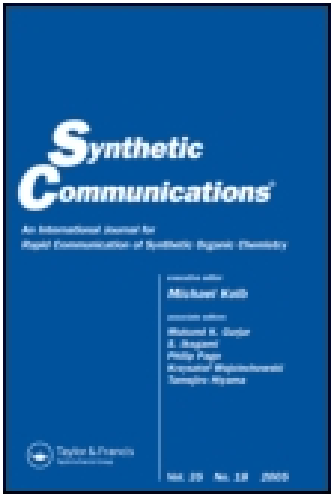


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Ring Opening of 5-(Bromomethyl)-2-Isoxazolines with Magnesium Metal in Absolute MeOH

Sung Jin Ha [b] , Ge Hyeong Lee [a] , In Kwon Yoon [b] & Chwang Siek Pak [a]

[a] Korea Research Institute of Chemical Technology , P.O.Box 107, Yusung, Taejeon, 305-600, Korea

[b] Pai Chai University, Department of Chemistry , Su-ku Domadong 439-6, Taejeon, 302-160, Korea

Published online: 17 Sep 2007.

To cite this article: Sung Jin Ha , Ge Hyeong Lee , In Kwon Yoon & Chwang Siek Pak (1999) Ring Opening of 5-(Bromomethyl)-2-Isoxazolines with Magnesium Metal in Absolute MeOH, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 29:18, 3165-3177, DOI: 10.1080/00397919908085941

To link to this article: http://dx.doi.org/10.1080/00397919908085941

SYNTHETIC COMMUNICATIONS, 29(18), 3165-3177 (1999)

RING OPENING OF 5-(BROMOMETHYL)-2-ISOXAZOLINES WITH MAGNESIUM METAL IN ABSOLUTE MeOH

Sung Jin Ha,[b] Ge Hyeong Lee,[a] In Kwon Yoon,[b] and Chwang Siek Pak*[a]

[a] Korea Research Institute of Chemical Technology, P.O.Box 107, Yusung, Taejeon 305-600, Korea. [b] Pai Chai University, Department of Chemistry, Su-ku Domadong 439-6, Taejeon 302-160, Korea

Abstract: Ring opening of 5-(bromomethyl)- and 5-(phenylsulfonylmethyl)-2-isoxazolines with magnesium in absolute methanol at -23 °C and room temperature afforded regiospecifically β,γ-enoximes and (*E*)-α,β-enoximes, respectively

In our continuing efforts to expand the synthetic utility and reaction mechanism of magnesium metal in absolute alcohol as a convenient electron transfer agent,[1] we have recently reported that magnesium metal in absolute methanol facilitates the *C-O* bond cleavage of 2-(halomethyl)oxiranes and 5-(halomethyl)-1,3-dioxolanes and β-alkoxy phenylsulfones to afford allylic alcohols[2] and *E*-alkenes[3], respectively. These results prompted the efforts described below. Here we report the results of reductive *C-O* bond cleavage of 5-

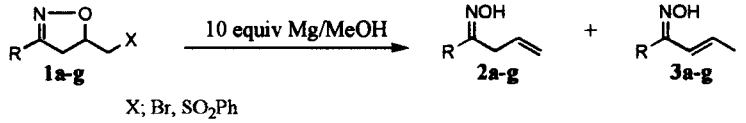
* To whom correspondence should be addressed.

(bromomethyl)- and 5-(phenylsulfonylmethyl)-2-isoxazolines with magnesium metal in absolute methanol to give regiospecifically β,γ-enoximes and (*E*)-α,β-enoximes, respectively, depending on the reaction conditions as shown in Table 1.

5-(Bromomethyl)-2-oxazolines (**1a-g**) were prepared from allyl halides or allyl sulfone and chlorooximes as precursors of nitrile oxides.[4] Except for **1g**, on treatment of **1a-f** with 10 equiv of magnesium metal in absolute MeOH at 0 °C for 2 h, *C-Br* and *C-S* bond cleavages take place to give **2a-f** and/or **3a-f**, depending upon the substrate, in very high yields (85-97%). Interestingly, however, regiospecific enoximes were obtained depending upon the reaction conditions, regardless of the substrate. At –23 °C, only β,γ-enoximes (**2a-f**) were obtained in high yield (93-99%). These β,γ-enoximes isomerized at room temperature to afford more thermodynamically stable (*E*)-α,β-enoximes (**3a-f**). In case of chloride **1g**, *C-Cl* bond was inert and the starting material was recovered quantitatively. It has been reported that the *C-Cl* bond is inert to magnesium metal in absolute MeOH.[2,5] This phenomenon is the same as the previous results[2,6] and the reaction mechanism of bond cleavage proceeds through the carbanion generated in a stepwise single electron transfer from magnesium metal to the substrate to cleave the *C-O* bond of oxazoline ring shown in Scheme I.

