The Catalytic Sakurai Reaction

Phil Ho Lee,*,† Kooyeon Lee,† Sun-young Sung,† and Sukbok Chang‡

Department of Chemistry, Kangwon National University, Chunchon 200-701, Republic of Korea, and Department of Chemistry, Ewha Womans University, Seoul 120-750, Republic of Korea

phlee@kangwon.ac.kr

Received June 4, 2001

Introduction

Sakurai reactions, Lewis acid additions of allyltrimethylsilane with conjugated enones to form δ,ϵ-enones,[1] have been extensively applied in organic synthesis, in natural product synthesis,[2] and in the preparation of some heterocyclic compounds.[3] They are now considered to be one of the most efficient means of C−C bond formation, and examples of both inter- and intramolecular reactions[4] have been reported. Sakurai reactions are regiospecific with regard to the newly formed C−C bond. The range of Lewis acids employed in Sakurai reactions is extensive, among which $TiCl_4$, $AlCl_3$, and BF_3:OEt_2 are in general the most effective for the allylations. In all cases, however, the procedures require a stoichiometric amount or even an excess of the Lewis acid to obtain reasonable reaction rates and acceptable yields of products. Although a few examples of catalytic Sakurai reactions have been reported,[4j,k] herein we disclose a novel and catalytic Sakurai reaction using catalytic amounts of $InCl_3$ in the presence of trimethylsilyl chloride (TMSCl).

Results and Discussion

During the course of our studies of indium-mediated organic transformation,[5] we observed an interesting result of Lewis acidity of $InCl_3$. When $InCl_3$ was added in a stoichiometric amount to a solution of 2-cyclohexen-1-one (**1**) in $CDCl_3$, the ^1H NMR spectrum of the resulting solution exhibited two peaks at 6.16 and 7.13 ppm, which correspond to the α- and β-protons, respectively (Scheme 1). Although chemical shifts of the α- and β-protons were shifted downfield relative to those of **1**, the enone moiety of **1** was maintained. In contrast, the enone moiety of **1** was entirely consumed to produce allylic carbocation species **3** in the presence of stoichiometric amounts of $TiCl_4$ indicating that the Ti complex coordinates to the enone irreversibly. These results strongly imply that although $InCl_3$ activates 2-cyclohexen-1-one, the extent of the activation is weak enough to have a reversible coordination; thus, $InCl_3$ may act as a catalyst in Sakurai reactions.

Representative results are summarized in Table 1. The choice of the solvent was important in this reaction, and of the solvents tested CH_2Cl_2, $CHCl_3$, THF, DMF and H_2O, CH_2Cl_2 and $CHCl_3$ were the only choices. When α,β-enone **1** was treated with allyltrimethylsilane in the presence of a stoichiometric amount of $InCl_3$ in dichloromethane, 1,4-addition product **4** was produced in a 62% yield (entry 1). When this reaction was carried out with 0.5 equiv of $InCl_3$, **4** was isolated in a 52% yield (entry 2). However, **4** was not obtained with 0.25 equiv of $InCl_3$ (entry 3). Thus, we next examined the effects of some additives on the reaction and found that the reaction could indeed be catalytic with $InCl_3$ in the presence of TMSCl. Of the catalytic systems examined, *the best results were obtained with the combination of 0.1 equiv of $InCl_3$ and 5 equiv of TMSCl* (entry 6). The use of less than 5 equivalents of TMSCl gave lower yields as well as longer reaction times (entry 5). Surprisingly, 1,4-addition product **4** was not produced at all with a catalytic amount of $TiCl_4$ and $AlCl_3$ regardless of the presence of TMSCl (entries 13−15). Even when InF_3 and $In(OTf)_3$, which are stronger Lewis acids than $InCl_3$, were used, the desired product was obtained in lower yield (entries 8−11).

To demonstrate the efficiency and scope of the present method, we applied this catalytic system to a variety of α,β-enones. The results are summarized in Table 2. Under the optimized conditions, methyl vinyl ketone was reacted to allyltrimethylsilane to afford 6-hepten-2-one in a 62% yield (entry 1). It should be noted that other acyclic α,β-enones (entries 2−6) containing a β-substitu-

* To whom correspondence should be addressed.
† Kangwon National University.
‡ Ewha Womans University.

