Intramolecular Cyclization of *tert*-Butyldiphenylallylsilane Units and Carbonyl Groups: Allylsilane Terminated Cyclization versus the Ene Reaction

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tert-Butyldiphenylsilylcopper reacts with allene to give an allylsilane-vinylcopper intermediate which upon treatment with α,β-unsaturated ketones leads to allylsilane containing ketones resulting from conjugate addition. These oxoallylsilanes bearing the bulky *tert*-butyldiphenylsilyl group undergo highly selective intramolecular cyclizations when treated with Lewis acid affording unsaturated cyclopentanols. Two reactivity patterns are observed: allylsilane terminated cyclization involving elimination of silicon or an ene reaction without losing the silyl group. The pathway depends on the ability of a hydrogen β to the carbonyl to be removed in an ene-type process. α,β-Unsaturated acid chlorides lead to silylated cyclopentenones.

The metallocupration of allenes and acetylenes is a powerful and synthetically useful reaction which has attracted considerable attention in the scientific community.[1,2] For the past 10 years,[3,4] we have been involved in the study of the silyl- and stannylcupration of allenes and acetylenes. These metallometalation reactions involve the addition of copper to one end of a multiple bond and of a silyl or stannyl group to the other, leading to a useful method for the synthesis of silicon or tin containing allyl- and vinylorganocuprates. The silylcupration of allenes is a reversible reaction whose regiochemistry depends on several factors such as temperature, structure of the allene, nature of the silyl group, and nature of the copper species.[5] The different regioselectivity found in the reaction of allene with phenyldimethylsilylcuprate[6] and *tert*-butyldiphenylsilylcuprate[7] (formally higher-order cuprates) provides a useful route for the selective synthesis of phenyldimethylvinylsilanes and *tert*-butyldiphenylallylsilanes, respectively.

The use of phenyldimethylsilylcopper[8] **1** as a silylating agent instead of the corresponding cuprate causes a dramatic change upon the regiochemistry of the silylcupration of allenes. Thus, the reaction of silylcopper species **1** with allene[8] is a highly regioselective method to obtain functionalized allylsilanes through a vinylcopper-allylsilane intermediate which readily reacts with different electrophiles (Scheme 1).

Interestingly enough, the use of α,β-unsaturated acid chlorides, aldehydes, and ketones affords allylsilanes containing divinyl ketones and oxoallylsilanes,[9,10a] which are valuable intermediates in the synthesis of methylenecyclopentanols and methylenecyclopentanones. Cyclopentane ring formation results from a stereocontrolled silicon-assisted intramolecular cyclization upon treat-

(1) Stoichiometric metallometalations: (a) Sharma, S.; Oehlschlager, A. C. *J. Org. Chem.* **1991**, *56*, 770. (b) Singer, R. D.; Hutzinger, M. W.; Oehlschlager, A. C. *J. Org. Chem.* **1991**, *56*, 4933. (c) Singer, R. D.; Hutzinger, M. W.; Oehlschlager, A. C. *J. Am. Chem. Soc.* **1990**, *112*, 9397. (d) Piers, E.; Gavai, A. V. *J. Org. Chem.* **1990**, *55*, 2374, 2380. (e) Piers, E.; Chong, J. M. *Can. J. Chem.* **1988**, *66*, 1425. (f) Cox, S. D.; Wudl, F. *Organometallics* **1983**, *2*, 184. (g) Lipshutz, B. H.; Sharma, S.; Reuter, D. C. *Tetrahedron Lett.* **1990**, *31*, 7253. (h) Lipshutz, B. H.; Reuter, D. C. *Tetrahedron Lett.* **1989**, *30*, 4617, 2065. (i) Magriotis, P. A.; Scott, M. E.; Kim, K. D. *Tetrahedron Lett.* **1991**, *32*, 6085. (j) Marino, J. P.; Edmonds, M. V. M.; Stengel, P. J.; Oliveira, A. R. M.; Simonelli, F.; Ferreira, J. T. B. *Tetrahedron Lett.* **1992**, *33*, 49. (k) Beaudet, I.; Parrain, J. L.; Quintard, J. P. *Tetrahedron Lett.* **1991**, *32*, 6333. (l) Marek, I.; Alexakis, A.; Normant, J. F. *Tetrahedron Lett.* **1991**, *32*, 6337. (m) Pereira, O. Z.; Chan, T. H. *Tetrahedron Lett.* **1995**, *36*, 8749. (n) Pereira, O. Z.; Chan, T. H. *J. Org. Chem.* **1996**, *61*, 5406. (o) See also ref 1c and citations therein.

(2) Catalytic metallometalations: (a) Sharma, S.; Oehlschlager, A. C. *Tetrahedron Lett.* **1986**, *27*, 6161. (b) Sharma, S.; Oehlschlager, A. C. *Tetrahedron Lett.* **1988**, *29*, 261. (c) Nozaki, K.; Wakamatsu, K.; Nonaka, T.; Tückmantel, W.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1986**, *27*, 2007. (d) Nonaka, T.; Okuda, Y.; Matsubara, S.; Oshima, K.; Utimoto, K.; Nozaki, H. *J. Org. Chem.* **1986**, *51*, 4716. (e) Mitchell, T. N.; Wickenkamp, R.; Amaria, A.; Dicke, R.; Schneider, U. *J. Org. Chem.* **1987**, *52*, 4868. (f) Mitchell, T. N. *J. Organomet. Chem.* **1992**, *437*, 127. (g) See also ref 1c and citations therein.

(3) SiCu of allenes and acetylenes: (a) Cuadrado, P.; González, A. M.; Pulido, F. J.; Fleming, I. *Tetrahedron Lett.* **1988**, *29*, 1825. (b) Barbero, A.; Cuadrado, P.; González, A. M.; Pulido, F. J.; Fleming, I.; Sánchez, A. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1525. (c) Blanco, F. J.; Cuadrado, P.; González, A. M.; Pulido, F. J. *Synthesis* **1996**, 42. (d) Barbero, A.; Blanco, Y.; García, C.; Pulido, F. J. *Synthesis* **2000**, 1223. (e) Barbero, A.; García, C.; Pulido, F. J. *Synlett* **2001**, 824.