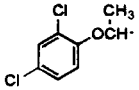
In contrast to the behaviour with zinc or zinc/copper,[7] the equilibrium takes between β,γ- and α,β-enoximes due to the presence of $Mg(OMe)_2$. To investigate the effect of $Mg(OMe)_2$ on the ratio of **2** to **3**, β,γ-enoxime **2b** was treated separately with 2 and 5 equiv of $Mg(OMe)_2$, respectively, in absolute MeOH at room temperature. After 3.5 h, when 5 equiv of $Mg(OMe)_2$ was used, only (*E*)-α,β-enoxime **3b** was obtained in 95% yield without contamination of **2b**.

Table 1. *C-O* Bond cleavage of 5-(bromomethyl)- and 5-(phenylsulfonylmethyl)-2-isoxazolines with magnesium metal in absolute methanol.



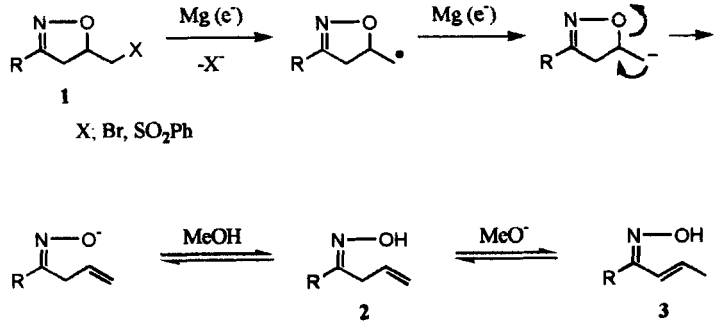
1a-g **2a-g** **3a-g**

X; Br, SO_2Ph

Substrate	R	X	Temp (°C)[a,b]	Time (h)	Ratio (**2/3**)[c]	Yields (%)[d]
1a	Bn	Br	A	1.5	1/0	97
			B	2	1/0	91
			C	6	0/1	90
1b	$PhCH_2CH_2$	Br	A	1.5	1/0	95
			B	0.5	1/0	48[e]
			B	2	1/7.93	91
			C	6	0/1	89
1c		Br	A	1.5	1/0	96
			B	2	0/1	91
			C	6	0/1	92
1d	cyclohexyl	Br	A	1.5	1/0	94
			B	2	1/16.5	90
			C	6	0/1	90
1e	n-C_6H_{13}	Br	A	1.5	1/0	93
			B	2	1.6/1	87
			C	6	0/1	91
1f	Bn	SO_2Ph	A	1.5	1/0	99
			B	2	3.2/1	97
			C	6	0/1	98
1g	Bn	Cl	C	6	-	-[f]

[a] $HgCl_2$ was used as catalyst at –23 °C. [b] A; -23 °C, B; 0 °C, C; 0 °C-rt. [c] Ratios were determined by ^1H NMR. [d] Isolated. [e] **1b** (50%) was recovered. [f] No reaction.

Scheme I

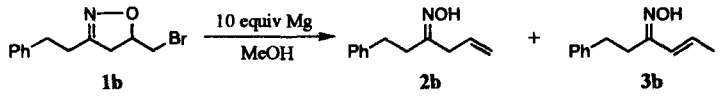


When 2 equiv of $Mg(OMe)_2$ was used, however, a mixture of **2b** and **3b** was quantitatively obtained in the ratio of 3:7, determined by ^1H NMR spectroscopy. This result indicates that only one isomer may be obtained, depending upon reaction conditions such as the reaction time and temperature. 5-Bromomethyl-3-phenethyloxazoline **1b** was treated with magnesium metal under various reaction conditions to give the expected results as shown in Table 2. Oxazoline **1b** gave only β,γ-enoxime **2b** in 95% yield at –23 °C and the isomerized (*E*)-α,β-enoxime **3b** in 89% yield at room temperature after 6 h.