(1) (a) Colvin, E. *Silicon in Organic Synthesis*; Butterworth: London, 1981; p 97. (b) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983; Vol. 12, p 173. (c) Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200. (d) Fleming, I.; Dunogues, J.; Smithers, R. *Org. React.* **1989**, *37*, 57. (e) Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, *95*, 1375. (f) Hosomi, A.; Sakurai, H. *J. Am. Chem. Soc.* **1977**, *99*, 1673. (g) Ojima, I.; Kumagai, M.; Miyazawa, Y. *Tetrahedron Lett.* **1977**, *18*, 1385. (h) Pardo, R.; Zahra, J.-P.; Santelli, M. *Tetrahedron Lett.* **1979**, *20*, 4557. (i) Fleming, I.; Paterson, I. *Synthesis* **1979**, 446. (j) Yanami, T.: Miyashita, M.: Yoshikoshi, A. *J. Org. Chem.* **1980**, *45*, 607. (k) Hosomi, K.: Kobayashi, H.; Sakurai, H. *Tetrahedron Lett.* **1980**, *21*, 955. (l) Majetich, G.; Casares, A. M.; Chapman, D.; Behnke, M. *Tetrahedron Lett.* **1983**, *24*, 1909. (m) Blumenkopf, T. A.; Heathcock, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 2354.

(2) (a) Tokoroyama, T.; Tsukamoto, M.; Asada, T.; Iio, H. *Tetrahedron Lett.* **1987**, *28*, 6645. (b) Nakamura, H.; Oya, T.; Murai, A. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 929. (c) Majetich, G.; Defauw, J. *Tetahedron* **1988**, *44*, 3833. (d) Yamamoto, Y.; Furuta, T. *J. Org. Chem.* **1990**, *55*, 3971. (e) Majetich, G.; Song, J.-S.; Ringold, C.; Nemeth, G. A. *Tetrahedron Lett.* **1990**, *31*, 2239. (f) Majetich, G.; Lowery, D.; Khetani, V.; Song, J.-S.; Hull, K.; Ringold, C. *J. Org. Chem.* **1991**, *56*, 3988. (g) Majetich, G.; Hull, K. *Tetrahedron* **1987**, *43*, 5621. (h) Dauben, W. G.; Friedrich, L. F.; Oberhansli, P.; Aoyagi, E. I. *J. Org. Chem.* **1972**, *37*, 9. (i) Majetich, G.; Ringold, C. *Heterocycles* **1987**, *25*, 271. (j) Majetich, G.; Behnke, M.; Hull, K. *J. Org. Chem.* **1985**, *50*, 3615. (k) Schinzer, D.; Feber, K.; Puppelt, M. *Justus Liebigs Ann. Chem.* **1992**, 139.

(3) (a) Heathcock, C. H.; Kleinman, E. F.; Binkley, E. S. *J. Am. Chem. Soc.* **1982**, *104*, 1054. (b) Majetich, G.; Song, J.-S.; Leigh, A. J.; Condon, S. M. *J. Org. Chem.* **1993**, *58*, 1030. (c) Kuroda, C.; Inoue, S.; Takemura, R.; Satoh, J. Y. *J. Chem. Soc., Perkin Trans. 1* **1994**, 521.

(4) (a) Schinzer, D. *Synthesis* **1988**, 263. (b) Schinzer, D.; Allagiannis, C.; Wichmann, S. *Tetrahedron* **1988**, *44*, 3851. (c) Schinzer, D.; Solyom, S.; Becker, M. *Tetrahedron Lett.* **1985**, *26*, 1831. (d) Majetich, G.; Desmond, R.; Casares, A. M. *Tetrahedron Lett.* **1983**, *24*, 1913. (e) Wilson, S. R.; Price, M. F. *J. Am. Chem. Soc.* **1982**, *104*, 1124. (f) Tokoroyama, T.; Tsukamoto, M.; Iio, H. *Tetrahedron Lett.* **1984**, *25*, 5067. (g) Schinzer, D. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 308. (h) Majetich, G.; Defauw, J.; Hull, K.; Shawe, T. *Tetrahedron Lett.* **1985**, *26*, 4711. (i) Majetich, G.; Hull, K.; Defauw, J.; Shawe, T. *Tetrahedron Lett.* **1985**, *26*, 2755. (j) Schinzer, D.; Ringe, K. *Synlett* **1994**, 463. (k) Kuhnert, N.; Peverley, J.; Robertson, J. *Tetrahedron Lett.* **1998**, *39*, 3215.

