evaporated to give *N,N*-dimethyl-*O*-(2,4-dinitrophenyl)-hydroxylamine (**17**) as orange crystals (0.15 g, 80%), mp 108–110 °C, homogeneous on TLC (S_4). Recrystallization from methanol afforded **17**, mp 111–113.5 °C. TLC (S_4) and paper electrophoresis of the material obtained after determination of the melting point showed only the presence of unchanged **17** in addition to traces of **9a**. UV max (ethanol) 211 (ε 14300), 244 (8800), 293 nm (10600); ^{1}H NMR ($CDCl_3$) δ 8.77 (d, 1, H_3, $J_{3,5}$ = 2.7 Hz), 8.39 (d of d, 1, H_5, $J_{5,3}$ = 2.7 Hz, $J_{5,6}$ = 9.3 Hz), 7.86 (d, 1, H_6, $J_{6,5}$ = 9.3 Hz), 2.90 (s, 6, $N(CH_3)_2$); EI-MS 227 (22.0, M), 184 (68.4, M − CH_2=NCH_3), 168 (6.1), 154 (30.2), 107 (36.9), 91 (46.2), 79 (37.4), 63 (100.0), 53 (68.4); in another run (JMS-D-100, mass range 40–240), fragments 42 (CH_2=N=CH_2), 43 (CH_3N=CH_2), and 44 ($(CH_3)_2N$) were detected; CI-MS 228 (66.8, M + 1), 227 (100.0, M) 185 (29.2, M + 1 − CH_3N=CH_2), 184 (26.5, M − CH_3N=CH_2), 168 (5.3), 154 (11.3), 125 (3.2), 107 (11.8). Anal. Calcd for $C_8H_9N_3O_5$: C, 42.29; H, 3.99; N, 18.50. Found: C, 42.37; H, 4.07; N, 18.60.

The slower moving minor bands gave a mixture of *N,N*-dimethyl- and *N*-methyl-2,4-dinitroaniline (**6a** and **8a**, 9 mg) in the ratio of 34:66 as determined by ^{1}H NMR[50] and a trace of 2,4-dinitrophenol (**9a**).

(50) Determined from the integration curve of CH_3 signals of **6a** and **8a**.

Acknowledgment. Thanks are due to Drs. Robin Hood, D. P. Lin, and Ole Mols from the Central Instrumentation Facility, Department of Chemistry, Wayne State University, for mass and 300-MHz NMR spectra. The 100-MHz spectra and some mass spectra were recorded by Dr. D. P. Lin and Walter Brukwinski at the Michigan Cancer Foundation. The work described herein was supported in part by U.S. Public Health Service Grant CA 21388 from the National Cancer Institute, Bethesda, MD, and in part by an institutional grant to the Michigan Cancer Foundation from the United Foundation of Greater Detroit.

Registry No. **1a**, 1867-73-8; **1b**, 71118-16-6; **2a**, 113509-54-9; **2b**, 113509-55-0; **3a**, 70230-70-5; **3b**, 71118-13-3; **3c**, 71118-15-5; **3d**, 71138-54-0; **4a**, 6741-88-4; **5**, 71118-18-8; **6a**, 1670-17-3; **6b**, 2554-75-8; **6c**, 5683-33-0; **7a**, 113509-56-1; **8a**, 2044-88-4; **8b**, 4093-89-4; **9a**, 51-28-5; **9b**, 5418-51-9; **10a**, 113509-57-2; **10a**·HCl, 113509-59-4; **10c**, 4465-60-5; **11**, 113509-58-3; **15a**, 3510-73-4; **15b**, 5987-73-5; **15c**, 5399-87-1; **16**, 70-34-8; **17**, 29746-97-2; $MeNH_2$·HCl, 593-51-1; Me_2NOH·HCl, 16645-06-0; 2-chloro-5-nitropyridine, 4548-45-2.