The resulting isomeric enoximes could be transformed to α,β-[8] or β,γ-enones[7a,7b] through known reactions. The (*E*)-α,β-enones were obtained in good yields (68%) from (*E*)-α,β- and/or β,γ-enoximes by the oxime exchange reaction with 1,1,1-trifluoro-2,4-pentanedione, as shown in Table 3.

In summary, through the ring opening of 5-(bromomethyl)- and 5-(phenylsulfonylmethyl)-2-isoxazolines with magnesium metal in absolute MeOH, (*E*)-α,β- and β,γ-enoximes can be obtained regiospecifically depending upon the reaction temperature.

Table 2. Reaction of **1b** with magnesium metal in various reaction conditions.

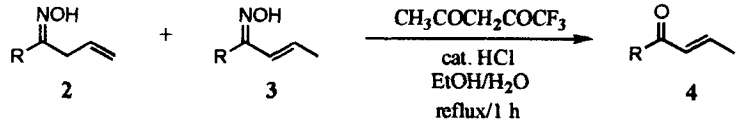


1b **2b** **3b**

Temperature (°C)	Time (h)	Ratio (**2b/3b**)[a]	Isolated yields (%)
-23	1.5	1/0	95[b]
0	0.5	1/0	48[c]
0	2	1/7.93	91
0	3	1/8.12	90
0-rt	6	0/1	89

[a] Ratios were determined by ^{1}H NMR. [b] $HgCl_2$ was used as catalyst. [c] **1b** (50%) was recovered.

Table 3. Reaction of enoximes with 1,1,1-trifluoro-2,4-pentanedione.



2 **3** **4**

Substrare	Product	Isolated yields (%)
3a	**4a**	70
2b/3b	**4b**	68
3c	**4c**	73
2d/3d	**4d**	75
2e/3e	**4e**	70

Experimental Section

General. Melting points were measured in open capillary tubes and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 200 MHz, unless otherwise specified, in $CDCl_3$ solution using tetramethylsilane as internal standard.

Analytical thin-layer chromatography was performed on precoated silica gel plates (0.25-mm 60 F-254 E. Merck). Methanol was dried over magnesium prior to use.

Representative Procedure for the Synthesis of Isoxazolines

Preparation of 3-Benzyl-5-bromethylisoxazoline (1a). To a stirred solution of 3-phenylpropionaldoxime (2.68 g, 20 mmol), allyl bromide (2.90 g, 24 mmol), and dry pyridine (0.32 g, 4 mmol) in $CHCl_3$ (50 mL) was added dropwise a solution of NaOCl (10%, 30 mL, 40 mmol) over 1.5 h at 0 °C. After 2 h, the organic layer was separated and washed with 2N HCl and saturated $NaHCO_3$ solution, respectively. The organic layer was dried over $MgSO_4$, filtered, and then concentrated *in vacuo* to afford a pale yellow oil, which was purified by flash column chromatography (SiO_2, n-hexane/EtOAc; 3/1) to give **1a** (2.68 g, 53%) as a colorless oil.

TLC R_f 0.37 (hexane/EtOAc; 3/1); ^{1}H NMR (200 MHz) δ 7.18-7.32 (m, aromatic, 5 H), 4.69-4.84 (m, 1 H), 3.67 (s, 2 H), 3.42 (dd, J = 10.2, 4.5 Hz, 1 H), 3.26 (dd, J = 10.2, 7.8 Hz, 1 H), 2.98 (dd, J = 17.0, 6.5 Hz, 1 H), 2.74 (dd, J = 17.0, 7.5 Hz, 1 H); MS *m/e* (rel intensity) 254 (M^+, 7.2), 91 (100). Anal. Calcd for $C_{11}H_{12}BrNO$: C, 51.99; H, 4.76. Found: C, 52.05; H, 4.71.

5-Bromomethyl-3-phenethylisoxazoline (1b): Yield 45%; TLC R_f 0.40 (hexane/EtOAc; 3/1); ^{1}H NMR (200 MHz) δ 7.13-7.28 (m, aromatic, 5 H), 4.63-4.74 (m, 1 H), 3.36 (dd, J = 10.3, 4.1 Hz, 1 H), 3.15 (dd, J = 10.3, 8.1 Hz, 1 H), 2.57-3.04 (m, 6 H); MS *m/e* (rel intensity) 268 (M^+, 2.9), 91 (100). Anal. Calcd for $C_{12}H_{14}BrNO$: C, 53.75; H, 5.26. Found: C, 53.94; H, 5.17.

