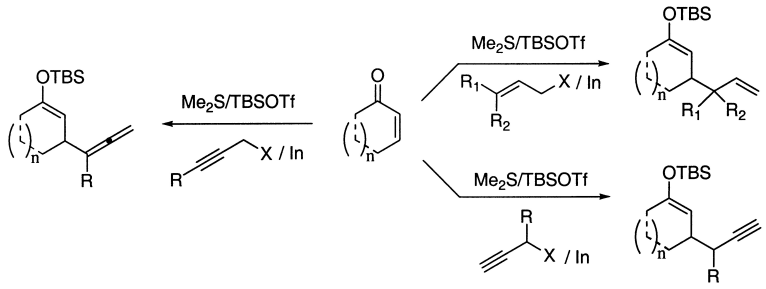
Article

Indium-Mediated β-Allylation, β-Propargylation, and β-Allenylation onto α,β-Unsaturated Ketones: Reactions of in-Situ-Generated 3-*tert*-Butyldimethylsilyloxyalk-2-enylsulfonium Salts with in-Situ-Generated Organoindium Reagents

Kooyeon Lee, Hyunseok Kim, Tomoya Miura, Koichi Kiyota, Hiroyuki Kusama, Sunggak Kim, Nobuharu Iwasawa, and Phil Ho Lee

J. Am. Chem. Soc., **2003**, 125 (32), 9682-9688• DOI: 10.1021/ja035988m • Publication Date (Web): 22 July 2003



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 2 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

J|A|C|S
ARTICLES
Published on Web 07/22/2003

Indium-Mediated β-Allylation, β-Propargylation, and β-Allenylation onto α,β-Unsaturated Ketones: Reactions of in-Situ-Generated 3-*tert*-Butyldimethylsilyloxyalk-2-enylsulfonium Salts with in-Situ-Generated Organoindium Reagents

Kooyeon Lee,[†] Hyunseok Kim,[†] Tomoya Miura,[‡] Koichi Kiyota,[‡] Hiroyuki Kusama,[‡] Sunggak Kim,[§] Nobuharu Iwasawa,*[,‡] and Phil Ho Lee*[,†]

Contribution from the Department of Chemistry, Kangwon National University, Chunchon 200-701, Republic of Korea, Department of Chemistry, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152-8551, Japan, and Center for Molecular Design and Synthesis and Department of Chemistry, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Republic of Korea

Received May 6, 2003; E-mail: phlee@kangwon.ac.kr

Abstract: 3-*tert*-Butyldimethylsilyloxyalk-2-enylsulfonium salts, generated in situ from the reaction of α,β-enones with dimethyl sulfide in the presence of TBSOTf, underwent a novel nucleophilic substitution with allylindiums to give silyl enol ethers of δ,ϵ-alkenyl ketones in good yields, which correspond to formal Michael addition products. In a similar manner, 1,4-propargylation of propargylindiums onto the sulfonium salts produced the corresponding silyl enol ethers of δ,ϵ-alkynyl ketones in good yields. Organoindium reagents derived from γ-substituted propargyl bromide and indium afforded the corresponding silyl enol ethers of β-allenyl ketones in good yields. The reaction proceeds via an addition-substitution mechanism involving the formation of allylic sulfonium salts. The presence of the intermediate sulfonium salt was confirmed by observation of the low-temperature ^{1}H NMR spectra.

Michael addition of organometallics to α,β-unsaturated carbonyl compounds is one of the most useful and important methods for C−C bond formation. It has been normally achieved by using organocopper and organomagnesium reagents in the presence of an additive such as copper halide.[1] Although β-substituted silyl enol ethers are generally obtained from α,β-enones by 1,4-addition of organocopper reagents followed by enolate trapping, such procedures are sometimes inconvenient, and the requisite reagents are difficult to obtain.[2] Furthermore, as far as we are aware, there have been very few reports on the preparation of silyl enol ethers having labile substituents such as alkoxycarbonyl or alkoxycarbonyl olefin.[3] Our interest in extending the scope of the Michael addition reaction and subsequent application of indium metal to modern organic synthesis[4] has led us to investigate indium-promoted Michael addition reactions. Generally, allylindiums reacted with α,β-unsaturated aldehydes to afford 1,2-addition products in good yields.[5] Reaction of 4-phenyl-3-buten-2-one, which is a unique example of an α,β-unsaturated ketone, with allylindiums produced a regioselective 1,2-addition product.[5] However, there are few reports on the Michael addition reaction of α,β-unsaturated ketones with allylindiums.[6] Recently, it was reported that indium-mediated allylation to 1,1-dicyano-2-arylethenes gave 1,4-addition products in aqueous media with good yields.[6a]

[†] Kangwon National University.
[‡] Tokyo Institute of Technology.
[§] Korea Advanced Institute of Science and Technology.

(1) (a) Posner, G. H. *Org. React.* **1972**, *19*, 1−113. (b) Posner, G. H. *An Introduction to Synthesis Using Organocopper Reagents*; Wiley-Interscience: New York, 1980. (c) Lee, P. H.; Shim, S. C.; Kim, S. *Bull. Korean Chem. Soc.* **1986**, *7*, 425. (d) Lipshutz, B. H. *Synthesis* **1987**, 325. (e) Taylor, R. J. K. *Organocopper Reagents*; Oxford University Press: Oxford, 1994. (f) Lee, P. H.; Park, J.; Lee, K.; Kim, H.-C. *Tetrahedron Lett.* **1999**, *40*, 7109.

(2) (a) Taylor, R. J. K. *Synthesis* **1985**, 364. (b) Hulce, M. *Org. React.* **1990**, *38*, 225. (c) Perlmutter, P. *Conjugate Addition Reactions in Organic Synthesis*; Pergamon Press: Oxford, 1992. (d) Lipshutz, B. H.; Sengupta, S. *Org. React.* **1992**, *41*, 135.

(3) (a) Horiguchi, Y.; Nakamura, E.; Kuwajima, I. *J. Org. Chem.* **1986**, *51*, 4323. (b) Pratt, D. V.; Hopkins, P. B. *J. Org. Chem.* **1988**, *53*, 5885.

(4) (a) Lee, P. H.; Bang, K.; Lee, 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. (c) Lee, P. H.; Bang, K.; Ahn, H.; Lee, K. *Bull. Korean Chem. Soc.* **2001**, *22*, 1385. (d) Lee, P. H.; Seomoon, S.; Lee, K. *Bull. Korean Chem. Soc.* **2001**, *22*, 1380. (e) Lee, P. H.; Lee, K.; Sung, S.-Y.; Chang, S. *J. Org. Chem.* **2001**, *66*, 8646. (f) Lee, P. H.; Lee, K.; Chang, S. *Synth. Commun.* **2001**, *31*, 3189. (g) Lee, P. H.; Bang, K.; Lee, K.; Sung, S.-Y.; Chang, S. *Synth. Commun.* **2001**, *31*, 3781. (h) Lee, P. H.; Sung, S.-Y.; Lee, K. *Org. Lett.* **2001**, *3*, 3201. (i) Lee, P. H.; Sung, S.-Y.; Lee, K.; Chang, S. *Synlett* **2002**, 146. (j) Bang, K.; Lee, K.; Park, Y. K.; Lee, P. H. *Bull. Korean Chem. Soc.* **2002**, *23*, 1272. (k) Lee, K.; Seomoon, D.; Lee, P. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 3901. (l) Lee, K.; Lee, J.; Lee, P. H. *J. Org. Chem.* **2002**, *67*, 8265. (m) Lee, P. H.; Seomoon, D.; Lee, K.; Heo, Y. *J. Org. Chem.* **2003**, *68*, 2510. (n) Lee, P. H.; Lee, S. W.; Lee, K. *Org. Lett.* **2003**, *5*, 1103.