(4) SnCu of allenes and acetylenes: (a) Barbero, A.; Cuadrado, P.; González, A. M.; Pulido, F. J.; Fleming, I. *J. Chem. Soc., Chem. Commun.* **1990**, 1030. (b) Barbero, A.; Cuadrado, P.; González, A. M.; Pulido, F. J.; Fleming, I. *J. Chem. Soc., Perkin Trans. 1* **1992**, 327. (c) Barbero, A.; Cuadrado, P.; González, A. M.; Pulido, F. J.; Fleming, I. *J. Chem. Res., Synop.* **1990**, *297*, 291. (d) See also ref 1c. (e) Barbero, A.; Cuadrado, P.; González, A. M.; Pulido, F. J.; Fleming, I. *J. Chem. Soc., Chem. Commun.* **1992**, 351. (f) Barbero, A.; Cuadrado, P.; González, A. M.; Pulido, F. J.; Rubio, R.; Fleming, I. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1657. (g) Barbero, A.; Cuadrado, P.; García, C.; Rincón, J. A.; Pulido, F. J. *J. Org. Chem.* **1998**, *63*, 7531. (h) Barbero, A.; Pulido, F. J.; Rincón, J. A.; Cuadrado, P.; Galisteo, D.; Martínez-García, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 2101.

(5) (a) Barbero, A.; Pulido, F. J. *Recent Res. Dev. Synth. Org. Chem.* **1999**, *2*, 1.

(6) (a) Fleming, I.; Pulido, F. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1010. (b) Cuadrado, P.; González, A. M.; Pulido, F. J.; Fleming, I.; Rowley, M. *Tetrahedron* **1989**, *45*, 413.

(7) Barbero, A.; Cuadrado, P.; González, A. M.; Pulido, F. J.; Fleming, I. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2811.

(8) Blanco, F. J.; Cuadrado, P.; González, A. M.; Pulido, F. J.; Fleming, I. *Tetrahedron Lett.* **1994**, *35*, 8881.

(9) Barbero, A.; García, C.; Pulido, F. J. *Tetrahedron Lett.* **1999**, *40*, 6652.

(10) (a) Barbero, A.; García, C.; Pulido, F. J. *Tetrahedron* **2000**, *56*, 2739. (b) Trost, B. M.; Coppola, B. P. *J. Am. Chem. Soc.* **1982**, *104*, 6879.

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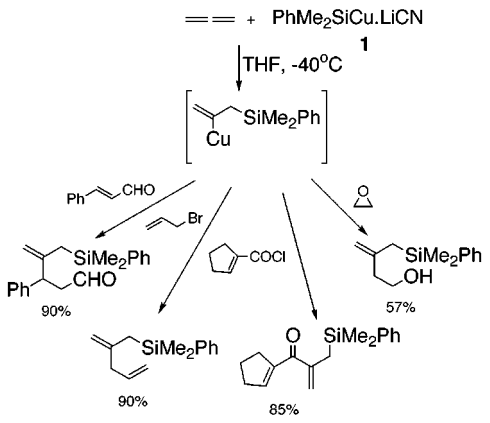
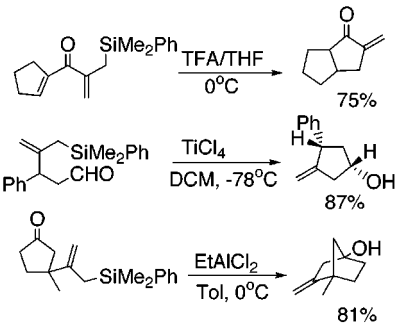
Scheme 1



Scheme 2



ment with a Lewis Acid[9,10a] (Scheme 2). Similar cyclizations using different silicon groups have been previously reported by Trost.[10b]

The chemistry of allylsilanes has been extensively studied.[11] They have proved to be versatile silicon-containing carbon nucleophiles which readily react with carbonyl electrophiles[12] and enones.[13] The reaction often shows high levels of stereocontrol and involves an intermediate carbocation which usually evolves with the loss of the silyl group. The ability of silicon to stabilize a developing β carbocation is believed to be responsible for the rate of such reactions.[14]

Scheme 3

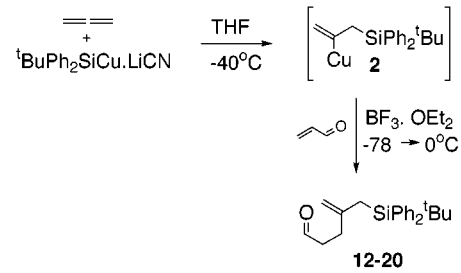
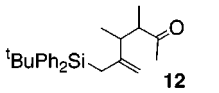
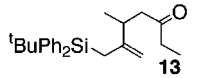
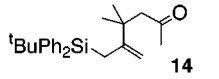
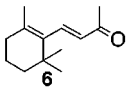
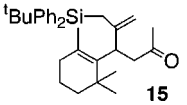
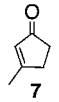
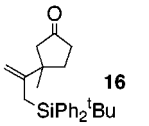
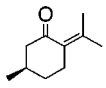
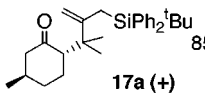
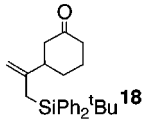
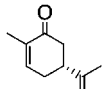
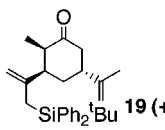
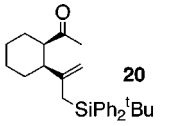


Table 1. Reaction of Vinylcopper 2 with Enones

Entry		Product	Yield (%)
1	 **3**	 **12**	88
2	 **4**	 **13**	89
3	 **5**	 **14**	90
4	 **6**	 **15**	85
5	 **7**	 **16**	87
6	 **8 (+)**	 **17a (+)**	85
7	 **9**	 **18**	87
8	 **10 (-)**	 **19 (+)**	75
9	 **11**	 **20**	81

From previous work, it is clear that the behavior of the *tert*-butyldiphenylsilyl group is perceptively different from that observed for the phenyldimethylsilyl group.[3b,7] We now describe the full results[15] of the reaction of **2** with enones as a valuable process to obtain carbonyl functionalized allyl-*tert*-butyldiphenylsilanes, which show an interesting reactivity pattern in acid-catalyzed cyclization reactions.

Thus, *tert*-butyldiphenylsilylcopper[10a] reacts with allene at −40 °C giving an allylsilane-vinylcopper intermediate **2** which was treated with different α,β-unsaturated ketones **3**−**11** to afford the products of conjugate addition **12**−**20** in very good yields (Scheme 3, Table 1).

The high selection of the vinylcopper species **2** for the 1,4-addition, in contrast with the preferred 1,2-addition

(11) (a) Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063. (b) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207. (c) Fleming, I.; Dunogues, J.; Smithers, R. *Org. React.* **1989**, *37*, 57. (d) Masse, C. E.; Panek, J. S. *Chem. Rev.* **1995**, *95*, 1293. (e) Nativi, C.; Ricci, A.; Taddei, M. In *Frontiers Of Organosilicon Chemistry*; Bassindale, A. R., Gaspar, P. P., Eds.; The Royal Society of Chemistry: Letchworth, 1991; p 332.