Trisubstituted Stannyllithium as a Double Electron Equivalent. Reaction with α,β-Enones[1]

Tadashi Sato,* Masami Watanabe, Toshiyuki Watanabe, Yasuo Onoda, and Eigoro Murayama[†]

Department of Applied Chemistry, Waseda University, Ookubo 3, Shinjuku-ku, Tokyo 160, Japan

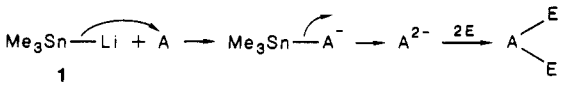
Received August 19, 1987

β-Stannyl ketones, easily available by the conjugate addition of (trimethylstannyl)lithium to α,β-enones, produced two types of ketones depending upon the substitution pattern by the treatment with titanium(IV) chloride. All the reactions proceeded through an intermediacy of cyclopropanol derivatives. The reaction involving the carbon skeleton rearrangement is promising as a synthetic method.

In our previous papers,[2] we described the versatility of the α-stannyl carbanion reagent as a synthetic tool. In these reactions, the reagent reacted with the electrophiles in two ways: first as an explicit carbanion, and second, as a latent carbanion. The net reaction is the replacement of two leaving groups in the substrate with a methylene group, so the reagent can be regarded as a methylene double anion equivalent. As another stannyl compound having an anionic center in the molecule, we chose (trimethylstannyl)lithium (**1**) which is easily available and known to react with electron acceptor A to produce stable stannyl compounds.[3] If electron-withdrawing groups still exist in the resulted stannyl compound, they can induce a heterolysis of the tin–carbon bond, leaving the bond electron on the substrate moiety as shown in Scheme I. Evidently the reagent could be regarded as a double electron equivalent, providing the electron-deficient substrate A with an ability to react with two electrophiles E. In the present study, we found that the reaction using α,β-enones as such an electron-deficient system proceeded in a unique manner and could be utilized as a synthetic method.

It has been known that stannyl compounds having a cationic center at the γ-position cyclize to cyclopropanes

Scheme I



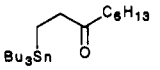
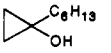
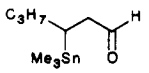
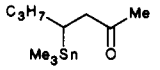
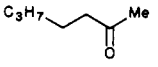
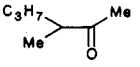
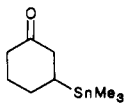
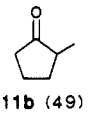
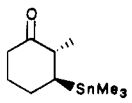
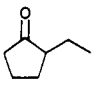
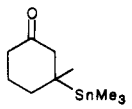
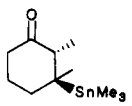
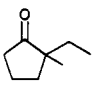
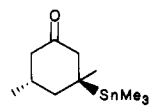
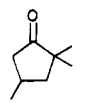
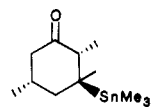
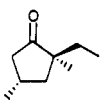
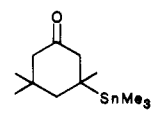
under various conditions.[4] Recently, we reported that γ,δ-epoxy stannyl compounds could be transformed into cyclopropyl-containing derivatives by treatment with Lewis acids.[5] Evidently, the developing cationic center at the oxygen-bearing carbon induced the heterolysis of the carbon–tin bond. The stereochemistry at the reacting centers has been elaborately investigated to conclude that the reaction proceeds with inversion of configuration at both reaction centers.[6] We expected that β-stannyl ketones would behave in a similar way and produce cyclo-

[†] Present address: New Drug Research Laboratory, Chugai Pharmaceutical Co. Ltd., Japan.

(1) Preliminary report: Sato, T.; Watanabe, M.; Murayama, E. *Tetrahedron Lett.* **1986**, *27*, 1621.
(2) Sato, T.; Matsuoka, H.; Igarashi, T.; Minomura, M.; Murayama, E. *J. Org. Chem.*, in press, and references cited therein (submitted).
(3) Still, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 4836.
(4) Hosomi, A.; Inaba, M.; Sakurai, H. *Chem. Lett.* **1983**, 1763 and references cited therein. Kadow, J. F.; Johnson, C. R.; *Tetrahedron Lett.* **1984**, *25*, 5255.
(5) Sato, T.; Watanabe, M.; Murayama, E. *Synth. Commun.* **1987**, *17*, 781.
(6) Fleming, I.; Urch, C. J. *J. Organomet. Chem.* **1985**, *285*, 173. Davis, D. D.; Johnson, H. T. *J. Am. Chem. Soc.* **1974**, *96*, 7576.