(5) (a) Araki, S.; Ito, H.; Butsugan, Y. *Synth. Commun.* **1988**, 453. (b) Araki, S.; Ito, H.; Butsugan, Y. *J. Org. Chem.* **1988**, *53*, 1831. (c) Araki, S.; Ito, H.; Katsumura, N.; Butsugan, Y. *J. Organomet. Chem.* **1989**, *369*, 291. (d) Hoppe, H. A.; Lloyd-Jones, G. C.; Murry, M.; Peakman, T. M.; Walsh, K. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 1545. (e) Loh, T.-P.; Cao, G.-Q.; Pei, J. *Tetrahedron Lett.* **1998**, *39*, 1453. (f) Capps, S. M.; Clarke, T. P.; Charmant, J. P. H.; Hoppe, H. A. F.; Lloyd-Jones, G. C.; Murry, M.; Peakman, T. M.; Stentifold, R. A.; Walsh, K. E.; Worthington, P. A. *Eur. J. Org. Chem.* **2000**, 963. (g) Loh, T.-P.; Song, H.-Y. *Synlett* **2002**, 2119. (h) Loh, T.-P.; Yin, Z.; Song, H.-Y.; Tan, K.-L. *Tetrahedron Lett.* **2003**, *44*, 911.

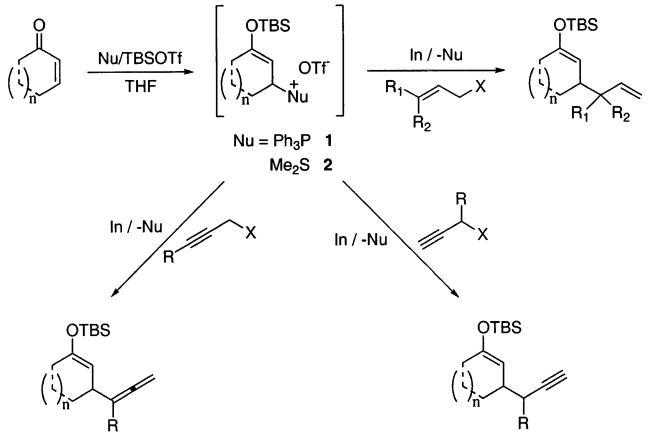
 10.1021/ja035988m CCC: $25.00

Tetraorganoindium ate-complexes reacted with α,β-unsaturated ketones in a 1,4-addition fashion.[6b] The reaction of allylindium with α,β-unsaturated carbonyl compounds, in which two electron-withdrawing groups were attached to alkenes, proceeded in a 1,2-addition mode, whereas a 1,4-addition reaction took place with 1,1-dicyano-2-arylethenes, which are extremely electron-deficient olefins.[6c] Although a variety of examples of the indium-mediated allylation to aldehydes and ketones have been reported,[7] as far as we are aware, few examples of the regioselective β-allylation to α,β-unsatursated ketones have been published.[6d] Recently, indium-mediated propargylation or allenylation to carbonyl compounds was reported.[8] However, 1,4-propargylation and allenylation onto α,β-unsaturated ketones is very difficult because the 1,2-addition mode of propargyl or allenyl group is a major pass. In addition, there is no example of the indium-mediated β-propargylation to α,β-unsaturated ketones.[9] As part of our continuing effort to expand the synthetic utility of indium, we now report on a novel nucleophilic substitution of in-situ-generated 3-*tert*-butyldimethylsilyloxyalk-2-enylsulfonium salts with organoindiums to obtain silyl enol ethers of δ,ϵ-alkenyl ketones, δ,ϵ-alkynyl ketones, and β-allenyl ketones, respectively, which correspond to Michael addition products (Scheme 1).[10]

Results and Discussion

Indium-Mediated β-Allylation onto α,β-Unsaturated Ketones. First, optimum conditions for In-mediated β-allylation were examined with 3-*tert*-butyldimethylsilyloxycyclohex-2-enylphosphonium salts (**1**),[11] which could be prepared from phosphoniosilylation of 2-cyclohexen-1-one. When **1** was treated with allylindium in THF at 60 °C for 2 h, the desired *tert*-butyldimethylsilyl enol ether **19** of 3-allylcyclohexanone was obtained in 15% yield (Table, entry 11). We next explored the feasibility of the corresponding sulfonium salts (**2**). Thus,

Scheme 1



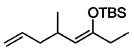
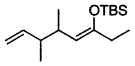
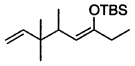
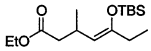
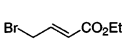
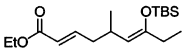
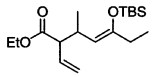
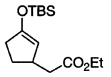
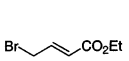
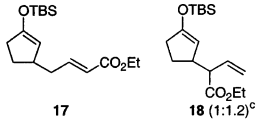
sulfonium salt (**2**) was generated in situ from 2-cyclohexen-1-one, dimethyl sulfide, and TBSOTf at −78 °C, and then treated with the allylindium reagent prepared separately from allyl bromide and indium. Among several reaction conditions examined, the best results were obtained with allylindium, which was generated in situ from the reaction of 1 equiv of indium with 1.5 equiv of allyl halide. The use of indium in less than 1 equiv and allyl halide in less than 1.5 equiv resulted in a sluggish reaction and gave lower yields as well as a longer reaction time. Because the sulfonium salt was thermally unstable, the reaction was carried out at low temperature (−78 °C) in THF.