(5) (a) Lee, P. H.; Bang, K.; Lee, C.-H.; Chang, S. *Tetrahedron Lett.* **2000**, *41*, 7521. (b) Lee, P. H.; Ahn, H.; Lee, K.; Sung, S.-Y.; Kim, S. *Tetrahedron Lett.* **2001**, *42*, 37.

10.1021/jo0105641 CCC: $20.00
Published on Web 11/10/2001

Scheme 1

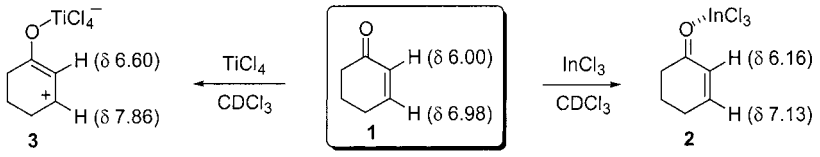
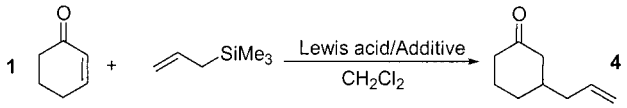


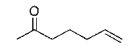
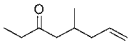
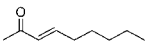
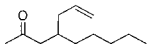
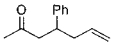
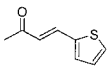
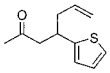
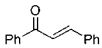
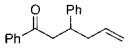
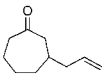
Table 1. Catalytic Activity of Several Lewis Acids in the Sakurai Reaction



entry	Lewis acid (equiv)	additive (equiv)	isolated yield, %[a]
1	$InCl_3$ (1.0)		62
2	$InCl_3$ (0.5)		52
3	$InCl_3$ (0.25)		0
4	$InCl_3$ (0.2)	TMSCl (1.0)	72
5	$InCl_3$ (0.1)	TMSCl (1.0)	56 (23)
6	**$InCl_3$ (0.1)**	**TMSCl (5.0)**	**73**
7	$InCl_3$ (0.1)	TMSCl (5.0)	64[b]
8	InF_3 (0.1)	TMSCl (5.0)	0
9	$In(OTf)_3$ (0.1)	TMSCl (5.0)	52
10	$InCl_3$ (0.1)	TMSOTf (5.0)	25
11	$In(OTf)_3$ (0.1)	TMSOTf (5.0)	32
12	$TiCl_4$ (1.0)		82[c]
13	$TiCl_4$ (0.1)		0
14	$TiCl_4$ (0.1)	TMSCl (5.0)	0
15	$AlCl_3$ (0.1)	TMSCl (5.0)	0

[a] Number in parentheses indicates recovered yield of 2-cyclohexen-1-one. [b] $CHCl_3$ was used. [c] From ref 1f.

Table 2. Indium Trichloride-Catalyzed Sakurai Reaction with Allyltrimethylsilane

entry	α,β-enone	product	isolated yield,%
1			62
2			77
3			82
4			81
5			89
6			89
7			64
8			73 75[a]
9			84
10			79

[a] Allylbenzyldimethylsilane was used.

ent underwent the catalytic Sakurai reaction with almost the same efficiency. Also, the reaction worked equally well with cyclic α,β-enones (entries 7−10). Unlike $TiCl_4$, when mesityl oxide, isophorone, pulegone, or 3-methyl-2-cyclohexen-1-one was treated with allyltrimethylsilane and a catalytic or stoichiometric amount of $InCl_3$ under the same reaction conditions, the desired products were not obtained. These results are consistent in that $InCl_3$ is the weaker acid and less oxophilic than $TiCl_4$. α,β-Unsaturated esters such as methyl acrylate and methyl methacrylate did not provide the added product, which is similar with $TiCl_4$.[1f]

Further synthetic utility of this catalytic procedure is shown in Scheme 2. (2-Methylallyl)trimethylsilane and 2-chloromethyl-3-trimethylsilyl-1-propene were reacted to α,β-enone **1** to produce 3-(2-methylallyl)cyclohexanone and 3-(2-chloromethylallyl)cyclohexanone, respectively, in good yields.