0022-3263/88/1953-1894$01.50/0

Table I. $TiCl_4$-Catalyzed Reaction of β-Stannyl Ketones

run	β-stannyl ketone (yield, %)[a]	product (yield, %) type A	type B	type C
1	 **8**			 **8c** (70)
2	 **9** (80)			 **9c** (100)[b]
3	 **10** (99)	 **10a** (8)	 **10b** (38)	
4	 **11** (69)	 **11a** (16)	 **11b** (49)	
5	 **12** (53)	 **12a** (39)	 **12b** (6)	
6	 **13** (51)		 **13b** (52)	
7	 **14** (54)		 **14b** (61)	
8	 **15** (85)		 **15b** (52)	
8	 **16** (55)		 **16b** (51)	
9	 **17** (87)		 **17b** (54)	

[a] Yields from the corresponding α,β-enones, except for 8. [b] Crude yield.

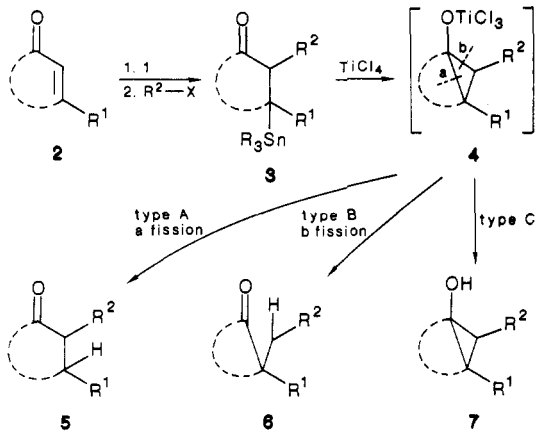
propanol derivatives, the carbonyl group inducing the heterolysis of the carbon–tin bond. The expected reaction was actually realized upon treatment of the β-stannyl ketones under acidic conditions, but we found that, in many cases, the reaction did not stop at the stage of cyclopropanol formation, but proceeded further with a C–C bond fission.

The β-stannyl ketones **3**, where R^2 = H or Me, were prepared by the well-known method of conjugate addition of reagent **1** to α,β-enones, **2**, followed by trapping the intermediate enolate with proton or methyl iodide, respectively.[3] Upon treatment with titanium(IV) chloride, the stannyl ketones underwent three types of reaction depending upon the substitution pattern of the substrate. The results are shown in Table I. The reactions seem to proceed through a common intermediate **4** shown in Scheme II. The reaction terminated at cyclopropanol formation (**7**, type C) only when the tin-bearing carbon had two hydrogen atoms, or, when the carbonyl compounds were aldehydes (runs 1 and 2). Otherwise, the reaction proceeded further with a C–C bond fission at either a (type A) or b (type B) position and afforded ketones **5** and/or **6**.

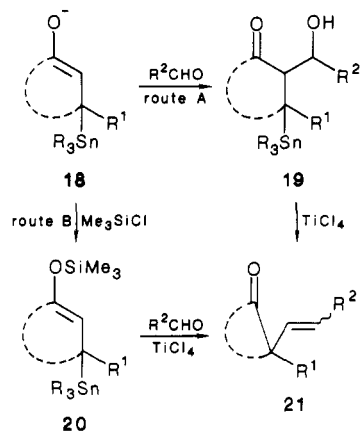
The acid- or base-induced ring opening of cyclopropanols or their derivatives has been well-documented, and the ring opening usually proceeds with protonation predominantly on the less substituted carbon.[7] The results shown in Table I are generally consistent with this trend. Evidently in runs 3 and 4, the reaction proceeded with the bond

(7) Gibson, D. H.; DePuy, C. H. *Chem. Rev.* **1974**, *74*, 605. Werstiuk, N. H. *Tetrahedron* **1983**, *39*, 205.