5-Bromomethyl-3-[1-(2,4-dichlorophenoxy)ethyl]isoxazoline (1c): Yield 33%; TLC R_f 0.54 (hexane/CH_2Cl_2; 1/1); ^{1}H NMR (200 MHz) δ 7.40 (d, J = 2.5 Hz, aromatic, 1 H), 7.19 (d, J = 2.5 Hz, aromatic, 1 H), 6.70-7.04 (m, aromatic, 1 H), 5.25-5.34 (m, 1 H), 4.82-4.93 (m, 1 H), 3.30-3.58 (m, 2 H), 2.90-3.28 (m, 2 H), 1.64-1.68 (m, 3 H); MS *m/e* (rel intensity) 353 (M^+, 13.0), 43 (100). Anal. Calcd for $C_{12}H_{12}BrCl_2NO_2$: C, 40.83; H, 3.43. Found: C, 41.01; H, 3.42.

5-Bromomethyl-3-cyclohexylisoxazoline (1d): Yield 51%; TLC R_f 0.36 (hexane/EtOAc; 10/1); ^{1}H NMR (200 MHz) δ 4.69-4.84 (m, 1 H), 3.43-3.51 (m, 1 H), 3.23 (dd, J = 10.8, 8.1 Hz, 1 H), 3.10 (dd, J = 17.3, 10.1 Hz, 1 H), 2.87 (dd, J = 17.3, 6.2 Hz, 1 H), 2.34-2.41 (m, 1 H), 1.67-1.84 (m, 5 H), 1.17-1.44 (m, 5 H); MS *m/e* (rel intensity) 246 (M^+, 5.1), 197 (36), 177 (39), 152 (79), 83 (69), 55 (100). Anal. Calcd for $C_{10}H_{16}BrNO$: C, 48.80; H, 6.55. Found: C, 48.97; H, 6.47.

5-Bromomethyl-3-hexylisoxazoline (1e): Yield 50%; TLC R_f 0.29 (hexane/CH_2Cl_2; 1/1); ^{1}H NMR (200 MHz) δ 4.72-4.87 (m, 1 H), 3.49 (dd, J = 10.3, 4.3 Hz, 1 H), 3.32 (dd, J = 10.3, 8.0 Hz, 1 H), 3.11 (dd, J = 17.4, 10.3 Hz, 1 H), 2.88 (dd, J = 17.4, 6.4 Hz, 1 H), 2.35 (t, J = 7.5 Hz, 2 H), 1.49-1.64 (m, 2 H), 1.26-1.41 (m, 6 H), 0.87 (t, J = 6.5 Hz, 3 H); MS *m/e* (rel intensity) 248 (M^+, 3.8), 179 (34), 154 (30), 43 (100). Anal. Calcd for $C_{10}H_{18}BrNO$: C, 48.40; H, 7.31. Found: C, 48.51; H, 7.25.

3-Benzyl-5-phenylsulfonylmethylisoxazoline (1f): Yield 68%; TLC R_f 0.37 (hexane/EtOAc; 2/1); ^{1}H NMR (200 MHz) δ 7.86-7.91 (m, aromatic, 1 H), 7.52-

7.72 (m, aromatic, 3 H), 7.15-7.53 (m, aromatic, 6 H), 4.84-4.92 (m, 1 H), 3.66 (s, 2 H), 3.51 (dd, J = 14.1, 4.7 Hz, 1 H), 3.01-3.26 (m, 2 H), 2.84 (dd, J = 17.5, 7.4 Hz, 1 H); MS *m/e* (rel intensity) 315 (M^+, 1.5), 43 (100). Anal. Calcd for $C_{17}H_{17}NO_3S$: C, 64.74; H, 5.43. Found: C, 64.82; H, 5.29.