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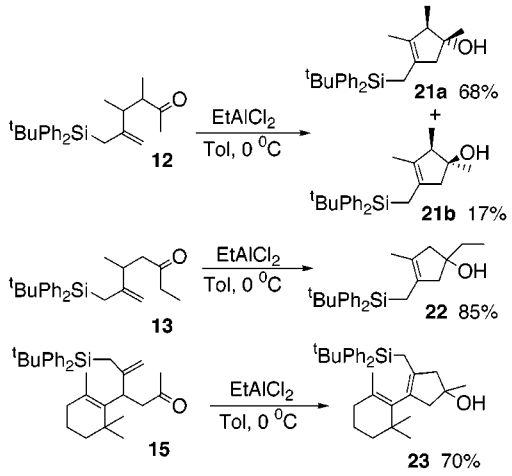
(13) See among others: (a) Hosomi, A.; Sakurai, H. *J. Am. Chem. Soc.* **1977**, *99*, 1673. (b) Knölker, H.-J.; Jones, P. G.; Pannek, J. B. *Synlett* **1990**, 429. (c) Knölker, H.-J.; Jones, P. G.; Pannek, J. B.; Weinkauf, A. *Synlett* **1991**, 147. (c) Knölker, H.-J.; Foitzik, N.; Goesmann, H.; Graf, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1081. (c) Organ, M. G.; Dragan, V.; Miller, M.; Froese, R. D. J.; Goddard, J. D. *J. Org. Chem.* **2000**, *65*, 3666.

(14) (a) Hanstein, W.; Berwin, H. J.; Traylor, T. G. *J. Am. Chem. Soc.* **1970**, *92*, 829. (b) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496. (c) Lambert, J. B.; Wang, G.-T.; Finzel, R. B.; Teramuda, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838. (d) Green, A. J.; Kuan, Y.-L.; White, J. M. *J. Org. Chem.* **1995**, *60*, 2734. (e) Gabelica, V.; Kresge, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 3838.

(15) A very preliminary result of the reaction was shown in ref 10.

Scheme 4

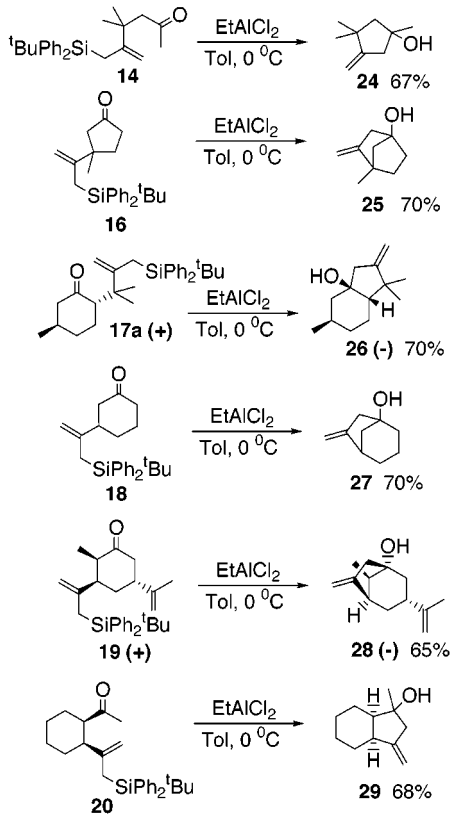


of the corresponding vinylcuprate,[7] indicates the softness of the former nucleophiles. All the reactions were carried out in the presence of $BF_3{\cdot}OEt_2$ which considerably increased the yield. Remarkably, the reaction of **10** and **11** with **2** was very stereoselective leading to the products **19** and **20** corresponding to the protonation of the intermediate enolate at the less-hindered face (opposite the silicon group). The stereochemistry of the optically active compound **19** was asigned on the basis of ^{1}H NMR and NOESY experiments. To prove the stereochemistry of compound **20**, a sample of the compound was treated with NaOH solution. Under such conditions, epimerization at C_α to carbonyl occurs giving the more stable trans isomer, whose sterochemistry could be proved with ^{1}H NMR and ^{1}H NMR/NOESY experiments. The regioselectivity of the reaction of **2** with the α,*β*-*γ*,*δ*-unsaturated dienone **6** which leads exclusively to the 1,4-addition product **15** is probably due to the higher accessibility of the bulky silylcopper reagent for the *β* position of the dienone. Reaction of the enantiomerically pure compound **8** with **2** gave a mixture of diastereomers cis/trans in a 1:1 ratio which could be separated. Nevertheless, when this mixture was treated with a diluted NaOH solution followed by neutralization, a single trans isomer **17a** could be isolated in 85% total yield (Table 1).

It is well known that the addition of allylsilanes to oxocompounds requires the assistance of a catalyst (usually a Lewis acid) to proceed at reasonable rates.[11] Among the Lewis acids tried in the cyclization reactions, Et_2AlCl showed the best results.

Thus, the intramolecular acid-catalyzed cyclization of allylsilane-ketones **12**, **13**, and **15** gave the cyclopentenols **21**−**23** which maintain the hindered silyl group, in sharp contrast with the observed behavior for the phenyldimethylsilyl analogues where the silyl moiety is always lost.[10a] Because of the low electrofugacity of the *tert*-butyldiphenylsilyl group, formation of an intermediate carbocation *β* to silicon could be followed by the loss of an adjacent hydrogen to form the double bond, which would account for the observed result. However, the reaction proved to be extremely regioselective leading to a unique allylsilane which corresponds to the elimination of a hydrogen *γ* to silicon and *β* to the carbonyl group (Scheme 4). Abstraction of hydrogen from other different positions was never observed. In fact, we were not able to detect, in any of the studied examples, the elimination of the allylic hydrogens α to silicon.

Scheme 5



These observations are not consistent with the intermediacy of a carbocation species. On the contrary, the intervention of an intramolecular ene reaction involving the carbonyl unit and the allylic moiety bearing the hydrogen *β* to carbonyl seems more feasible.