When a mixture of 4-(2-oxopropyl)-2-cyclohexen-1-one (**5**)[6] and allyltrimethylsilane in dichloromethane was treated with $InCl_3$ (0.1 equiv) and TMSCl (5 equiv), the allyl group was added chemoselectively to the C=C double bond to afford **6** in a 73% yield (Scheme 3). However, allyltrimethylsilane in the presence of a catalytic or stoichiometric amount of $TiCl_4$ and $AlCl_3$ did not react with either the ketone or the enone moiety.

We briefly studied catalytic intramolecular Sakurai reactions, and the results are shown in Table 3. Treatment of **7**[7] with $InCl_3$ (0.1 equiv) and TMSCl (5 equiv) in dichloromethane for 2 h diastereoselectively afforded **8** (α:β = 1:34) in an excellent yield.[8] Ordinarily, these reactions proceed only when 1.3 equiv of $EtAlCl_2$ is used, which was the most effective in the intramolecular Sakurai reaction to afford the desired product **8** (α:β = 4:1).[4a]

Although the role of the TMSCl in the Sakurai reaction is not clear at the present moment, we believe that the TMSCl traps the enolate intermediate to drive the equilibrium to completion.[9] This and other plausible mechanistic pathways are under investigation, especially with regard to the design of enantioselective catalytic systems.

In conclusion, we have shown that catalytic amounts of $InCl_3$ promote inter- and intramolecular Sakurai reactions in the presence of TMSCl. The present method complements existing synthetic methods due to its mild reaction conditions and some of the advantageous properties of indium metal over other metals such as ease of

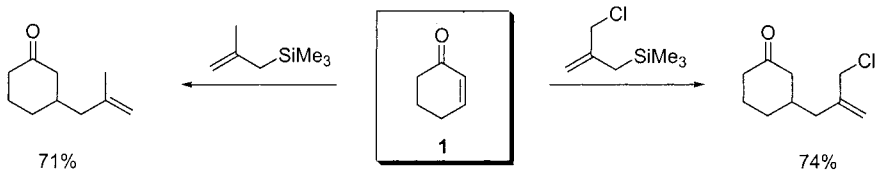
(6) Compound **5** was prepared from 1,3-cyclohexadione in five steps (PhH, EtOH, *p*-TsOH/LDA, allyl iodide/DiBAL-H/H_3O^+/Wacker oxidation).

(7) Compound **7** was prepared from 1,3-cyclohexadione in seven steps (PhH, EtOH, *p*-TsOH/LDA, allyl iodide/Sia_2BH, H_2O_2, NaOH/Swern oxidation/$Ph_3P{=}CHCH_2TMS$/DIBAL-H/H_3O^+).

(8) Stork, G.; Reynolds, M. E. *J. Am. Chem. Soc.* **1988**, *110*, 6911.

(9) Support for the formation of such TMSCl/α,β-enone complexes is lacking; ^1H NMR measurement for a mixture of 2-cyclohexen-1-one and TMSCl failed to detect the Lewis acid/Lewis base complex. ^{29}Si NMR measurement for a mixture of TMSCl and $InCl_3$ failed to detect the TMS^+InCl_4 or TMSCl → $InCl_3$ complex: (a) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1985**, *26*, 6015. (b) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1985**, *26*, 6019.

Scheme 2



Scheme 3

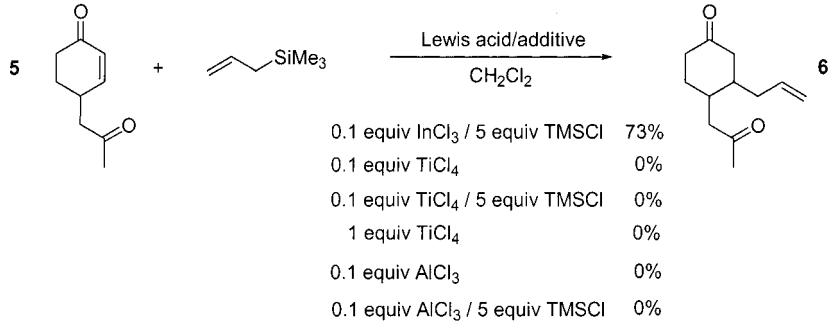
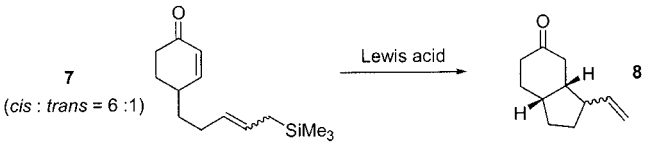