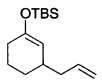
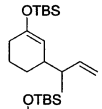
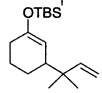
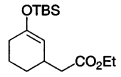
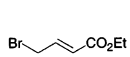
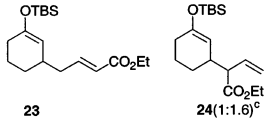
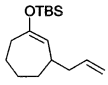
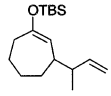
To demonstrate the efficiency and scope of the present method, we applied these optimum conditions to numerous α,β-enones and allyl halides. The results are summarized in Table 1. The sulfonium salt **2** reacted with allyl bromide and indium to produce 1,4-addition product **19** in 65% yield (Table 1, entry 11). Reaction of **2** with organoindiums, which were obtained from crotyl bromide and prenyl bromide in THF, gave **20** and **21** in 62% and 61% yields, respectively, at −78 °C for 10 min (Table 1, entries 12 and 13). It should be noted that the substitution reaction showed an exclusive γ-regioselectivity. Consequently, these two-step conversions in one pot correspond to the conjugate addition of organoindiums to α,β-enones. Treatment of sulfonium salt **2** with organoindium derived from ethyl iodoacetate afforded **22** in 62% yield under the optimized conditions (Table 1, entry 14). Similarly, when **2** was reacted with ethoxycarbonyled allylindium, the desired products **23** and **24** were obtained in 42% and 22% yields, respectively (Table 1, entry 15). It is interesting to note that sulfonium salts are easily displaced by organoindiums derived from ethyl iodoacetate and ethyl bromocrotonate in which substituents possessing labile alkoxycarbonyl or alkoxycarbonyl olefin are present at the β-position. Generally, lithium, magnesium, or copper reagents containing these groups are difficult to obtain. Several sulfonium salts of other cyclic α,β-enones (**4** and **6**) underwent this novel nucleophilic substitution with the same efficiency. Also, the reaction worked equally well with the sulfonium salt of acyclic 4-hexen-3-one (**3**).

Indium-Mediated β-Propargylation and β-Allenylation onto α,β-Unsaturated Ketones. Iwasawa recently reported a novel $W(CO)_5(L)$-catalyzed cyclization of ω-acetylenic silyl enol ethers,[12] where 5-siloxy-5-en-1-ynes undergo 6-*endo* cyclization,[12a] while 7-siloxy-6-en-1-ynes undergo either 5-*exo* or 6-*endo* cyclization by an appropriate choice of the reaction

(6) (a) Wang, L.; Sun, X.; Zhang, Y. *Synth. Commun.* **1998**, *28*, 3263. (b) Araki, S.; Shimizu, T.; Jin, S.-J.; Butsugan, Y. *Chem. Commun.* **1991**, 824. (c) Araki, S.; Horie, T.; Kato, M.; Hirashita, T.; Yamamura, H.; Kawai, M. *Tetrahedron Lett.* **1999**, *40*, 2331. (d) Lee, P. H.; Ahn, H.; Lee, K.; Sung, S.-Y.; Kim, S. *Tetrahedron Lett.* **2001**, *42*, 37.
(7) (a) Li, C.-J.; Chan, T.-H. *Tetrahedron Lett.* **1991**, *32*, 7017. (b) Beuchet, P.; Marrec, N. L.; Mosset, P. *Tetrahedron Lett.* **1992**, *33*, 5959. (c) Kim, E.; Gordon, D. M.; Schmid, W.; Whitesides, G. M. *J. Org. Chem.* **1993**, *58*, 5500. (d) Li, C.-J. *Chem. Rev.* **1993**, *93*, 2023. (e) Bindra, W. H.; Prenner, R. H.; Schmid, W. *Tetrahedron* **1994**, *50*, 749. (f) Isaac, M. B.; Chan, T.-H. *Tetrahedron Lett.* **1995**, *36*, 8957. (g) Chan, T.-H.; Lee, M.-C. *J. Org. Chem.* **1995**, *60*, 4228. (h) Li, C.-J. *Tetrahedron* **1996**, *52*, 5643. (i) Li, X.-R.; Loh, T.-P. *Tetrahedron: Asymmetry* **1996**, *7*, 1535. (j) Loh, T.-P.; Ho, D. S.-C.; Chua, G.-L.; Sim, K.-Y. *Synlett* **1997**, 563. (k) Li, C.-J.; Chan, T.-H. *Organic Reactions in Aqueous Media*; Wiley: New York, 1997. (l) Loh, T.-P.; Ho, D. S.; Xu, K.-C.; Sim, K.-Y. *Tetrahedron Lett.* **1997**, *38*, 865. (m) Chan, T.-H.; Lu, W. *Tetrahedron Lett.* **1998**, *39*, 8605. (n) Li, C.-J.; Chan, T.-H. *Tetrahedron* **1999**, *55*, 11149.
(8) (a) Isaac, M. B.; Chan, T.-H. *Chem. Commun.* **1995**, 1003. (b) Yi, X.-H.; Meng, Y.; Hua, X.-G.; Li, C.-J. *J. Org. Chem.* **1998**, *63*, 7472. (c) Nair, V.; Jayan, C. N.; Ros, S. *Tetrahedron* **2001**, *57*, 9453.
(9) For some previously reported examples using other reagents, see: (a) Paquette, L. A.; Han, Y.-K. *J. Am. Chem. Soc.* **1981**, *103*, 1831. (b) Corey, E. J.; Rucker, C. *Tetrahedron Lett.* **1982**, *23*, 719. (c) Haruta, J.; Nishi, K.; Matsuda, S.; Akai, S.; Tamura, Y.; Kita, Y. *J. Org. Chem.* **1990**, *55*, 4853. (d) Shibata, I.; Kano, T.; Kanazawa, N.; Fukuoka, S.; Baba, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1389.
(10) For a preliminary letter of this work, see: (a) Lee, P. H.; Lee, K.; Kim, S. *Org. Lett.* **2001**, *3*, 3205. (b) Iwasawa, N.; Miura, T.; Kiyota, K.; Kusama, H.; Lee, K.; Lee, P. H. *Org. Lett.* **2002**, *4*, 4463. (c) Miura, T.; Kiyota, K.; Kusama, H.; Lee, K.; Kim, H.; Kim, S.; Lee, P. H.; Iwasawa, N. *Org. Lett.* **2003**, *5*, 1725.
(11) (a) Kozikowski, A. P.; Jung, S. H. *J. Org. Chem.* **1986**, *51*, 3402. (b) Kim, S.; Lee, P. H. *Tetrahedron Lett.* **1988**, *29*, 5413. (c) Kim, S.; Lee, P. H.; Kim, S. S. *Bull. Korean Chem. Soc.* **1989**, *10*, 218. (d) Lee, P. H.; Kim, S. *Tetrahedron Lett.* **1992**, *13*, 580. (e) Lee, P. H.; Kim, J. S.; Kim, Y. C.; Kim, S. *Tetrahedron Lett.* **1993**, *34*, 7583. (f) Lee, P. H.; Kim, H. S.; Kim, S. *Chem. Lett.* **1994**, 2401. (g) Lee, P. H.; Cho, M.; Han, I.-S.; Kim, S. *Tetrahedron Lett.* **1999**, *40*, 6975.