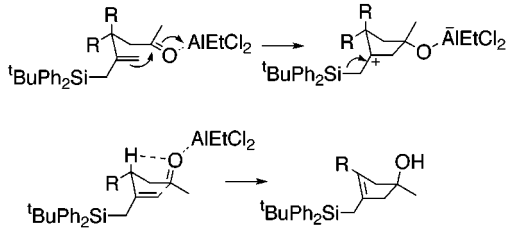
Accordingly, we wondered what would happen if the hydrogen was not in that position. For that purpose, we used the *β*,*β*-disubstituted ketones **5**, **7**, and **8**. This time, the cyclization reaction of the oxoallylsilanes **14**, **16**, and **17a** led to cyclopentenols **24**−**26**, where the lack of a hydrogen *β* to the carbonyl group caused the silyl group to come off, probably following the usual S_E mechanism involving stabilized carbocations *β* to silicon (Scheme 5).

Allylsilane terminated cyclizations of the ketones **18**−**20** gave cyclopentanols **27**−**29** losing the silicon group again (Scheme 5). Although compounds **18**−**20** have a hydrogen *β* to the carbonyl, the sterical requirements of these cyclic ketones do not favor a low-energy transition state for the ene reaction. Moreover, the angular position of the hydrogen would lead to a very strained structure having a double bond on a bridgehead carbon which is an unfavorable process as stated by Bredt.

The high stereocontrol observed in the succesive transformation of **10** → **19** → **28** allows the conversion of (−)-carvone in a bicyclic alcohol where three new stereogenic centers of defined configuration are formed with a simple protocol.

From the above results, it seems quite a general trend that if the oxoallylsilane comes from an open-chain α,*β*-unsaturated ketone and it has an accessible hydrogen *γ* to silicon and *β* to a carbonyl group, this is lost during cyclization, giving allylsilane containing cyclopentenols. Otherwise, the *tert*-butyldiphenylsilyl group is the leaving group, as happens with other silyl groups in a typical allylsilane terminated cyclization.

Scheme 6



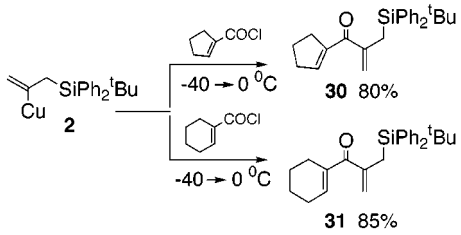
On the basis of the former considerations, two mechanistic alternatives could be put forward to account for the different behavior of the oxoallylsilanes **12**, **13**, and **15** toward oxoallylsilanes **14**, **16**−**20**. β,β-Disubstituted ketone **14** and cyclic ketones **16**−**20** follow the classical S_E reaction through a carbocation β to silicon losing the silyl group, despite the poor leaving group ability of the *tert*-butyldiphenylsilyl group. On the other hand, linear oxoallylsilanes **12**, **13**, and **15** react through an ene mechanism to give allylsilanes as final products (Scheme 6). This behavior is not found with the phenyl dimethylsilyl group where loss of silicon is always the observed process.

Allylsilanes are known to give ene reactions,[16] either under thermal or acid-catalyzed conditions. From the classical mechanism standpoint, it is generally agreed upon that the concerted ene reaction involves a highly asynchronous transition state featuring a well-developed C−C bond prior to a relatively late proton transfer toward the oxygen.[17] This will be favored by the stabilization of the partial positive charge at the β carbon atom to silicon.

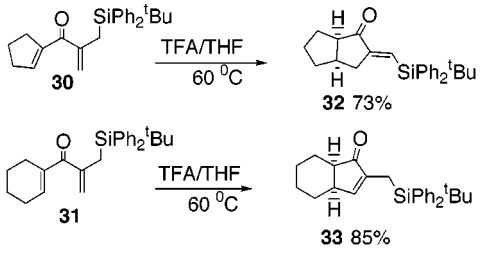
It was noted before that only hydrogens β to carbonyl are involved in the ene reaction, whereas allylic hydrogens α to silicon seem to be unreactive. The high level of regioselectivity obtained in the ene reaction could be interpreted in terms of the greater accessibility of the hydrogen β to the carbonyl group to be abstracted, probably due to the bulky *tert*-butyldiphenylsilyl group which hinders the hydrogens α to silicon.

To complete the study, divinyl ketones **30** and **31** were obtained with excellent yield by reaction of **2** with α,β-unsaturated acid chlorides (Scheme 7). The silicon-assisted Nazarov[18] reaction of divinyl ketones **30** and **31**, in the presence of TFA, affords a good yield of methylenecyclopentanones **32** and **33**, which maintain the hindered silyl group (Scheme 8). This time the loss of the hydrogen is not univocal leading to vinylsilane **32** and allylsilane **33** without apparent differentiation, which allows us to think about an intermediate carbocation β to silicon in which both hydrogens α and γ to silicon can be lost.

Scheme 7



Scheme 8



In conclusion, the reaction of allyl-*tert*-butyldiphenylsilylcopper **2** with α,β-unsaturated acid chlorides and ketones provides a useful way of synthesis of divinyl ketones and oxoallylsilanes, which upon treatment with a Lewis acid undergo highly regio- and stereoselective intramolecular silicon-assisted cyclization reactions to give silylated cyclopentenones, methylenecyclopentanols, and allylsilane containing cyclopentenols. Formation of the latter compounds depends on the ability of a hydrogen β to the ketone to be lost in an ene-type reaction. When this is not possible, an intramolecular allylsilane terminated cyclization is the normal process. The low electrofugacity of the *tert*-butyldiphenylsilyl group as compared with other silyl groups is responsible for the formation of silicon containing cyclic products when both reactions can compete.

Experimental Section

All melting points are uncorrected. All reagents were of commercial quality from freshly opened containers or were purified before use. THF was distilled under N_2 from purple solutions of sodium benzophenone ketyl. Allene (97%) was supplied by Air-Products in lecture bottles. Commercial reagents **3**−**11** were purchased from Aldrich. The preparation of α,β-unsaturated acid chlorides was reported previously.[10a] IR spectra were recorded on a FT/IR spectrophotometer as neat liquid films. ^{1}H and ^{13}C NMR spectra were taken at 300 and 50 MHz, respectively. GC/MS spectra were recorded operating either in the CI mode or in the EI mode (70 eV). The purification of the products was performed by flash chromatography on Silica Gel 60 (Merck, 230−400 mesh). Nonaqueous reactions were carried out under nitrogen atmosphere. Compounds **25**, **27**, and **29** were described in a previous article.[10a] Unless otherwise noted, yields of all compounds are of purified material. The stereochemistry of the compounds has been assigned on the basis of ^{1}H NMR and NOESY experiments.