Scheme II



Scheme III



cleavage at the bond to the secondary carbon, rather than to tertiary carbon, in the presumed cyclopropanol intermediate, giving type B product as the major component. However, in run 5, where the both carbons in the cyclopropanol are tertiary, path A predominated probably because of the greater stability of the six-membered ring system than that of the five-membered system. Quite understandably, the bond cleavage at the b position became an exclusive reaction pattern when the C-3 was quarternarized by introducing a substituent (runs 6–9).

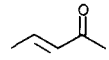
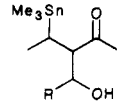
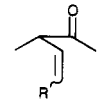
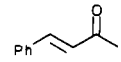
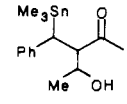
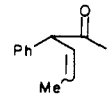
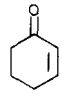
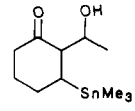
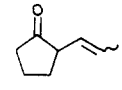
Synthetically, the type B reaction is particularly interesting because it involves a carbon skeleton rearrangement, producing substituted cyclopentanones. Generally, the system could be prepared by introducing appropriate substituents into the cyclopentanone ring, but, under this strategy, the attainment of the stereo- and regioselectivity becomes a major problem. Evidently, the present reaction has the advantage that no regiochemical problems could arise, and it afforded substituted cyclopentanones without any contamination of the position isomers. It was hoped that the merit of the reaction could be further enhanced, if we could attain the introduction of the substituents with definite stereochemistry.

In view of the ^1H NMR and GLC analyses, the product **16b** appeared to be a single isomer. The ^{13}C NMR spectrum of various substituted cyclohexanones and cyclopentanones have been reported,[8] and it was shown that the chemical shifts of the carbon atoms in the ring as well as in the substituents were different among stereoisomers. Since the ^{13}C NMR spectrum of **16b** indicated nine well-defined signals only, we concluded that the product was diastereometricaly pure. Although the present data were not sufficient for the full assignment of the absolute stereochemistry, we speculated the stereochemistry from the following consideration.

It has been established that the 2- and 5-methyl groups in **12** and **15**, respectively, are both in a trans relation against the stannyl group.[3,9] In analogy, therefore, we assigned *t*-2-methyl-*r*-3-stannyl-*t*-5-methyl structure as **16**. With the steric inversion at the tin-bearing carbon in the nucleophilic reaction having been definitely established,[6] we assigned *c*-2-methyl-*t*-2-ethyl-*r*-4-methylcyclopentanone as **16b**. We are elucidating the stereochemical problem by investigating the reaction with substrates having some functionality in the substituents.

Although the type B reaction which involves the carbon skeleton rearrangement is promising particularly from the synthetic viewpoint, the selectivity between type A and type B was not necessarily satisfactory with substrates having a hydrogen atom at the C-3 position (runs 3–5). In order to improve the selectivity, we attempted to introduce a leaving group into the side chain on the C-2 position. This was accomplished by the aldol reaction of the intermediate enolates **18** with aldehydes[10] (Scheme III). When the resulting aldols **19** were treated with titanium(IV) chloride, the selective type B reaction occurred as expected to afford β,γ-enones **21** (route A). The results are shown in Table II. The reaction could be most reasonably schemed as proceeding through the intermediacy of cyclopropanol intermediate **22**, which would undergo bond cleavage only at the b position with a concomitant elimination of the hydroxyl group. Evidently the tin–carbon bond in **19** attacked the carbonyl carbon rather than the alcohol carbon, both at the γ-position from the stannyl group. The same type reaction was also effected by starting from a silyl enol ether **20**, which was obtained by trapping the enolate **18** with trimethylsilyl chloride. The titanium(IV) chloride catalyzed reaction with an aldehyde gave β,γ-enones directly (Table III, route B).