Table 3. Indium Trichloride-Catalyzed Intramolecular Sakurai Reaction



Lewis acid	solvent	temp, °C	isolated yield, %[a]
1.3 equiv $EtAlCl_2$[b]	$PhCH_3$	−78	92 (4:1)
1.3 equiv $EtAlCl_2$[b]	$PhCH_3$	0	84 (1:1)
0.1 equiv $EtAlCl_2$	$PhCH_3$	−78	10
0.1 equiv $InCl_3$[c]	CH_2Cl_2	25	89 (1:34)

[a] Ratio in parentheses indicates the ratio of α to β. [b] From ref 4c. [c] A 5 equiv quantity of TMSCl was used.

handling, high reactivity and selectivity, low toxicity, and operational simplicity.

Experimental Section

Typical Experimental Procedure. To a suspension of indium trichloride (22.0 mg, 0.1 mmol) in CH_2Cl_2 (3 mL) was added sequentially *trans*-chalcone (208.0 mg, 1.0 mmol), chlorotrimethylsilane (543.0 mg, 5.0 mmol), and allyltrimethylsilane (126.0 mg, 1.1 mmol) at room temperature under nitrogen atmosphere. After 30 min, the reaction mixture was quenched with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with ether (3 × 25 mL), and the combined organics were washed with water (20 mL) and brine (20 mL), dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/EtOAc = 20/1) leading to 1,3-diphenyl-1-oxo-5-hexene (223.0 mg, 89%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 7.28 Hz, 2H), 7.52 (t, J = 7.29 Hz, 1H), 7.41 (t, J = 7.85 Hz, 2H), 7.29−7.22 (m, 4H), 7.17 (t, J = 6.96 Hz, 1H), 5.69 (ddt, J = 17.15, 10.11, 7.05 Hz, 1H), 5.00 (d, J = 17.10 Hz, 1H), 4.96 (d, J = 10.08 Hz, 1H), 3.48 (quint, J = 7.08 Hz, 1H), 3.29 (d, J = 6.04 Hz, 2H), 2.48−2.44 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 198.90, 144.34, 137.20, 136.26, 132.92, 128.51, 128.42, 128.00, 127.56, 126.36, 116.78, 44.53, 40.72, 40.68 ppm; IR (film) 3010, 2950, 1670, 1430, 1400 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{19}O$ [M + H]$^+$ 251.1436, found 251.1440.

6-Hepten-2-one: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (ddt, J = 17.01, 10.26, 6.78 Hz, 1H), 5.02 (d, J = 17.01 Hz, 1H), 4.98 (d, J = 10.26 Hz, 1H), 2.44 (t, J = 7.43 Hz, 2H), 2.14 (s, 3H), 2.06 (q, J = 7.22 Hz, 2H), 1.68 (quint, J = 7.49 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 209.01, 137.95, 115.25, 42.85, 33.03, 30.95, 22.77 ppm; IR (film) 3020, 2950, 1700, 1430, 1410 cm^{-1}; HRMS (EI) calcd for $C_7H_{12}O$ M$^+$ 112.0888, found 112.0886.

5-Methyl-7-octen-3-one: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (ddt, J = 17.53, 10.34, 7.10 Hz, 1H), 5.01 (d, J = 10.34 Hz, 1H), 5.00 (d, J = 17.53 Hz, 1H), 2.49−2.41 (m, 3H), 2.24 (dd, J = 15.72, 7.88 Hz, 1H), 2.17−1.71 (m, 3H), 1.06 (t, J = 5.87 Hz, 3H), 0.94 (d, J = 6.47 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 211.47, 136.72, 116.39, 48.94, 41.20, 36.56, 28.97, 19.81, 7.79 ppm; IR (film) 3060, 3000, 1720, 1440, 1430 cm^{-1}; HRMS (EI) calcd for $C_9H_{16}O$ M$^+$ 140.1201, found 140.1203.

4-Allyl-2-nonanone: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (ddt, J = 16.97, 9.95, 6.60 Hz, 1H), 5.01 (d, J = 9.95 Hz, 1H), 5.00 (d, J = 16.97 Hz, 1H), 2.35 (ddd, J = 35.03, 16.46, 6.33 Hz, 2H), 2.12 (s, 3H), 2.04−1.952 (m, 2H), 1.32−1.21 (m, 9H), 0.88 (t, J = 6.65 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 209.09, 136.61, 116.54, 48.05, 38.30, 33.85, 33.47, 32.00, 30.57, 26.41, 22.62, 14.06 ppm; IR (film) 3020, 2960, 2800, 1700, 1430, 1410 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{22}O$ [M + H]$^+$ 183.1749, found 183.1745.