Table 1. Indium-Mediated β-Allylation onto α,β-Unsaturated Ketones

Entry	α,β-Enones	Allyl Halides	Product	Isolated Yield(%)[a]
1	 **3**			**7** 65
2				**8** 69(1:1.1)[c]
3				**9** 62
4				**10** 72
5				**11** 70(1:4.8)[d]
				**12** (1:1)[c]
6	 **4**			**13** 62
7				**14** 64(1:1)[c]
8				**15** 61
9				**16** 74
10			 **17**	**18** (1:1.2)[c] 72(1:3)[d]

Entry	α,β-Enones	Allyl Halides	Product	Isolated Yield(%)[a]
11	 **5**			**19** 15[e] 25[f] 0[g] 65
12				**20** 62(1:1)[c]
13				**21** 61
14				**22** 62
15			 **23** **24**(1:1.6)[c]	64(1:1.9)[d]
16	 **6**			**25** 65
17				**26** 69(1:1)[c]
18				**27** 66
19				**28** 71
20			**29** **30**(1:1)[c]	60(1:1.9)[d]

[a] Reaction performed with 1.0 equiv of enone, 1.0 equiv of In, 1.5 equiv of propargyl bromide, 1.2 equiv of Me_2S, and 1.05 equiv of TBSOTf, unless otherwise noted. [b] Isomeric ratio of crotyl bromide; cis:trans = 1:5. [c] The ratios in parentheses indicate the diastereomeric ratio. [d] The ratios in parentheses indicate the ratios of constitutional isomers. [e] Phosphonium salt was used. [f] 2-Cyclohexen-1-one:In:allylbromide = 1.0:0.67:1.0. [g] Me_2S was not used.

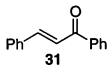
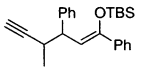
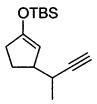
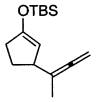
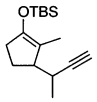
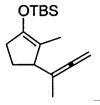
conditions.[12b] On the other hand, only one specific example was disclosed for the 5-*endo* cyclization of the 6-siloxy-5-en-1-yne derivative.[12a] One reason for this scarcity is the lack of a good and simple method for preparation of the requisite substrates. Therefore, it is highly desirable to develop a concise method for the direct 1,4-propargylation onto α,β-unsaturated ketones with simultaneous silylation of the produced enolates.[13,14] On the basis of the above-mentioned indium-mediated β-allylation onto α,β-unsaturated ketones, we applied in-situ-generated organoindium reagents, which are derived from the reaction of indium with propargyl halides, to a variety of α,β-unsaturated ketones to obtain silyl enol ethers of δ,ϵ-alkynyl ketones and β-alkenyl ketones.[10b] The results are summarized in Table 2. The sulfonium salt **2** was treated with the indium reagent generated from propargyl bromide and indium to produce the conjugate addition product **42** in 86% yield (Table 2, entry 8). It is especially noteworthy that the substitution reaction showed an exclusive α-regioselectivity. There is no allenic compound formed in the reaction. Consequently, these two-step conversions in one pot correspond to the 1,4-propargylation of organoindium reagents to α,β-enones. Treatment of sulfonium salt **2** with organoindium reagents derived from 3-bromobutyne gave **43** in 81% yield with α-regioselectivity under the optimized conditions (Table 2, entry 9). However, the reaction of **2** with 1-bromo-2-butyne having a methyl group at the γ-position in

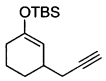
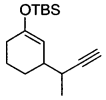
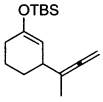
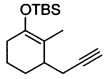
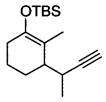
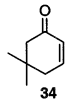
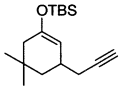
(12) (a) Maeyama, K.; Iwasawa, N. *J. Am. Chem. Soc.* **1998**, *120*, 1928. (b) Iwasawa, N.; Maeyama, K.; Kusama, H. *Org. Lett.* **2001**, *3*, 3871. (c) Miura, T.; Iwasawa, N. *J. Am. Chem. Soc.* **2002**, *124*, 518. (d) Kusama, H.; Yamabe, H.; Iwasawa, N. *Org. Lett.* **2002**, *4*, 2562. References for the $W(CO)_5$(L)-promoted reactions are cited therein. See also: (e) Imamura, K.; Yoshikawa, E.; Gevorgyan, V.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 4081. (f) Imamura, K.; Yoshikawa, E.; Gevorgyan, V.; Sudo, T.; Asao, N.; Yamamoto, Y. *Can. J. Chem.* **2001**, *79*, 1624.

(13) Generally, 1,4-propargylation onto α,β-unsaturated ketones is not an easy process because 1,2-addition of propargyl (or allenyl) metallic reagents usually occurs preferentially. Some exceptions are reported using allenyltin and several other reagents; see: (a) Shibata, I.; Kano, T.; Kanazawa, N.; Fukuoka, S.; Baba, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1389. (b) Haruta, J.; Nishi, K.; Matsuds, S.; Akai, S.; Tamura, Y.; Kita, Y. *J. Org. Chem.* **1990**, *55*, 4853. (c) Corey, E. J.; Rucker, C. *Tetrahedron Lett.* **1982**, *23*, 719. (d) Paquette, L. A.; Han. Y.-K. *J. Am. Chem. Soc.* **1981**, *103*, 1831.

(14) Reaction with allyltri-*n*-butyltin with chalcone in the presence of $TaCl_5$ and TMSCl gave the conjugate adduct as a silyl enol ether.[14a] When we carried out the conjugate addition of allenyltri-*n*-butyltin with chalcone in the presence of $TaCl_5$ and a silyl chloride such as TMSCl or TBSCl, only hydrolyzed conjugate adduct was obtained, and none of the desired silyl enol ether was detected in the crude mixtures.

Table 2. Indium-Mediated β-Propargylation and β-Allenylation onto α,β-Unsaturated Ketones

Entry	α,β-Enones	Propargyl Halides	Product		Isolated Yield(%)[a]
1	 **31**			**35**	74[b](1:2.6)[c]
2	 **4**			**36**	82
3				**37**	71(1:2.1)[c]
4				**38**	69[d]
5	 **32**			**39**	81
6				**40**	85(1:.2.6)[c]
7				**41**	73[d]

Entry	α,β-Enones	Propargyl Halides	Product		Isolated Yield(%)
8	 **5**			**42**	86
9				**43**	81(1:1.3)[c]
10				**44**	64[d]
11	 **33**			**45**	76[e]
12				**46**	64[b](1:1.1)[c]
13	 **34**			**47**	48[e]

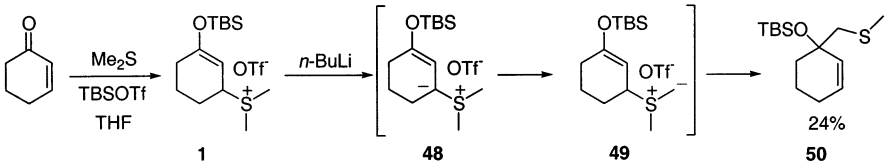
[a] Reaction performed with 1.0 equiv of enone, 1.0 equiv of In, 1.5 equiv of propargyl bromide, 1.2 equiv of Me_2S, and 1.05 equiv of TBSOTf, and silica gel was treated with 5% Et_3N in hexane prior to column, unless otherwise noted. [b] Reaction performed with 1.0 equiv of enone, 2.0 equiv of In, 3.0 equiv of propargyl bromide, 1.3 equiv of Me_2S, and 1.1 equiv of TBSOTf, and silica gel was treated with 5% Et_3N in hexane prior to column, unless otherwise noted. [c] The ratios in parentheses indicate the diastereomeric ratio. [d] One equivalent of LiI was used. [e] Reaction performed with 1.0 equiv of enone, 2.0 equiv of In, 3.0 equiv of propargyl bromide, 1.3 equiv of Me_2S, and 1.1 equiv of TBSOTf, unless otherwise noted.