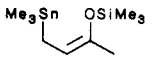
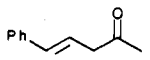
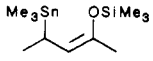
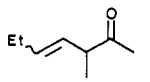
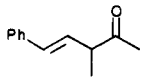
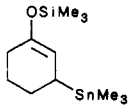
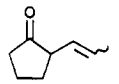
Table II. Preparation and $TiCl_4$-Catalyzed Reaction of β-Hydroxy β′-Stannyl Ketones (Route A)

run	α,β-enone	aldehyde	β-hydroxy β′-stannyl ketone (yield, %)	β,γ-enone (yield, %)
		RCHO		
11	**23a**	R = Me	**23b** (22)	**23c** (21)
12	**23a**	R = Et	**24b** (45)	**24c** (47)
13	**23a**	R = *n*-Bu	**25b** (58)	**25c** (47)
14	 **26a**	MeCHO	 **26b** (49)	 **26c** (18)
15	 **27a**	MeCHO	 **27b** (75)	 **27c** (74)

Although each of the β,γ-enones thus obtained showed a single peak on a GLC analysis, the product **26c** was found to be a cis–trans mixture (cis:trans = 5:12), in view of the integrated areas of the signals of the proton on the phe-

(8) Stothers, J. B.; Tan, C. T. *Can. J. Chem.* **1974**, *52*, 308.
(9) Kitching, W. *J. Org. Chem.* **1982**, *47*, 3788.
(10) Nakamura, E.; Shimizu, M.; Kuwajima, I.; Sakata, J.; Yokoyama, K.; Noyori, R. *J. Org. Chem.* **1983**, *48*, 932.

Table III. $TiCl_4$-Catalyzed Reaction of Stannyl Silyl Enol Ethers with Aldehydes (Route B)

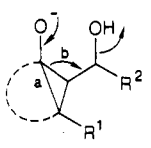
run	stannyl silyl enol ether (yield, %)[a]	aldehyde	β,γ-enone
16	 **28a** (81)	PhCHO	 **28b** (40)
17	 **29a** (69)	EtCHO	 **29b** (47)
18	**29a**	PhCHO	 **30b** (64)
19	 **31a** (55)	MeCHO	 **31b** (42)

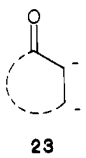
[a] Yields from the corresponding α,β-enones.

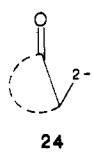
nyl-bearing carbon at δ 4.16 and 4.51.[11] On the other hand, it was concluded that **30b** was a single isomer of trans geometry, because the olefinic protons showed a well-defined AB quartet with J = 16 Hz (the upper half of the signals further split into doublets by the neighboring methine proton). The coupling pattern of the olefinic signals in the ^1H NMR spectrum of **28b** was not completely identical with that reported for trans[12] or cis[13] isomers. However, we concluded it to be trans, since it is known that the cis isomer gradually transforms into the trans isomer upon standing,[13] and **28b** was completely identical with that prepared independently from an epoxy ketone as reported in our earlier paper.[14] The cyclopentanone derivative **27c** from route A was a 1:3 cis–trans mixture, while **31b** from route B was a 3:5 cis–trans mixture in view of the ^{13}C NMR spectra.[15] All the other products also seemed to be cis–trans mixtures in view of the ^{13}C NMR spectra. The formation of the β,γ-enones **21** as cis–trans mixtures might be ascribable to the poor diastereoselectivity in the aldol condensation. Actually, the ^{13}C NMR spectrum of **27b** showed four distinct signals of the carbonyl carbon in a ratio of 6.0:2.1:1.7:1.0, implying that the product is a diastereomeric mixture. The stereochemical relations between the aldols and the β,γ-enones are now under vigorous investigation, which will be reported elsewhere.

All the reactions described in the present paper are explicit examples of the equivalence of the reagent **1** to a double electron reagent. By using the reagent, the α,β-enone is equivalent to α,β-dianion **23** in the type A reaction, while it is equivalent to β,β-dianion **24** in the type B reaction.