Silylcupration of Allene. Preparation of Intermediate 2. A solution of *tert*-butyldiphenylsilyllithium[19] (3 mmol) prepared in THF (3 mL) was added by syringe to a stirred suspension of copper(I) cyanide (269 mg, 3 mmol) in THF (5 mL) at 0 °C. The resulting green-black mixture was stirred at this temperature for 30 min and then used immediately. The solution of *tert*-butyldiphenylsilylcopper (3 mmol) in THF (8 mL) was cooled at −40 °C, and a slight excess of allene was

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added from a balloon. The mixture was stirred for 1 h, and the reagent **2** was used immediately.

Reaction of Intermediate 2 with α,β-Unsaturated Ketones. $BF_3{\cdot}Et_2O$ (0.38 mL, 3 mmol) was added at −78 °C to a stirred solution of cuprate **2** (3 mmol), and the mixture was stirred for 10 min at this temperature. A solution of 3.6 mmol of ketones **3**−**11** in THF (5 mL) was then added dropwise at −78 °C, and the resulting mixture was kept at this temperature for 1 h. After gentle warming to 0 °C (over 0.5 h), the mixture was quenched with basic saturated ammonium chloride solution and extracted twice with Et_2O. The organic layer was dried ($MgSO_4$), evaporated, and chromatographed (EtOAc:hexanes) to give the allylsilanes **12**−**20**.

5-*tert*-Butyldiphenylsilylmethyl-3,4-dimethyl-5-hexen-2-one (12). 88% from **3**. Colorless oil. IR (neat): 1700, 1625, 1100. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.72−7.27 (10H, m), 4.70 (1H, s), 4.64 (1H, s), 2.50 (1H, dq, J = 9.0, 7.0), 2.22 (1H, d, J = 15.5), 2.08−2.02 (2H, m), 2.01 (3H, s), 1.06 (9H, s), 0.86 (3H, d, J = 7.0), 0.74 (3H, d, J = 7.0). ^{13}C NMR ($CDCl_3$, 75 MHz): 212.7, 147.6, 136.2, 136.1, 134.6, 134.2, 129.1, 127.5, 112.2, 51.5, 44.3, 28.7, 27.8, 18.5, 17.5, 17.4, 15.3. MS(EI) *m*/*z*: 321 ($M^+ - {}^t$Bu, 19%), 243, 199 (100). Anal. Calcd for $C_{25}H_{34}OSi$: C, 79.31; H, 9.05. Found: C, 79.45; H, 9.12.

6-*tert*-Butyldiphenylsilylmethyl-5-methyl-6-hepten-3-one (13). 89% from **4**. Colorless oil. IR (neat): 1700, 1620, 1100. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.68−7.33 (10H, m), 4.61 (1H, s), 4.60 (1H, s), 2.30−2.13 (5H, m), 2.20 (2H, s), 1.07 (9H, s), 0.96 (3H, t, J = 7.2), 0.80 (3H, d, J = 6.5). ^{13}C NMR ($CDCl_3$, 75 MHz): 210.6, 150.6, 136.3, 134.5, 129.1, 127.4, 108.9, 48.6, 36.6, 35.8, 27.8, 19.4, 18.7, 18.5, 7.7. MS(EI) *m*/*z*: 321 ($M^+ - {}^t$Bu, 19%), 243, 199 (100). Anal. Calcd for $C_{25}H_{34}OSi$: C, 79.31; H, 9.05. Found: C, 79.50; H, 9.20.

5-*tert*-Butyldiphenylsilylmethyl-4,4-dimethyl-5-hexen-2-one (14). 90% from **5**. Colorless oil. IR (neat): 1700, 1620, 1100. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.72−7.27 (10H, m), 4.72 (1H, s), 4.64 (1H, s), 2.47 (2H, s), 2.16 (2H, s), 2.08 (3H, s), 1.05 (6H, s), 1.04 (9H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): 208.5, 150.4, 136.2, 134.5, 129.0, 127.4, 112.0, 53.5, 39.8, 32.2, 27.8, 26.8, 18.4, 12.8. MS(EI) *m*/*z*: 321 ($M^+ - {}^t$Bu, 15%), 263, 199 (100), 43. Anal. Calcd for $C_{25}H_{34}OSi$: C, 79.31; H, 9.05. Found: C, 79.58; H, 9.27.

5-*tert*-Butyldiphenylsilylmethyl-4-[2,6,6-trimethyl-1-cyclohexen-1-yl]-5-hexen-2-one (15). 85% from **6**. Colorless oil. IR (neat): 1710, 1625, 1100. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.76−7.33 (10H, m), 4.62 (1H, s), 4.57 (1H, s), 3.53 (1H, d, J = 8.7), 3.04 (1H, dd, J = 18 and 8.7), 2.46 (1H, d, J = 18), 2.17 (1H, d, J = 18), 2.09 (3H, s), 1.97 (1H, d, J = 18), 1.92 (2H, t, J = 6), 1.58 (2H, t, J = 6), 1.50−1.40 (2H, m), 1.44 (3H, s), 1.04 (3H, s), 1.01 (9H, s), 0.99 (3H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): 207.3, 145.9, 138.7, 136.3, 134.7, 130.7, 129.0, 127.5, 127.3, 112.2, 48.2, 42.1, 40.2, 36.0, 34.0, 30.0, 28.5, 27.8, 21.4, 19.4, 18.4, 16.3. MS(EI) *m*/*z*: 415 ($M^+ - {}^t$Bu, 5%), 357, 199 (73). Anal. Calcd for $C_{32}H_{44}OSi$: C, 81.30; H, 9.38. Found: C, 81.59; H, 9.55.

3-(3-*tert*-Butyldiphenylsilyl-1-propen-2-yl)-3-methylcyclopentan-1-one (16). 87% from **7**. Colorless oil. IR (neat): 1730, 1100, 900. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.82−7.34 (10H, m), 4.69 (1H, s), 4.67 (1H, s), 2.24 (1H, d, J = 17.6), 2.17 (2H, s), 2.27−2.13 (2H, m), 2.03 (1H, d, J = 17.6), 1.97−1.80 (2H, m), 1.11 (3H, s), 1.01 (9H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): 219.0, 150.0, 136.3, 134.5, 129.2, 127.5, 111.4, 51.0, 46.3, 36.5, 33.5, 27.9, 25.6, 18.5, 13.2. MS(EI) *m*/*z*: 319 ($M^+ - {}^t$Bu, 18%), 239, 199, 41 (100). Anal. Calcd for $C_{25}H_{32}OSi$: C, 79.73; H, 8.56. Found: C, 79.91; H, 8.69.