the presence of indium afforded selectively allene **44** with γ-regioselectivity in 64% yield in THF at −78 °C for 10 min (Table 2, entry 10). In the case of 2-methyl-2-cyclohexen-1-one, the desired β-propargylation products were obtained with propargyl bromide and 3-bromobutyne in 76% and 64% yields, respectively (Table 2, entries 11 and 12). Exposure of 5,5-dimethyl-2-cyclohexen-1-one (**34**) to propargylindium gave the desired product **47** in 48% yield because of steric hindrance (Table 2, entry 13). The case of 4,4-dimethyl-2-cyclohexen-1-one gave only the 1,2-addition product in 74% yield (ratio of α to γ = 1.2:1). 2-Cyclopenten-1-one and 2-methyl-2-cyclopenten-1-one underwent β-propargylation with organoindium reagents to produce the desired compounds in good yields (Table 2, entries 2, 3, 5, and 6). When **4** and **32** were selectively reacted with indium reagents derived from 1-bromo-2-butyne, allene products **38** and **41** were obtained in good yields, respectively (Table 2, entries 4 and 7). However, the reaction of 2-cyclohepten-1-one with propargylindium yielded 1-(1′-ethynyl)-methylenyl-2-cycloheptene, which was produced by the 1,2-addition reaction of propargylindium followed by the elimination reaction of water, in 72% yield. Although chalcone **31** was treated with 3-bromobutyne in the presence of indium to give the 1,4-addition product **35** (Table 2, entry 1), other acyclic α,β-enones [4-hexen-3-one, 3-methylene-2-norbornanone, and *trans*-4-(2-thienyl)-3-buten-2-one] produced 1,2-addition products.

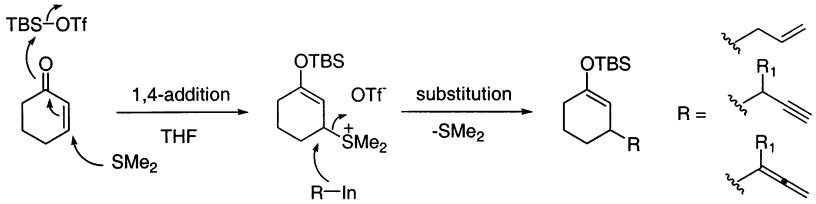
Addition-Substitution Mechanism of β-Allylation, β-Propargylation, and β-Allenylation. The preparation of sulfonium salts is classified into several parts on the basis of the structural nature of the sulfides.[15] It is well known that dialkyl sulfides have enough nucleophilicity for smooth reaction with primary alkyl halides under mild conditions.[16] The sulfonium salts are easily prepared by the reaction of dialkyl sulfides with primary alkyl halides, but secondary and tertiary alkyl halides do not give good results because of the low reactivity toward dialkyl sulfides. Thus, silver tetrafluoroborate is added for metal assisted substitution.[17] In 1952, Schoberl reported that dialkyl sulfides underwent a conjugate addition to α,β-unsaturated carboxylic acid in the presence of anhydrous hydrogen chloride.[18] In contrast with dialkyl sulfides, the reaction of aryl sulfides with alkyl halides takes place only in the presence of silver or mercury(II) salts because the nucleophilicity of aryl sulfides is appreciably weaker than that of dialkyl sulfides.[19] It has been known that conjugate addition of triphenylphosphine to α,β-unsaturated carbonyl compounds occurs in the presence of the carbonyl group activation reagents such as hydrogen chloride

(15) Stirring, C. J. M. *The Chemistry of the Sulfonium Compound*; Wiley: New York, 1981.
(16) Speziale, A. J.; Tung, C. C.; Ratts, K. W.; Yao, A. *J. Am. Chem. Soc.* **1965**, *87*, 962.
(17) Trost, B. M.; Hammen, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 962.
(18) Schoberl, A.; Lang, G. *Angew. Chem.* **1952**, *64*, 224.
(19) Franzen, V.; Schmidt, H. J.; Mertz, C. *Chem. Ber.* **1961**, *94*, 2942.

Scheme 2



Scheme 3



and TMSCl.[11,20] Although dialkyl sulfides are much less nucleophilic than triphenylphosphine, it may be possible that dialkyl sulfide undergoes conjugate addition onto α,β-unsaturated carbonyl compounds. We have investigated their sulfoniosilylation reactions in the presence of TBSOTf. As is shown in Scheme 2, to prove the sulfoniosilylation, *n*-butyllithium was added to the reaction mixture of sulfonium salt **1** at −78 °C, and sulfide **50** was isolated in 24% yield. It is assumed that sulfide **50** might be produced via 2,3-sigmatropic rearrangement of intermediate **49**. Because the present result indicates the existence of the sulfonium salt **1** in an indirect manner, direct and definite proof for the formation of sulfonium salt **1** must be sought. Direct evidence was then obtained by low-temperature ^{1}H NMR spectroscopy.

2-Cyclohexen-1-one was treated with 1.1 equiv of TBSOTf and an excess amount of dimethyl sulfide in chloroform-*d* at −50 °C, and the reaction mixture was slowly warmed to room temperature. Low-temperature ^{1}H NMR spectroscopy in chloroform-*d* at −50 °C exhibited two singlets at δ 4.51 and 4.86 ppm resulting from an olefinic proton and the proton adjacent to the dimethylsulfonium group (Figure 1). However, sulfonium salt **1** was decomposed above −45 °C. That is to say, after 2-cyclohexen-1-one was gradually regenerated above −45 °C, a clear ^{1}H NMR spectrum of 2-cyclohexen-1-one was obtained at −20 °C.

Furthermore, diphenyl sulfide, which is less nucleophilic than dimethyl sulfide, did not undergo conjugate addition to α,β-enones. In summary, the sulfonium salts are highly unstable species, and their existence could only be detected by low-temperature ^{1}H NMR spectroscopy. The reaction proceeds via an addition-substitution mechanism involving the formation of allylic sulfonium salts. The addition of dimethyl sulfide to α,β-enones in the presence of TBSOTf produced the allylic sulfonium salts. Substitutions of dimethyl sulfide by in-situ-generated allylindium, propargylindium, and allenylindium reagents then yielded the desired products (Scheme 3).