3-Benzyl-5-Chloromethylisoxazoline (1g): Yield 41%; TLC R_f 0.32 (hexane/EtOAc; 5/1); ^{1}H NMR (200 MHz) δ 7.13-7.34 (m, aromatic, 5 H), 4.66-4.77 (m, 1 H), 3.66 (s, 2 H), 3.37-3.59 (m, 2 H), 2.68-3.02 (m, 2 H); MS *m/e* (rel intensity) 209 (M^+, 19.3), 160 (25), 91 (100). Anal. Calcd for $C_{11}H_{12}ClNO$: C, 63.01; H, 5.77. Found: C, 63.17; H, 5.82.

Representative Procedure for the Ring Cleavage of Isoxazoline with magnesium metal: A mixture of isoxazoline **1a-g** (2.0 mmol), magnesium (468 mg, 20.0 mmol, -50 mesh), and a few crystals of $HgCl_2$ (without at 0 °C and 0 °C-rt) in absolute MeOH was stirred for 1.5 h at –23 °C (2 h at 0 °C and 6 h at 0 °C-rt). The reaction mixture was poured into cold 0.5 N HCl solution and extracted with ether (50 mL x 2). The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried ($MgSO_4$), filtered, and then concentrated *in vacuo* to give product (**2a-f** and/or **3a-f**) which was purified by flash column chromatography (SiO_2).

1-Phenyl-5-hexen-3-one oxime (2b): TLC R_f 0.34 (hexane/EtOAc; 5/1); ^{1}H NMR (200 MHz) δ 9.40 (br s, OH, 1 H), 7.13-7.31 (m, 5 H), 5.78-5.95 (m, 1 H), 5.07-

5.18 (m, 2 H), 3.17 (td, J = 6.8, 1.4 Hz, 2 H), 2.79-2.89 (m, 2 H), 2.40-2.55 (m, 2 H); MS *m/e* (rel intensity) 189 (M^+, 3.1), 43 (100). HRMS calcd. for $C_{12}H_{15}NO$: 189.1154; found: 189.1163.

2-(2,4-Dichlorophenoxy)-5-hexen-3-one oxime (2c): TLC R_f 0.18 (hexane/CH_2Cl_2; 1/1); ^1H NMR (200 MHz) δ 8.36 (br s, OH, 1 H), 7.35 (d, J = 2.5 Hz, aromatic, 1 H), 7.11 (dd, J = 8.8, 2.5 Hz, aromatic, 1 H), 6.89 (d, J = 8.8 Hz, aromatic, 1 H), 5.64-5.94 (m, 1 H), 4.88-5.17 (m, 3 H), 3.18 (d, J = 6.6 Hz, 2 H), 1.56 (d, J = 6.6 Hz, 3 H); MS *m/e* (rel intensity) 274 (M^+, 4.3), 162 (31), 112 (89), 81 (100). HRMS calcd. for $C_{12}H_{13}Cl_2NO_2$: 273.0323; found: 273.0330.

1-Cyclohexyl-3-buten-1-one oxime (2d): TLC R_f 0.32 (hexane/EtOAc; 10/1); ^1H NMR (200 MHz) δ 8.92 (br s, OH, 1 H), 5.77-5.97 (m, 1 H), 5.03-5.15 (m, 2 H), 3.11 (td, J = 6.5, 1.5 Hz, 2 H), 2.08-2.21 (m, 1 H), 1.60-1.89 (m, 5 H), 1.16-1.38 (m, 5 H); MS *m/e* (rel intensity) 167 (M^+, 5.3), 83 (30), 41 (100). HRMS calcd. for $C_{10}H_{17}NO$: 167.1310; found: 167.1322.

1-Decen-4-one oxime (2e): TLC R_f 0.31 (hexane/EtOAc; 10/1); ^1H NMR (200 MHz) δ 8.93 (br s, OH, 1 H), 5.85-5.96 (m, 1 H), 5.00-5.25 (m, 2 H), 2.17-2.24 (m, 2 H), 1.88-1.92 (m, 2 H), 1.22-1.55 (m, 8 H), 0.86-0.92 (m, 3 H); MS *m/e* (rel intensity) 169 (M^+, 8.2), 99 (53), 84 (32), 41 (100). HRMS calcd. for $C_{10}H_{19}NO$: 169.1467; found: 169.1466.