3-(3-*tert*-Butyldiphenylsilyl-1-propen-2-yl)cyclohexanone (18). 87% from **9**. Colorless oil. IR (neat): 1705, 1630, 1100. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.65−7.32 (10H, m), 4.73 (1H, s), 4.59 (1H, s), 2.22 (2H, s), 2.20−2.02 (4H, m), 1.89−1.63 (3H, m), 1.41−1.11 (2H, m), 1.07 (9H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): 211.4, 149.0, 136.5, 134.4, 134.3, 129.2, 127.5, 109.2, 46.8, 45.0, 41.1, 30.1, 27.8, 24.7, 19.3, 18.5. MS(EI) *m*/*z*: 319 ($M^+ - {}^t$Bu, 12%), 239, 199, 41 (100). Anal. Calcd for $C_{25}H_{32}OSi$: C, 79.73; H, 8.56. Found: C, 80.01; H, 8.77.

[2*S*,5*R*]-2-(3-*tert*-Butyldiphenylsilylmethyl-2-methyl-3-buten-2-yl)-5-methyl-cyclohexan-1-one (17a). 44% from **8**. Colorless oil. $[\alpha]^{20}_D$ +3.57 (*c* 1.10, $CHCl_3$). IR (neat): 1710, 1640, 1110. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.73−7.35 (10H, m), 4.72 (1H, s), 4.65 (1H, s), 2.55 (1H, dd, J = 12.0 and 4.5), 2.33 (1H, ddd J = 12.0, 3.9, and 2.1), 2.13−2.01 (3H, m), 1.88−1.82 (3H, m), 1.39−1.29 (2H, m), 1.18 (3H, s), 1.07 (3H, s), 1.04 (9H, s), 1.02 (3H, d, J = 6.0). ^{13}C NMR ($CDCl_3$, 75 MHz): 211.5, 150.7, 136.2, 136.0, 134.8, 134.4, 129.0, 127.4, 113.0, 55.4, 52.4, 41.4, 36.2, 34.8, 28.9, 27.9, 24.6, 22.3, 21.9, 18.5, 12.4. MS(EI) *m*/*z*: 375 ($M^+ - {}^t$Bu, 7%), 239, 199. Anal. Calcd for $C_{29}H_{40}OSi$: C, 80.49; H, 9.32. Found: C, 80.61; H, 9.41.

[2*R*,5*R*]-2-(3-*tert*-Butyldiphenylsilylmethyl-2-methyl-3-buten-2-yl)-5-methyl-cyclohexan-1-one (17b). 41% from **8**. Colorless oil. $[\alpha]^{20}_D$ +44.3 (*c* 0.90, $CHCl_3$). IR (neat): 1710, 1640, 1110. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.72−7.34 (10H, m), 4.72 (1H, s), 4.66 (1H, s), 2.58−2.50 (2H, m), 2.27 (1H, m), 2.11 (1H, d, J = 16.8), 2.0 (1H, d, J = 16.8), 2.08 (1H, m), 1.78 (1H, m), 1.69−1.63 (2H, m), 1.53 (1H, m), 1.12 (3H, s), 1.05 (3H, s), 1.03 (9H, s), 0.95 (3H, d, J = 7.0). ^{13}C NMR ($CDCl_3$, 75 MHz): 212.9, 150.5, 136.2, 136.1, 134.8, 134.3, 129.0, 127.4, 113.2, 55.2, 50.5, 42.0, 32.2, 31.4, 27.9, 25.1, 24.7, 22.7, 19.7, 18.5, 12.4. MS(EI) *m*/*z*: 375 ($M^+ - {}^t$Bu, 15%), 239, 199. Anal. Calcd for $C_{29}H_{40}OSi$: C, 80.49; H, 9.32. Found: C, 80.84; H, 9.55.

[2*R*,3*R*,5*R*]-3-(3-*tert*-Butyldiphenylsilyl-1-propen-2-yl)-5-isopropenyl-2-methylcyclohexanone (19). 75% from **10**. Colorless oil. $[\alpha]^{20}_D$ +34.6 (*c* 1.20, $CHCl_3$). IR (neat): 1705, 1640, 1100. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.65−7.31 (10H, m), 4.8 (1H, s), 4.7 (1H, s), 4.6 (1H, s), 4.4 (1H, s), 2.54 (1H, tt, J = 9.5 and 4.5), 2.47−2.34 (3H, m), 2.22 (1H, d, J = 13.8), 2.13 (1H, d, J = 13.8), 2.2 (1H, m), 1.93 (1H, dt, J = 13.6 and 4.5), 1.62 (3H, s), 1.54 (1H, ddd, J = 13.6, 9.5, and 4.5), 1.04 (9H, s), 0.76 (3H, d, J = 6.5). ^{13}C NMR ($CDCl_3$, 75 MHz): 213.7, 147.0, 144.7, 136.2, 136.1, 134.4, 134.1, 129.2, 127.5, 112.9, 110.5, 46.8, 45.4, 44.4, 39.8, 31.0, 22.7, 21.1, 20.1, 18.5, 11.6. MS(EI) *m*/*z*: 373 ($M^+ - {}^t$Bu, 18%), 332, 239, 199. Anal. Calcd for $C_{29}H_{38}OSi$: C, 80.87; H, 8.89. Found: C, 81.08; H, 8.97.

***cis*-1-Acetyl-2-(3-*tert*-butyldiphenylsilyl-1-propen-2-yl-)cyclohexane (20).** 81% from **11**. White solid, mp 91−92 °C. IR (neat): 1700, 1625, 1100. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.70−7.33 (10H, m), 4.80 (1H, s), 4.58 (1H, s), 2.83 (1H, m), 2.42 (1H, d, J = 14.3), 2.15 (1H, d, J = 14.3), 2.0 (3H, s), 1.79−1.50 (6H, m), 1.10 (9H, s), 1.30−1.0 (3H, m). ^{13}C NMR ($CDCl_3$, 75 MHz): 212.7, 148.0, 136.2, 136.1, 134.4, 134.2, 129.1, 127.5, 110.8, 48.6, 45.3, 31.6, 27.8, 27.5, 26.0, 25.6, 21.7, 20.3, 18.6. MS(EI) *m*/*z*: 404 (M^+, 1%), 347, 269, 199 (100). Anal. Calcd for $C_{27}H_{36}OSi$: C, 80.14; H, 8.97. Found: C, 80.39; H, 9.09.