The present reaction could be contrasted to the conventional method of cyclopropanol preparation through the Simmons–Smith cyclopropanation of enol derivatives.[16]


22


23


24

The reaction is synthetically attractive because the β-stannyl ketones are easily available by the conjugate addition of the stannyl anion to α,β-enones, and more importantly, the net reaction is an introduction of two nucleophiles into an α,β-enone, in some cases with carbon skeleton rearrangement.

Experimental Section

General Procedure and Instrumentation. All the experiments were carried out in the same way as described in our preceding paper.[2]

(Trimethylstannyl)lithium. A solution of trimethylstannyl chloride (1.000 g, 5 mmol) in THF (6.3 mL) was added to a suspension of small pieces of lithium (0.174 g, 25 mol) in THF (6.3 mL) at 0 °C. The mixture was stirred for 15 min at this temperature and kept in an ultrasonic vessel for 2 h. The remaining lithium was removed by decantation, and the resulting solution was used directly for the next step.

General Procedure for the Preparation of β-Stannyl Ketones 9–17. Except for **8**, all stannyl ketones **9–17** were prepared in the following way. To a THF solution of (trimethylstannyl)lithium prepared as described above (1.5 equiv) was added dropwise a THF solution of the corresponding α,β-enone (1 M, 1 equiv) at 0 °C under N_2. After being stirred for 15 min at 0 °C, the solution was quenched with water or methyl iodide (1.2 equiv). The product was extracted with ether and dried over $MgSO_4$, and the solvent was removed in vacuo. Chromatography on silica gel (first with hexane and then with $CHCl_3$) gave pure material.

3-(Trimethylstannyl)-1-hexanal (9). The product was obtained from 2-hexenal (0.251 g, 2.56 mmol) in 80% yield (0.538 g). ^1H NMR (CCl_4): δ 0.00 (s, 9 H), 0.65–1.85 (m, 8 H), 2.53–2.77 (m, 2 H), 9.70 (br s, 1 H).

4-(Trimethylstannyl)-2-heptanone (10). The product was obtained from 3-hepten-2-one (1.505 g, 13.4 mmol) in 99% yield (3.686 g). ^1H NMR (CCl_4): δ 0.00 (s, 9 H), 0.65–1.70 (m, 8 H), 2.08 (s, 3 H), 2.50–2.80 (m, 2 H).

3-(Trimethylstannyl)cyclohexanone (11). The product was obtained from 2-cyclohexen-1-one (0.72 g, 7.5 mmol) in 69% yield (1.35 g). ^1H NMR (CCl_4): δ 0.05 (s, 9 H), 1.20–2.70 (m, 9 H).

***trans*-2-Methyl-3-(trimethylstannyl)cyclohexanone (12).**[3] The product was obtained from 2-cyclohexen-1-one (0.335 g, 3.49 mmol) and methyl iodide (4.19 mmol) in 53% yield (0.512 g). ^1H NMR (CCl_4): δ 0.08 (s, 9 H), 0.95 (d, J = 6 Hz, 3 H), 1.35–2.70 (m, 8 H).

3-Methyl-3-(trimethylstannyl)cyclohexanone (13). The product was obtained from 3-methyl-2-cyclohexen-1-one (0.353 g, 3.20 mmol) in 51% yield (0.451 g). MS, m/z: 276 (M^+), 261, 231, 165 (base peak), 151, 135, 120, 111, 83, 69, 53. ^1H NMR (CCl_4): δ 0.00 (s, 9 H), 1.12 (s, 3 H), 1.40–2.55 (m, 8 H). Exact mass: calcd for $C_{10}H_{20}OSn$ (M) 276.0536, obsd 276.0500.