Conclusions

In conclusion, 3-*tert*-butyldimethylsilyloxyalk-2-enylsulfonium salts in-situ-generated from the reaction of α,β-enones with dimethyl sulfide in the presence of TBSOTf underwent a novel nucleophilic substitution with allylindium reagents generated from indium and allyl halides to give silyl enol ethers of α,β-unsaturated ketones in good yields, which correspond to Michael addition products. Also, facile β-propargylation and β-allenylation occurred by the reaction of sulfonium salts with various organoindium reagents derived from propargyl bromide and indium to produce silyl enol ethers of δ,ϵ-alkynyl ketones and β-allenyl ketones, respectively, in good yields. The reaction proceeds via an addition-substitution mechanism involving the formation of allylic sulfonium salts, which are highly unstable species. The addition of a dimethyl sulfide to α,β-enones in the presence of TBSOTf produced the allylic sulfonium salts. Substitutions of dimethyl sulfide by in-situ-generated allylindium, propargylindium, and allenylindium then yielded the desired products. Although β-substituted silyl enol ethers are

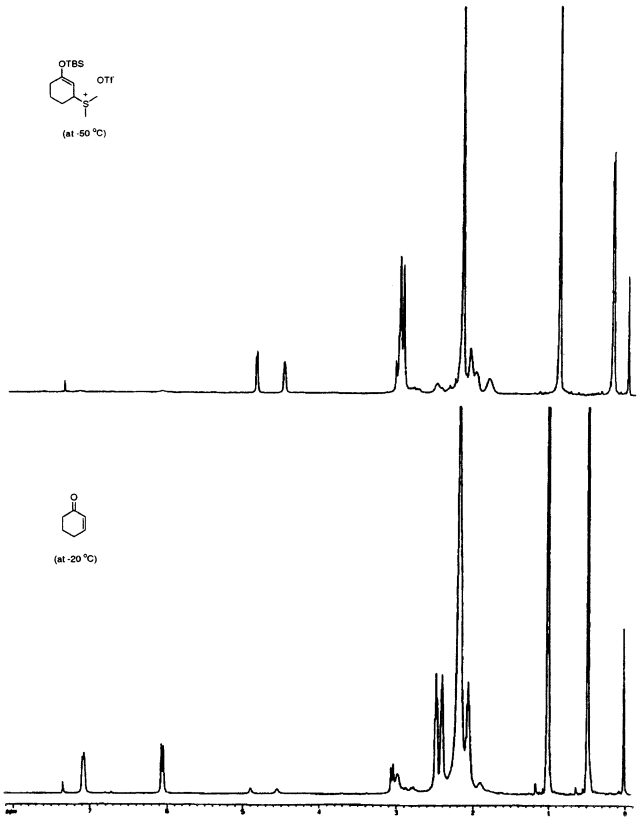


Figure 1. ^{1}H NMR spectrum of 3-(*tert*-butyldimethylsilyloxy)-2-cyclohexenyldimethylsulfonium trifluoromethanesulfonate in $CDCl_3$ at −50 and −20 °C, respectively.

(20) Kraus, G. A.; Gottschalk, P. *Tetrahedron Lett.* **1983**, *24*, 2727.

generally accessible to α,β-enones by conjugate addition of copper reagent to α,β-enones followed by enolate trapping, few reports for the Michael addition reaction of allyl, propargyl, and allenyl reagents to α,β-enones have been published.[5,6] Thus, the present method would find an abundant use as a synthetic method, for example, for cyclopentene annulation. Also, because sulfonium salts have been utilized mainly in the generation of sulfur ylides[21] and have seldom been used as leaving groups,[22] the present method enhances the synthetic utility of 3-*tert*-butyldimethylsilyloxylalk-2-enylsulfonium salts.

Experimental Section

General. Reactions were carried out in oven-dried glassware under a nitrogen atmosphere. All commercial reagents were used without purification, and all solvents were reaction grade. THF was freshly distilled from sodium/benzophenone under nitrogen. All reaction mixtures were stirred magnetically and were monitored by thin-layer chromatography using Merck silica gel 60 F_{254} precoated glass plates, which were visualized with UV light and then developed by using Fluka silica gel 60 (0.040−0.063 mm, 230−400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brucker DPX FT(400 MHz) spectrometer. Deuterated chloroform was used as the slovent, and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent (δ 7.24 for ^{1}H and δ 77.0 for ^{13}C). High-resolution mass spectra were recorded on a VG Autospec Ulpima. Infrared spectra were recorded on a JASCO FT/IR-460 plus FT-IR spectrometer as either a thin film pressed between two sodium chloride plates or a solid suspended in a potassium bromide disk.

Typical Experimental Procedure of β-Allylation onto α,β-Enones. Dimethyl sulfide (75.0 mg, 1.2 mmol) and TBSOTf (278 mg, 1.05 mmol) were added successively to a stirred solution of 2-cyclohexen-1-one (96.0 mg, 1.0 mmol) in THF (1.5 mL) at −78 °C under a nitrogen atmosphere. After 10 min, allylindium reagent, which is generated from allyl bromide (218 mg, 1.5 mmol) and indium (115 mg, 1.0 mmol) in THF (1.5 mL), was added, and the mixture was stirred at −78 °C for 30 min. The reaction mixture was quenched with $NaHCO_3$ (saturated aqueous). The aqueous layer was extracted with ether (3 × 20 mL), and combined organics were washed with water and brine (20 mL), dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using *n*-hexane to give 1-(*tert*-butyldimethylsiloxy)-3-(prop-2-enyl)cyclohexene (163 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.78 (ddt, J = 17.38, 10.13, 7.09 Hz, 1H), 4.95 (d, J = 17.38 Hz, 1H), 4.92 (d, J = 10.13 Hz, 1H), 4.80 (s, 1H), 2.21−2.19 (m, 1H), 2.05−1.97 (m, 4H), 1.77−1.66 (m, 2H), 1.56−1.53 (m, 1H), 1.16−1.07 (m, 1H), 0.92 (s, 9H), 0.12 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.90, 137.35, 115.70, 108.84, 41.38, 34.54, 29.96, 28.67, 25.73, 21.71, 18.06, −4.32, −4.49. IR (film): 3053, 2930, 1664, 1472, 1366, 1265, 1180 cm^{-1}. HRMS (EI): calcd for $C_{15}H_{28}OSi$ M^+ 252.1909, found 252.1905.

Typical Experimental Procedure of β-Propargylation onto α,β-Enones. Dimethyl sulfide (75.0 mg, 1.2 mmol) and TBSOTf (278 mg, 1.05 mmol) were added successively to a stirred solution of 2-cyclohexen-1-one (96.0 mg, 1.0 mmol) in THF (1.5 mL) at −78 °C under a nitrogen atmosphere. After 10 min, propargylindium reagent, which is generated from propargyl bromide (80% in toluene, 223.0 mg, 1.5 mmol) and indium (115 mg, 1.0 mmol) in THF (1.5 mL), was added, and the mixture was stirred at −78 °C for 30 min. The reaction mixture was quenched with $NaHCO_3$ (saturated aqueous). The aqueous layer was extracted with ether (3 × 20 mL), and combined organics were washed with water and brine (20 mL), dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel, which was treated with 5% Et_3N in hexane, column chromatography using *n*-hexane to give 1-(*tert*-butyldimethylsiloxy)-3-(prop-2-ynyl)-cyclohexene (215 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.83 (br s, 1H), 2.40−2.30 (m, 1H), 2.12 (dd, J = 7.2, 2.7 Hz, 2H), 2.01−1.90 (m, 2H), 1.93 (t, J = 2.7 Hz, 1H), 1.80−1.60 (m, 2H), 1.68−1.43 (m, 1H), 1.29−1.16 (m, 1H), 0.90 (s, 9H), 0.11 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 107.8, 83.4, 68.9, 34.3, 29.8, 28.3, 25.8, 25.7, 21.4, 18.0, −4.3, −4.5. IR (film): 3313, 2929, 2858, 2118, 1666, 1200 cm^{-1}. HRMS (EI): calcd for $C_{15}H_{26}OSi$ M^+ 250.1753, found 250.1759.