***(E)*-1-Phenyl-3-penten-2-one oxime (3a):** TLC R_f 0.35 (hexane/EtOAc; 5/1); ^1H

NMR (200 MHz) δ 8.92 (br s, OH, 1 H), 7.13-7.35 (m, 5 H), 6.74-6.86 (m, 1 H), 6.12-6.31 (m, 1 H), 3.70 (s, 2 H), 1.78 (m, 3 H); MS *m/e* (rel intensity) 175 (M^+, 4.9), 43 (100). HRMS calcd. for $C_{11}H_{13}NO$: 175.0997; found: 175.0993.

(*E*)-1-Phenyl-4-hexen-3-one oxime (3b): TLC R_f 0.34 (hexane/EtOAc; 5/1); ^1H NMR (200 MHz) δ 9.05 (br s, OH, 1 H), 7.17-7.36 (m, 5 H), 6.85 (qd, J = 1.7, 1.6 Hz, 1 H), 6.26 (qd, J = 16.2, 6.7 Hz, 1 H), 2.82-2.92 (m, 2 H), 2.62-2.73 (m, 2 H), 1.91 (dd, J = 6.7, 1.7 Hz, 3 H); MS *m/e* (rel intensity) 189 (M^+, 7.2), 43 (100). HRMS calcd. for $C_{12}H_{15}NO$: 189.1154; found: 189.1160.

(*E*)-1-Cyclohexyl-2-buten-1-one oxime (3d): TLC R_f 0.32 (hexane/EtOAc; 10/1); ^1H NMR (200 MHz) δ 8.92 (br s, OH, 1 H), 6.63-6.74 (m, 1 H), 6.14-6.39 (m, 1 H), 3.09-3.13 (m, 2 H), 2.34-2.5- (m, 1 H), 1.60-1.89 (m, 5 H), 1.16-1.38 (m, 5 H); MS *m/e* (rel intensity) 167 (M^+, 7.3), 83 (50), 41 (100). HRMS calcd. for $C_{10}H_{17}NO$: 167.1310; found: 167.1317.

(*E*)-2-Decen-4-one oxime (3e): TLC R_f 0.31 (hexane/EtOAc; 10/1); ^1H NMR (200 MHz) δ 8.93 (br s, OH, 1 H), 6.17-6.29 (m, 1 H), 5.08-5.18 (m, 1 H), 2.32-2.39 (m, 2 H), 1.88-1.92 (m, 2 H), 1.22-1.55 (m, 8 H), 0.86-0.92 (m, 3 H); MS *m/e* (rel intensity) 169 (M^+, 5.9), 99 (73), 84 (59), 67 (48), 41 (100). HRMS calcd. for $C_{10}H_{19}NO$: 169.1467; found: 169.1459.

Representative Oxime-exchange Reaction of α,β- and/or β,γ-enoximes with 1,1,1-trifluoro-2,4-pentadione: A solution of a,b- and/or b,g-enoxime (1.0 mmol),

1,1,1-trifluoro-2,4-pentadione (1.5 mmol), and catalytic amount of conc. HCl in aqueous ethanol ($EtOH/H_2O$; 1/1) was refluxed for 1 h. The reaction mixture was allowed to cool to room temperature and extracted with ether (30 mL x 2). The combined organic layer was washed with 1 N NaOH solution and brine, dried ($MgSO_4$), filtered, and then concentrated *in vacuo* to give (*E*)-α,β-enone (**4**) which was purified by flash column chromatography (SiO_2).

(*E*)-1-Pneyl-3-penten-2-one (4a): TLC R_f 0.26 (hexane/EtOAc; 10/1); ^{1}H NMR (200 MHz) δ 7.17-7.36 (m, 5 H), 6.92 (qd, J = 14.0, 6.9 Hz, 1 H), 6.15 (qd, J = 14.0, 1.6 Hz, 1 H), 3.80 (s, 2 H), 1.86 (dd, J = 6.9, 1.6 Hz, 3 H); MS *m/e* (rel intensity) 160 (M^+, 2.5), 149 (15), 91 (100). HRMS calcd. for $C_{11}H_{12}O$: 160.0888; found: 160.0879.

(*E*)-1-Phenyl-4-hexen-3-one (4b): TLC R_f 0.29 (hexane/EtOAc; 5/1); ^{1}H NMR (200 MHz) δ 7.17-7.34 (m, 5 H), 6.77-6.92 (m, 1 H), 6.09-6.19 (m, 1 H), 2.82-3.01 (m, 4 H), 1.90 (dd, J = 6.9, 1.6 Hz, 3 H); MS *m/e* (rel intensity) 174 (M^+, 66), 159 (94), 105 (64), 91 (78), 69 (100). HRMS calcd. for $C_{12}H_{14}O$: 174.1045; found: 174.1051.