2,3-Dimethyl-3-(trimethylstannyl)cyclohexanone (14). The product was obtained from 3-methyl-2-cyclohexen-1-one (0.652 g, 5.92 mmol) and methyl iodide (7.10 mmol) in 54% yield (0.922 g). MS, m/z: 290 (M^+), 275, 247, 217, 165 (base peak), 151, 135, 125, 120, 97, 83, 69, 53. ^1H NMR (CCl_4): δ 0.17 (s, 9 H), 1.04 (d, J = 6 Hz, 3 H), 1.17 (s, 3 H), 1.65–3.05 (m, 7 H). Exact mass: calcd for $C_{11}H_{22}OSn$ (M) 290.0692, obsd 290.0660.

3,5-Dimethyl-3-(trimethylstannyl)cyclohexanone (15).[3] The product was obtained from 3,5-dimethyl-2-cyclohexen-1-one (0.469 g, 3.78 mmol) in 85% yield (0.928 g). MS, m/z: 290 (M^+), 275, 233, 205, 165 (base peak), 151, 135, 125, 120, 83, 69, 53. ^1H NMR (CCl_4): δ 0.11 (s, 9 H), 1.11 (d, J = 5.5 Hz, 3 H), 1.25 (s, 3 H), 1.60–2.80 (m, 7 H). ^{13}C NMR ($CDCl_3$): δ −10.67, 22.02, 28.63, 30.62, 32.11, 47.20, 48.42, 53.24, 208.28. Exact mass: calcd for $C_{11}H_{22}OSn$ (M) 290.0692, obsd 290.0718.

(11) Dana, G.; Thuan, S. L. T.; Gharbi-Benarous, J. *Bull. Soc. Chim. Fr.* **1973**, 1676.
(12) Fayos, J.; Clardy, J.; Dolby, L. J.; Jarnham, T. *J. Org. Chem.* **1977**, *42*, 1349.
(13) Hegedus, L. S.; Stiverson, R. K. *J. Am. Chem. Soc.* **1974**, *96*, 3250.
(14) Sato, T.; Kikuchi, T.; Sootome, N.; Murayama, E. *Tetrahedron Lett.* **1985**, *26*, 2205.
(15) The ratio was evaluated from the peak intensities of the ^{13}C NMR signals. The assignment of the respective geometry for each of the component has not been achieved.
(16) Wenkert, E. *Acc. Chem. Res.* **1980**, *13*, 27.

2,3,5-Trimethyl-3-(trimethylstannyl)cyclohexanone (16). The product was obtained from 3,5-dimethyl-2-cyclohexen-1-one (0.444 g, 3.58 mmol) and methyl iodide (4.30 mmol) in 55% yield (0.591 g). MS, m/z: 304 (M^+), 289, 247, 165 (base peak), 150, 135, 120, 111, 97, 69, 53. ^1H NMR (CCl_4): δ 0.18 (s, 9 H), 1.18 (d, J = 7 Hz, 6 H), 1.31 (s, 3 H), 1.61–2.95 (m, 6 H). ^{13}C NMR ($CDCl_3$): δ −10.67, 10.34, 21.84, 22.78, 31.13, 31.90, 40.34, 44.37, 51.35, 211.76. Exact mass: calcd for $C_{12}H_{24}OSn$ (M) 304.0849, obsd 304.0903.

3,5,5-Trimethyl-3-(trimethylstannyl)cyclohexanone (17). The product was obtained from 3,5,5-trimethyl-2-cyclohexen-1-one (0.619 g, 4.48 mmol) in 87% yield (1.183 g). MS, m/z: 304 (M^+), 289, 233, 205, 165 (base peak), 150, 135, 120, 83, 69, 53. ^1H NMR (CCl_4): δ 0.18 (s, 9 H), 1.08 (s, 3 H), 1.17 (s, 3 H), 1.35 (s, 3 H), 1.65–2.90 (m, 6 H). Exact mass: calcd for $C_{12}H_{24}OSn$ (M) 304.0849, obsd 304.0837.