Typical Experimental Procedure of β-Allenylation onto α,β-Enones. Dimethyl sulfide (75.0 mg, 1.2 mmol) and TBSOTf (278 mg, 1.05 mmol) were added successively to a stirred solution of 2-cyclohexen-1-one (96.0 mg, 1.0 mmol) in THF (1.5 mL) at −78 °C under a nitrogen atmosphere. After 10 min, allenylindium reagent, which is generated from 1-bromo-2-butyne (199.0 mg, 1.5 mmol), indium (115 mg, 1.0 mmol), and lithium iodide (134 mg, 1.0 mmol) in THF (1.5 mL), was added, and the mixture was stirred at −78 °C for 30 min. The reaction mixture was quenched with $NaHCO_3$ (saturated aqueous). The aqueous layer was extracted with ether (3 × 20 mL), and combined organics were washed with water and brine (20 mL), dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel, which was treated with 5% Et_3N in hexane, column chromatography using *n*-hexane to give 1-(*tert*-butyldimethylsiloxy)-3-(1-methyl-1,2-propadienyl)cyclohexene (169 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.97 (bs, 1H), 4.76−4.70 (m, 2H), 2.87−2.84 (m, 1H), 2.12−1.85 (m, 4H), 1.81 (t, J = 3.11 Hz, 3H), 1.71−1.67 (m, 2H), 1.04 (s, 9H), 0.14 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.32, 151.35, 107.09, 102.62, 74.69, 38.79, 29.84, 27.37, 25.87, 21.59, 18.02, 16.86, −4.21, −4.57. IR (film): 2929, 2242, 1446, 1383, 1350 cm^{-1}. HRMS (EI): calcd for $C_{16}H_{28}OSi$ M^+ 262.4784, found 262.4781.

(*Z*)-1-(*tert*-Butyldimethylsilyloxy)-4-methyl-1,3-diphenylhex-1-en-5-yne (35). ^{1}H NMR (400 MHz, $CDCl_3$) major isomer: δ 7.64−7.44 (m, 10H), 5.63 (d, J = 10.10 Hz, 1H), 4.06 (dd, J = 10.10, 7.13 Hz, 1H), 3.03−2.99 (m, 1H), 2.21 (d, J = 6.49, 1H), 1.39 (d, J = 7.02 Hz, 3H), 1.19 (s, 9H), 0.07 (s, 6H). Minor isomer: δ 7.64−7.44 (m, 10H), 5.72 (d, J = 10.10 Hz, 1H), 4.14 (dd, J = 10.10, 7.13 Hz, 1H), 3.08−3.06 (m, 1H), 2.28 (d, J = 6.49, 1H), 1.42 (d, J = 7.02 Hz, 3H), 1.16 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) major isomer: δ 150.26, 142.31, 139.64, 128.64, 128.12, 127.81, 127.69, 126.58, 126.36, 112.66, 87.33, 70.16, 46.45, 32.61, 25.91, 19.21, 18.29, −4.02, −3.75. Minor isomer: δ 151.07, 143.37, 139.81, 128.36, 128.08, 127.96, 127.69, 126.25, 110.87, 86.93, 65.86, 45.95, 33.28, 25.91, 19.71, 15.28, −4.02, −3.75. IR (film): 3303, 3055, 2986, 1645, 1265 cm^{-1}. HRMS (EI): calcd for $C_{25}H_{32}OSi$ M^+ 376.2222, found 376.2228.

1-(*tert*-Butyldimethylsiloxy)-3-(prop-2-ynyl)cyclopentene (36). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.66 (s, 1H), 2.85−2.81 (m, 1H), 2.30−2.08 (m, 5H), 1.92 (t, J = 2.68 Hz, 1H), 1.58−1.55 (m, 1H), 0.92 (s, 9H), 0.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.58, 106.28, 84.16, 68.76, 41.68, 33.59, 27.85, 26.32, 26.07, 18.55, −4.20, −4.27. IR (film): 3303, 3053, 2931, 1686, 1264 cm^{-1}. HRMS (EI): calcd for $C_{14}H_{24}OSi$ M^+ 236.1596, found 236.1578.

1-(*tert*-Butyldimethylsiloxy)-3-(1-methylprop-2-ynyl)cyclopentene (37). ^{1}H NMR (400 MHz, $CDCl_3$) major isomer: δ 4.71 (bs, 1H), 2.70−2.67 (m, 1H), 2.36−2.27 (m, 4H), 2.05−2.00 (m, 2H), 1.14 (d, J = 7.00 Hz, 3H), 0.93 (s, 9H), 0.173 (s, 3H), 0.168 (s, 3H). Minor isomer: δ 4.63 (bs, 1H), 2.70−2.67 (m, 1H), 2.36−2.27 (m, 4H), 2.05−2.00 (m, 2H), 1.15 (d, J = 7.00 Hz, 3H), 0.93 (s, 9H), 0.173 (s, 3H), 0.168 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) major isomer: δ 156.33, 104.59, 88.42, 68.36, 47.47, 33.49, 31.73, 25.69, 25.44, 18.19, 15.29, −4.55, −4.66. Minor isomer: δ 153.90, 101.59, 87.76, 69.06, 41.09, 33.23, 30.97, 26.18, 25.44, 18.50, 14.13, −4.55, −4.66. IR (film): 3303, 3053, 2932, 1687, 1265 cm^{-1}. HRMS (EI): calcd for $C_{15}H_{26}OSi$ M^+ 250.1753, found 250.1799.

(21) (a) Johnson, A. W. *Ylide Chemistry*; Academic Press: New York, 1966. (b) Trost, B. M.; Melvin, L. S., Jr. *Sulfur Ylide*; Academic Press: New York, 1975.
(22) (a) Trost, B. M.; Shibata, T. *J. Am. Chem. Soc*. **1982**, *104*, 3225. (b) Trost, B. M.; Martin, S. J. *J. Am. Chem. Soc*. **1984**, *106*, 4263. (c) Matsuyama, H.; Nakamura, T.; Kamigata, N. *J. Org. Chem*. **1989**, *54*, 5218.