4-Phenyl-6-hepten-2-one: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.13 (m, 5H), 5.64 (ddt, J = 17.10, 10.08, 7.04 Hz, 1H), 4.99 (d, J = 17.10 Hz, 1H), 4.96 (d, J = 10.08 Hz, 1H), 3.25 (quint, J = 7.13 Hz, 1H), 2.76 (dd, J = 16.24, 6.34 Hz, 1H), 2.70 (dd, J = 16.23 Hz, 7.54, 1H), 2.33 (dd, J = 8.84, 7.10 Hz, 2H), 2.02 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) 207.75, 144.05, 136.16, 128.48, 127.45, 126.45, 116.78, 49.50, 40.87, 40.69, 30.68 ppm; IR (film) 3010, 2950, 1700, 1440, 1420, 1400 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{17}O$ [M + H]$^+$ 189.1279, found 189.1282.

4-(2-Thienyl-)-6-hepten-2-one: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, J = 5.10 Hz, 1H), 6.91 (dd, J = 5.06, 3.50 Hz, 1H), 6.81 (d, J = 3.37 Hz, 1H), 5.71 (ddt, J = 16.47, 13.29, 6.86 Hz, 1H), 5.04 (d, J = 16.47 Hz, 1H), 5.03 (d, J = 13.29 Hz, 1H), 3.62 (quint, J = 6.99 Hz, 1H), 2.78 (d, J = 1.95 Hz, 1H), 2.76 (d, J = 2.78 Hz, 1H), 2.43−2.39 (m, 2H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 207.17, 147.95, 135.64, 126.59, 123.91, 123.11, 117.28, 50.19, 41.56, 35.89, 30.69 ppm; IR (film) 3040, 2970, 1710, 1420, 1410 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{14}OS$ [M + H]$^+$ 195.0480, found 195.0474.

3-Allylcyclopentanone: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (ddt, J = 17.03, 10.19, 6.83 Hz, 1H), 5.04 (d, J = 17.03 Hz, 1H), 5.03 (d, J = 10.19 Hz, 1H), 2.40−2.11 (m, 7H), 2.38 (dd, J = 17.71, 9.0 Hz, 1H), 1.64−1.53 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 219.70, 136.28, 116.48, 44.71, 39.56, 38.36, 36.68, 29.00 ppm; IR (film) 3020, 2960, 2900, 1680, 1430, 1410 cm^{-1}; HRMS (EI) calcd for $C_8H_{12}O$ M$^+$ 124.0888, found 124.0891.

3-Allylcyclohexanone: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 (ddt, J = 17.83, 10.87, 7.22 Hz, 1H), 5.04 (d, J = 17.83 Hz, 1H), 5.04 (d, J = 10.87 Hz, 1H), 2.44−2.25 (m, 3H), 2.12−1.83 (m, 6H), 1.67−1.60 (m, 1H), 1.41−1.34 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 211.61, 135.60, 116.70, 47.64, 41.30, 40.71, 38.67, 30.78,

25.05 ppm; IR (film) 3020, 2960, 2900, 1680, 1430, 1410 cm^{-1}; HRMS (EI) calcd for $C_9H_{15}O$ $[M + H]^+$ 139.1123, found 139.1118.

3-Allyl-4,4-dimethylcyclohexanone: ^1H NMR (400 MHz, $CDCl_3$) δ 5.67 (ddt, J = 16.86, 10.87, 8.40 Hz, 1H), 5.02 (d, J = 10.87 Hz, 1H), 5.01 (d, J = 16.86 Hz, 1H), 2.45−2.24 (m, 4H), 2.04 (dd, J = 16.00, 11.97 Hz, 1H), 1.78−1.56 (m, 4H), 1.06 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 211.98, 136.78, 116.62, 46.40, 42.60, 40.36, 38.32, 35.42, 32.78, 28.75, 19.56 ppm; IR (film) 3040, 2940, 2910, 1700, 1410 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{19}O$ $[M + H]^+$ 167.1436, found 167.1436.