Allylsilane Terminated Cyclizations.[10] $EtAlCl_2$ (2.4 mmol, 1.8 M in toluene) was added slowly to a solution of **12**−**20** (2 mmol) in toluene (8 mL) at 0 °C under nitrogen. After stirring for 1 h at 0 °C, brine was added (5 mL), and the mixture was extracted with Et_2O, dried, and evaporated. Purification by flash chromatography gave **21**−**29**. Compounds **25**, **27**, and **29** were prepared before.[10a,b]

(*E*)-1,4,5-Trimethyl-3-*tert*-butyldiphenylsilylmethyl-3-cyclopenten-1-ol (21a). 68% from **12**. Colorless oil. IR (neat): 3530, 3450, 1100, 900. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.65−7.27 (10H, m), 2.17 (1H, d, J = 15), 2.15 (1H, d, J = 15), 2.10−2.0 (1H, m), 2.06 (1H, d, J = 15.5), 1.87 (1H, d, J = 15.5), 1.46, (3H, s), 1.40 (1H, s), 1.08 (9H, s), 0.98 (3H, s), 0.65 (3H, d, J = 7.0). ^{13}C NMR ($CDCl_3$, 75 MHz): 136.1, 136.0, 134.6, 134.3, 133.2, 129.1, 129.0, 127.4, 79.2, 55.6, 51.7, 27.6, 22.4, 18.4, 14.1, 12.7, 12.1. MS(EI) *m*/*z*: 378 (M^+, 8%), 321 ($M^+ - {}^t$Bu, 8%), 239, 199 (100). Anal. Calcd for $C_{25}H_{34}OSi$: C, 79.31; H, 9.05. Found: C, 79.57; H, 9.19.

(*Z*)-1,4,5-Trimethyl-3-*tert*-butyldiphenylsilylmethyl-3-cyclopenten-1-ol (21b). 17% from **12**. Colorless oil. IR (neat): 3530, 3450, 1100, 900. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.65−7.27 (10H, m), 2.20 (1H, d, J = 15), 2.09−2.03 (3H, m), 1.89 (1H, d, J = 15), 1.40 (3H, s), 1.07 (9H, s), 1.06 (3H, s), 0.80 (1H, s), 0.75 (3H, d, J = 7.0). ^{13}C NMR ($CDCl_3$, 75 MHz): 136.1, 136.0, 134.7, 134.3, 131.9, 129.3, 129.2, 127.4, 127.3, 77.9, 52.4, 52.3, 27.6, 25.4, 18.3, 12.3, 11.9, 11.1. MS(EI) *m*/*z*: 378 (M^+, 7%), 321 ($M^+ - {}^t$Bu, 8%), 239, 199 (100). Anal. Calcd for $C_{25}H_{34}OSi$: C, 79.31; H, 9.05. Found: C, 79.70; H, 9.29.

1-Ethyl-4-methyl-3-*tert*-butyldiphenylsilylmethyl-3-cyclopenten-1-ol (22). 85% from **13**. Colorless oil. IR (neat):

3400, 1100. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.65−7.34 (10H, m), 2.24 (1H, d, J = 16.5), 2.17 (2H, s), 2.06 (1H, d, J = 16.5), 2.03 (1H, d, J = 16.5), 1.85 (1H, d, J = 16.5), 1.47 (3H, s), 1.38 (2H, q, J = 7.2), 1.20 (1H, s), 1.10 (9H, s), 0.76 (3H, t, J = 7.2). ^{13}C NMR ($CDCl_3$, 75 MHz): 136.0, 134.8, 134.6, 129.6, 129.1, 127.4, 127.3, 79.4, 51.9, 51.4, 33.0, 27.6, 18.3, 14.2, 12.2, 8.7. MS(EI) *m*/*z*: 378 (M^+, 5%), 321 ($M^+ - {}^t$Bu, 5%), 239, 199 (100). Anal. Calcd for $C_{25}H_{34}OSi$: C, 79.31; H, 9.05. Found: C, 79.61; H, 9.24.

3-*tert*-Butyldiphenylsilylmethyl-4-[2,6,6-trimethyl-1-cyclohexen-1-yl]-3-cyclopenten-1-ol (23). 77% from **15**. Colorless oil. IR (neat): 3590, 3400, 1100, 920. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.96−7.32 (10H, m), 2.46 (1H, dd, J = 16.3 and 6.6), 2.27−1.97 (5H, m), 2.09 (2H, s), 1.67 (2H, t, J = 6), 1.62 (1H, s), 1.43 (2H, qn, J = 6), 1.33 (3H, s), 1.14 (3H, s), 1.03 (9H, s), 0.94 (3H, s), 0.84 (3H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): 135.7, 134.8, 134.7, 136.1, 132.7, 132.6, 129.1, 128.7, 127.4, 77.3, 54.4, 52.6, 40.0, 35.4, 31.8, 30.1, 29.3, 27.9, 27.6, 20.8, 19.2, 18.2, 12.9. MS(EI) *m*/*z*: 472 (M^+, 3%), 199 (100), 57. Anal. Calcd for $C_{32}H_{44}OSi$: C, 81.30; H, 9.38. Found: C, 81.62; H, 9.59.

3-Methylene-1,4,4-trimethylcyclopentan-1-ol (24). 67% from **14**. Colorless oil. IR (neat): 3350, 3400, 1660, 880. ^{1}H NMR ($CDCl_3$, 300 MHz): 4.89 (1H, s), 4.83 (1H, s), 2.55 (1H, d, J = 15.7), 2.47 (1H, d, J = 15.7), 1.77 (1H, d, J = 13.6), 1.73 (1H, d, J = 13.6), 1.44 (1H, s), 1.35 (3H, s), 1.24 (3H, s), 1.12 (3H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): 160.7, 105.0, 77.3, 56.3, 49.3, 41.4, 31.1, 30.1, 28.2. MS(EI) *m*/*z*: 140 (M^+, 3%). Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.48; H, 11.76.

[1*S*,3*R*,6*S*]-3,7,7-Trimethyl-8-methylenebicyclo[4.3.0]-nonan-1-ol (26). 70% from **17**. White solid, mp 83−84 °C. $[\alpha]^{20}_D$ −39.16 (*c* 0.95, $CHCl_3$). IR (neat): 3600, 3450, 1645, 880. ^{1}H NMR ($CDCl_3$, 300 MHz): 4.93 (1H, m), 4.88 (1H, m), 2.80 (1H, dt, J = 16.8 and 2.9), 2.24 (1H, ddd, J = 16.8, 3.4, and 1.6), 1.93 (1H, ddd, J = 12.9, 3.4, and 2.3), 1.76 (1H, m), 1.64 (1H, m), 1.49 (1H, ddd, J = 12.3, 5.7, and 1.9), 1.38 (3H, s), 1.36−1.30 (2H, m), 1.17 (1H, t, J = 12.6), 1.07−0.86 (2H, m), 1.03 (3H, s), 0.91 (3H, d, J = 6.1). ^{13}C NMR ($CDCl_3$, 75 MHz): 160.8, 105.9, 80.0, 56.0, 46.3, 45.2, 44.2, 34.0, 33.9, 30.4, 28.2, 25.9, 22.2. MS(EI) *m*/*z*: 194 (M^+, 11%), 176. Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.51; H, 11.52.