1-(*tert*-Butyldimethylsiloxy)-3-(1-methyl-1,2-propadienyl)cyclopentene (38). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.85 (bs, 1H), 4.65−4.54 (m, 2H), 2.74−2.72 (m, 1H), 2.38−2.06 (m, 4H), 1.89 (t, J = 2.71 Hz, 3H), 0.94 (s, 9H), 0.12 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.15, 152.11, 106.28, 94.16, 73.15, 41.94, 37.99, 25.70, 18.10, 14.84, 10.60, −3.99, −4.07. IR (film): 2930, 2248, 1446, 1383, 1350 cm^{-1}. HRMS (EI): calcd for $C_{15}H_{26}OSi$ M^+ 250.1753, found 250.1750.

1-(*tert*-Butyldimethylsiloxy)-2-methyl-3-(1-methyl-1,2-propadienyl)-cyclopentene (40). ^{1}H NMR (400 MHz, $CDCl_3$) major isomer: δ 2.77−2.63 (m, 2H), 2.28−2.21 (m, 2H), 1.99 (d, J = 2.44, 1H), 1.98−1.90 (m, 1H), 1.76−1.69 (m, 1H), 1.50 (s, 3H), 1.01 (d, J = 7.04 Hz, 3H), 0.94 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H). Minor isomer: δ 2.77−2.63 (m, 2H), 2.28−2.21 (m, 2H), 1.98−1.90 (m, 1H), 1.91 (d, J = 2.74 Hz, 1H), 1.76−1.69 (m, 1H), 1.54 (s, 3H), 1.15 (d, J = 7.04 Hz, 3H), 0.13 (s, 3H), 0.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) major isomer: δ 156.73, 104.99, 101.99, 88.91, 68.75, 47.87, 37.69, 33.89, 32.19, 26.09, 18.89, 18.58, −4.15, −4.25. Minor isomer: δ 157.00, 105.12, 104.82, 88.82, 69.46, 41.49, 38.43, 33.62, 32.13, 26.23, 19.54, 18.54, −4.15, −4.25. IR (film): 3303, 3053, 2931, 1686, 1264 cm^{-1}. HRMS (EI): calcd for $C_{16}H_{28}OSi$ M^+ 264.1909, found 264.1945.

1-(*tert*-Butyldimethylsiloxy)-2-methyl-3-(1-methyl-1,2-propadienyl)-cyclopentene (41). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.57−4.54 (m, 2H), 3.09−3.06 (m, 1H), 2.32−2.22 (m, 2H), 2.11−2.04 (m, 1H), 1.73−1.66 (m, 1H), 1.57 (t, J = 3.14 Hz, 3H), 1.48 (s, 3H), 0.94 (s, 9H), 0.12 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.25, 148.22, 114.08, 100.96, 73.15, 49.94, 32.99, 25.70, 25.61, 18.10, 14.84, 10.60, −3.99, −4.07. IR (film): 2929, 2245, 1440, 1350 cm^{-1}. HRMS (EI): calcd for $C_{16}H_{28}OSi$ M^+ 264.1909, found 264.1909.

1-(*tert*-Butyldimethylsiloxy)-3-(1-methylprop-2-ynyl)cyclohexene (43). ^{1}H NMR (400 MHz, $CDCl_3$) major isomer: δ 4.95 (s, 1H), 2.41−2.33 (m, 1H), 2.24−2.22 (m, 1H), 2.03 (t, J = 2.58 Hz, 1H), 2.01−1.96 (m, 2H), 1.84−1.73 (m, 2H), 1.58−1.52 (m, 1H), 1.40−1.19 (m, 1H), 1.17 (d, J = 7.00 Hz, 3H), 0.92 (s, 9H), 1.52 (s, 3H), 0.14 (s, 3H). Minor isomer: δ 4.84 (s, 1H), 2.41−2.33 (m, 1H), 2.24−2.22 (m, 1H), 2.03 (t, J = 2.58 Hz, 1H), 2.01−1.96 (m, 2H), 1.84−1.73 (m, 2H), 1.58−1.52 (m, 1H), 1.40−1.19 (m, 1H), 1.17 (d, J = 7.00 Hz, 3H), 0.92 (s, 9H), 0.15 (s, 3H), 0.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) major isomer: δ 152.02, 106.63, 88.20, 68.99, 40.14, 31.38, 29.88, 26.50, 25.74, 22.07, 17.94, −4.19, −4.57. Minor isomer: δ 152.11, 106.86, 88.14, 68.97, 39.95, 31.26, 29.95, 26.50, 25.72, 21.70, 18.13, −4.19, −4.54. IR (film): 3302, 3053, 2932, 1664, 1262 cm^{-1}. HRMS (EI): calcd for $C_{16}H_{28}OSi$ M^+ 264.1909, found 264.1927.

1-(*tert*-Butyldimethylsiloxy)-2-methyl-3-(1-methylprop-2-ynyl)cyclohexene (46). ^{1}H NMR (400 MHz, $CDCl_3$) major isomer: δ 2.89−2.84 (m, 1H), 2.41−1.18 (m, 7H), 1.93 (d, J = 2.47 Hz, 1H), 1.56 (s, 3H), 0.99 (d, J = 7.08 Hz, 3H), 0.94 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H). Minor isomer: δ 2.89−2.84 (m, 1H), 2.41−1.18 (m, 7H), 2.04 (d, J = 2.47 Hz, 1H), 1.63 (s, 3H), 1.19 (d, J = 7.21 Hz, 3H), 0.123 (s, 3H), 0.116 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) major isomer: δ 146.70, 112.17, 87.23, 69.18, 44.14, 30.91, 28.37, 25.90, 24.11, 22.02, 18.76, 14.87, 13.70, −3.71, −3.82. Minor isomer: δ 145.95, 113.44, 89.11, 68.50, 43.08, 30.77, 27.09, 25.86, 23.77, 21.84, 18.18, 14.13, 13.97, −3.99, −4.09. IR (film): 3310, 3054, 2986, 1421, 1265 cm^{-1}. HRMS (EI): calcd for $C_{17}H_{30}OSi$ M^+ 278.2066, found 278.2063.

3-(*tert*-Butyldimethylsilyloxy)cyclohex-2-enyldimethylsulfonium Trifluoromethanesulfonate. ^{1}H NMR (400 MHz, $CDCl_3$, at −50 °C): δ 4.86 (d, J = 4.98 Hz, 1H), 4.50 (bs, 1H), 2.99 (s, 3H), 2.95 (s, 3H), 2.75−1.88 (m, 6H), 0.91 (s, 9H), 0.20 (s, 3H), 0.19 (s, 3H).

Acknowledgment. This work was supported by Grant No. R02-2003-000-10023-0 of the Basic Research Program of the Korea Science & Engineering Foundation, the CMDS at KAIST, and a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. T.M. has been granted a Research Fellowship of the Japan Society for the Promotion of Science for Young Scientists. We thank Prof. S. Chang (Department of Chemistry, KAIST) for HRMS measurements. The gas chromatograms were provided by the GC facility, supported by the Research Center for Advanced Mineral Aggregate Composite Products.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra for all new compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA035988M