3-Allylcycloheptanone: ^1H NMR (400 MHz, $CDCl_3$) δ 5.75 (ddt, J = 17.33, 10.40, 7.11 Hz, 1H), 5.04 (d, J = 10.40 Hz, 1H), 5.03 (d, J = 17.33 Hz, 1H), 2.52−2.46 (m, 3H), 2.38 (dd, J = 10.90, 6.00 Hz, 1H), 2.08−1.57 (m, 7H), 1.44−1.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 214.81, 136.58, 117.31, 49.93, 44.35, 42.18, 36.97, 36.23, 29.03, 23.73 ppm; IR (film) 3080, 3020, 2960, 1720, 1450, 1470 cm^{-1}; HRMS (EI) calcd for $C_{10}H_{17}O$ $[M + H]^+$ 153.1279, found 153.1277.

3-(2-Methylallyl)cyclohexanone: ^1H NMR (400 MHz, $CDCl_3$) δ 4.77 (s, 1H), 4.68 (s, 1H), 2.41−2.26 (m, 3H), 2.10−1.88 (m, 6H), 1.74−1.60 (m, 1H), 1.69 (s, 3H), 1.33−1.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 211.90, 142.83, 112.38, 47.93, 45.25, 41.47, 36.76, 31.19, 25.18, 22.13 ppm; IR (film) 3000, 2940, 1690, 1440, 1400, 1250, 1240 cm^{-1}; HRMS (CI) calcd for $C_{10}H_{17}O$ M^+ 152.1201, found 152.1200.

3-(2-Chloromethylallyl)cyclohexanone: ^1H NMR (400 MHz, $CDCl_3$) δ 5.21 (s, 1H), 4.97 (s, 1H), 4.01 (s, 2H), 2.43−2.27 (m, 4H), 2.18−1.91 (m, 5H), 1.70−1.64 (m, 1H), 1.37−1.34 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 211.66, 142.60, 117.15, 48.29, 48.16, 41.76, 40.66, 37.08, 31.60, 25.42 ppm; IR (film) 3000, 2960, 1690, 1410, 1250 cm^{-1}; HRMS (EI) calcd for $C_{10}H_{16}ClO$ $[M + H]^+$ 187.0890, found 187.0895.

3-Allyl-4-(2-oxopropyl)cyclohexanone: ^1H NMR (400 MHz, $CDCl_3$) δ 5.69 (ddt, J = 16.90, 10.04, 7.04 Hz, 1H), 5.08 (d, J = 10.4 Hz, 1H), 5.04 (d, J = 16.90 Hz, 1H), 2.75 (dd, J = 17.00, 4.02 Hz, 1H), 2.32−1.78 (m, 9H), 1.85 (s, 3H), 1.43−1.40 (m, 1H), 1.22−1.44 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (major isomer) 211.15, 207.62, 134.59, 117.79, 46.81, 45.60, 41.77, 40.32, 38.05, 35.11, 31.08, 30.68 ppm, (minor isomer) 210.90, 207.45, 135.75, 117.23, 44.51, 43.80, 40.22, 39.22, 34.26, 33.37, 30.51, 28.22 ppm; IR (film) 3000, 2940, 1690, 1400 cm^{-1}; HRMS (CI) calcd for $C_{12}H_{19}O_2$ $[M + H]^+$ 195.1385, found 195.1380.

9-Vinylbicyclo[4.3.0]nonan-3-one: ^1H NMR (400 MHz, $CDCl_3$) δ 5.65 (ddt, J = 17.52, 10.13, 7.59 Hz, 1H), 5.02 (d, J = 17.52, 1H), 4.97 (d, J = 10.13 Hz, 1H), 2.46 (dd, J = 15.19, 6.48 Hz, 1H), 2.35−1.89 (m, 9H), 1.71−1.61 (m, 1H), 1.46−1.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (major isomer) 213.65, 141.03, 114.68, 50.66, 43.77, 41.46, 38.47, 36.97, 32.02, 31.11, 27.64 ppm, (minor isomer) 214.14, 138.65, 115.27, 48.21, 43.13, 39.19, 37.57, 37.39, 28.92, 28.30, 27.53 ppm; IR (film) 3000, 2940, 2920, 1690, 1400 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{16}O$ $[M + H]^+$ 164.1201, found 164.1205.

Acknowledgment. This work was supported by Korea Science and Engineering Foundation (KOSEF-2000-1-123-002-5). Gas chromatograms were provided by the GC facility supported by Research Center for Advanced Mineral Aggregate Composite Products.

JO0105641