(*E*)-2-(2,4-Dichlorophenoxy)-4-hexen-3-one (4c): TLC R_f 0.50 (hexane/EtOAc; 5/1); ^{1}H NMR (200 MHz) δ 7.39 (d, J = 1.5 Hz, aromatic, 1 H), 7.07-7.19 (m, aromatic, 2 H), 6.62 (d, J = 13.2 Hz, 1 H), 6.47-6.56 (m, 1 H), 4.71 (q, J = 6.9 Hz, 1 H), 1.91 (dd, J = 7.0, 1.5 Hz, 3 H), 1.58 (d, J = 6.9 Hz, 3 H); MS *m/e* (rel

intensity) 259 (M^+, 0.9), 181 (31), 97 (66), 69 (100). HRMS calcd. for $C_{11}H_{12}Cl_2O_2$: 258.0214; found: 258.0222.

(*E*)-1-Cyclohexyl-2-buten-1-one (4d): TLC R_f 0.38 (hexane/EtOAc; 10/1); ^{1}H NMR (200 MHz) δ 6.88 (qd, J = 15.4, 6.8 Hz, 1 H), 6.13-6.23 (m, 1 H), 2.47-2.60 (m, 1 H), 1.89 (dd, J = 6.5, 1.4 Hz, 3 H), 1.62-1.82 (m, 5 H), 1.22-1.45 (m, 5 H); MS *m/e* (rel intensity) 152 (M^+, 3.8), 137 (43), 86 (67), 84 (100), 69 (92), 55 (89). HRMS calcd. for $C_{10}H_{16}O$: 152.1201; found: 152.1211.

(*E*)-2-Decen-4-one (4e): TLC R_f 0.50 (hexane/EtOAc; 5/1); ^{1}H NMR (200 MHz) δ 6.75-6.90 (m, 1 H), 6.06-6.16 (m, 1 H), 2.51 (t, J = 7.5 Hz, 2 H), 1.90 (dd, J = 7.0, 1.6 Hz, 3 H), 1.51-1.67 (m, 2 H), 1.20-1.37 (m, 6 H), 0.85-0.91 (m, 3 H); MS *m/e* (rel intensity) 154 (M^+, 8.3), 97 (47), 84 (100). HRMS calcd. for $C_{10}H_{18}O$: 154.1358; found: 154.1351.

Acknowledgement. We thank the Ministry of Science and Technology for financial support.

REFERENCES

1. (a) Lee, G. H.; Lee, H. K.; Choi, E. B.and Pak, C. S. *Bull. Korean Chem. Soc.* **1995**, *16*, 1141. (b) Lee, G. H.; Choi, E. B.; Lee, E. and Pak, C. S. *J Org. Chem.* **1994**, *59*, 1428.
2. Lee, G. H.; Choi, E. B.; Lee, E, and Pak, C. S. *J Org. Chem.* **1993**, *58*, 1523.

3. Lee, G. H.; Lee, H. K.; Choi, E. B.; Kim, B. T. and Pak, C. S. *Tetrahedron Lett.* **1995**, *36*, 5607.

4. (a) Huisgen, R. *J. Org. Chem.* **1976**, *41*, 403. (b) Christl, M. and Huisgen, R. *Chem. Ber.* **1973**, *106*, 3345.

5. Hutchins, R. O. and Suchismita *Synth. Commun.* **1989**, *19*, 1519.

6. Lee, G. H.; Choi, E. B.; Lee, E. and Pak, C. S. *Tetrahedron Lett.* **1993**, *34*, 4541.

7. (a) Jäger, V.; Grund, H. and Schwab, W. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 78. (b) Timms, G. H. and Wildsmith, E. *Tetrahedron Lett.* **1971**, 195. (c) Corey, E. J. and Richman, J. E. *J. Am. Chem. Soc.* **1970**, *92*, 5276.

8. Kim, J. N.; Chung, K. H. and Ryu, E. G. *Bull. Korean Chem. Soc.* **1991**, *12*, 8.

Received in the UK 30 November 1998