[1*S*,3*R*,5*R*,8*R*]-8-Methyl-6-methylene-3-isopropenyl-bicyclo[3.2.1]octan-1-ol (28). 65% from **19**. White solid, mp 80−82 °C. $[\alpha]^{20}_D$ −12.2 (*c* 1.05, $CHCl_3$). IR (neat): 3340, 1650, 880. ^{1}H NMR ($CDCl_3$, 300 MHz): 4.87 (2H, s), 4.70 (2H, s), 2.45−2.33 (4H, m), 1.90 (1H, ddd, J = 11.8, 5, and 1), 1.70 (3H, s), 1.67−1.55 (4H, m), 1.45 (1H, td, J = 11.8 and 2), 0.95 (3H, d, J = 7). ^{13}C NMR ($CDCl_3$, 75 MHz): 151.7, 148.5, 108.8, 107.2, 78.9, 50.3, 48.6, 45.4, 40.7, 39.3, 38.9, 20.8, 13.7. MS-(EI) *m*/*z*: 192 (M^+, 15%), 177, 159. Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.38; H, 10.57.

Reaction of Intermediate 2 with Acid Chlorides. A solution of the acid chlorides in THF (3.6 mmol) was added to the cuprate reagent **2** (3 mmol) at −40 °C, and the resulting solution was stirred at this temperature for 1 h. After gentle warming to 0 °C (over 0.5 h), the mixture was quenched with basic saturated ammonium chloride solution and extracted twice with Et_2O. The organic layer was dried over $MgSO_4$ and rotoevaporated. Purification by flash chromatography (EtOAc: hexanes) gave the allylsilanes **30**−**31**.

1-(1-Cyclopentenyl)-2-*tert*-butyldiphenylsilylmethyl-2-propen-1-one (30). 80%. Colorless oil. IR (neat): 1700, 1620, 1600, 1090 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.66−7.27 (10H, m), 5.91 (1H, m), 5.34 (1H, s), 5.24 (1H, s), 2.58 (2H, s), 2.40−2.27 (4H, m), 1.77 (2H, qn, J = 7.5), 1.06 (9H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): 195.5, 146.0, 145.0, 143.2, 136.4, 133.7, 129.1, 127.4, 121.8, 33.8, 31.3, 27.7, 22.5, 18.5, 14.8. MS(EI) *m*/*z*: 374 (M^+, 4%), 317 (100), 239. Anal. Calcd for $C_{25}H_{30}OSi$: C, 80.16; H, 8.07. Found: C, 80.41; H, 8.28.

1-(1-Cyclohexenyl)-2-*tert*-butyldiphenylsilylmethyl-2-propen-1-one (31). 85%. Colorless oil. IR (neat): 1690, 1640, 1610, 1110. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.65−7.31 (10H, m), 6.0 (1H, m), 5.25 (1H, s), 5.17 (1H, s), 2.60 (2H, s), 2.07−2.03 (2H, m), 1.96−1.90 (2H, m), 1.55−1.43 (4H, m), 1.07 (9H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): 199.4, 144.8, 142.0, 137.0, 136.4, 133.6, 129.1, 127.4, 121.5, 27.7, 25.7, 23.5, 21.9, 21.4, 18.5, 15.3. MS(EI) *m*/*z*: 388 (M^+, 5%), 331, 199. Anal. Calcd for $C_{26}H_{32}$-OSi: C, 80.36; H, 8.30. Found: C, 80.53; H, 8.39.

Directed Nazarov Reactions. A solution of **30** or **31** (2 mmol) in THF (3 mL) was stirred at room temperature, and TFA (0.46 mL, 6 mmol) was added with continuous stirring. The solution was heated to 60 °C and stirred for an additional period of 1 h. The reaction was quenched with a saturated solution of sodium bicarbonate (5 mL). After extraction with Et_2O, the ethereal layer was washed twice with brine, dried, and concentrated. The crude product was purified by flash chromatography (EtOAc:hexanes) to give **32** or **33**.

(*E*)-2-*tert*-Butyldiphenylsilylmethylene-*cis*-bicyclo[3.3.0]-octan-2-one (32). 73% from **30**. Colorless oil. IR (neat): 1690, 1110, 900. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.69−7.28 (10H, m), 7.17 (1H, t, J = 2.6), 2.68 (1H, td, J = 9.2 and 4), 2.43 (1H, dqn, J = 2 and 8), 2.19 (1H, ddd, J = 18.4, 8.4, and 3.2), 2.06−1.84 (3H, m), 1.70−1.60 (2H, m), 1.15 (2H, qn, J = 7), 1.08 (9H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): 209.8, 156.0, 135.9, 133.2, 133.0, 129.4, 129.2, 128.5, 127.8, 52.1, 37.7, 34.5, 33.8, 30.0, 27.2, 26.1, 18.4. MS(EI) *m*/*z*: 374 (M^+, 5%), 317 ($M^+ - {}^t$Bu, 100), 239. Anal. Calcd for $C_{25}H_{30}OSi$: C, 80.16; H, 8.07. Found: C, 80.38; H, 8.17.

***cis*-2-*tert*-Butyldiphenylsilylmethylbicyclo[3.3.0]oct-3-en-2-one (33).** 75% from **31**. Colorless oil. IR (neat): 1690, 1110, 810. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.66−7.34 (10H, m), 6.45 (1H, d, J = 1.1), 2.55 (1H, m), 2.32 (1H, d, J = 14.8), 2.22−2.15 (2H, m), 1.68−1.53 (3H, m), 1.53−1.10 (5H, m), 1.06 (9H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): 211.5, 160.0, 140.3, 136.1, 134.0, 133.7, 129.2, 127.5, 127.4, 44.7, 38.4, 27.8, 27.7, 22.7, 21.1, 21.0, 18.4, 6.3. MS(EI) *m*/*z*: 331 ($M^+ - {}^t$Bu, 90), 253, 199, 57 (100). Anal. Calcd for $C_{26}H_{32}OSi$: C, 80.36; H, 8.30. Found: C, 80.66; H, 8.48.

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Supporting Information Available: X-ray figure and data of *cis*-3-methylene-4-phenylcyclopentan-1-ol (phenylurethane derivative). This material is available free of charge via the Internet at http://pubs.acs.org.

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