1-(Tributylstannyl)-3-nonanone (8). 3-(Tributylstannyl)-1-propanol (1.474 g, 23%) was prepared from allyl alcohol (2.11 g, 36.3 mmol) and Bu_3SnH (5.28 g, 18.1 mmol) by refluxing for 5 h without any solvent. To a solution of *N*-chlorosuccinimide (NCS) (0.580 g, 4.34 mmol) and Me_2S (0.342 g, 5.50 mmol) in toluene (10 mL) was added the 3-(tributylstannyl)-1-propanol (0.758 g, 2.17 mmol) in toluene (2.0 mL), and the solution was stirred for 3 h at −30 °C. After Et_3N (0.61 mL) was added, the solution was stirred for another 20 min while warming up the solution to 0 °C. The workup after addition of NH_4Cl (saturated aqueous, 11 mL) gave 3-(tributylstannyl)propanal (0.642 g, 85%). To a Grignard solution prepared from hexyl bromide (1.138 g, 6.89 mmol) was added a solution of the 3-(tributylstannyl)propanal (0.600 g, 1.72 mmol) in ether (5 mL). The solution was stirred for 3 h at −20 °C, and workup afforded 1-(tributylstannyl)-3-nonanol (0.375 g, 50%). NCS oxidation of the 1-(tributylstannyl)-3-nonanol (0.375 g) in the same way as described above gave 8 (0.325 g, 87%). ^1H NMR (CCl_4): δ 0.60–1.77 (m, 40 H), 2.28 (t, J = 7 Hz, 2 H), 2.55 (t, J = 7 Hz, 2 H).

General Procedure for the Reaction of β-Stannyl Ketones 8–17 with Titanium(IV) Chloride. To a CH_2Cl_2 solution of β-stannyl ketone (1 M, equiv) was added a solution of $TiCl_4$ (0.5 M, 1 equiv) in CH_2Cl_2, and the solution was stirred for 15 min at 0 °C under N_2. The reaction was quenched by adding $NaHCO_3$ (saturated aqueous) and the product was extracted with CH_2Cl_2. The crude material obtained by removing the solvent in vacuo was chromatographed on silica gel ($CHCl_3$) to give pure material.

Reaction of 8. The product **8c** was obtained from **8** (0.050 g, 0.115 mmol) at −78 °C in 70% yield (0.011 g). ^1H NMR (CCl_4): δ 0.30–1.90 (m, 17 H), 1.95 (br s, 1 H).

Reaction of 9. The product **9c** was obtained from **9** (0.040 g, 0.152 mmol) at −78 °C in 100% (crude) yield (0.015 g). ^1H NMR (CCl_4): δ 0.30–1.67 (m, 10 H), 2.00 (br s, 1 H), 3.00–3.07 (m, 1 H).

Reaction of 10. The product obtained in 46% yield from **10** (1.805 mmol) was a 17:83 mixture of **10a** and **10b** by GLC. The GC-MS and ^1H NMR analyses of **10a** showed identical results as those of the commercial sample. For **10b**: MS, m/z 114 (M^+), 85, 72 (base peak), 43.

Reaction of 11. The product obtained in 65% yield from **11** (0.766 mmol) was determined to be a 25:75 mixture of cyclohexanone (**11a**) and 2-methylcyclopentanone (**11b**),[17] by comparison with the respective authentic samples on GLC and GC-MS analyses.

Reaction of 12. The product obtained in 45% yield from **12** (0.789 mmol) at −78 °C was determined to be a 87:13 mixture of **12a** and **12b**,[17] by comparison with the respective authentic samples on GC-MS and ^1H NMR analyses. The IR analysis of the mixture showed two carbonyl bands at 1740 and 1710 cm^{-1}.

Reaction of 13. The product **13b** was obtained from **13** (0.200 g, 0.77 mmol) in 52% yield (0.045 g). MS, m/z: 112 (M^+), 97, 79, 69 (base peak), 54. ^1H NMR (CCl_4): δ 1.05 (s, 6 H), 1.50–2.50 (m, 6 H). Exact mass: calcd for $C_7H_{12}O$ (M) 112.0888, obsd 112.0895. The ^1H NMR spectrum was identical with that reported.[18]

Reaction of 14. The product **14b** was obtained from **14** (0.112 g, 0.388 mmol) in 61% yield (0.030 g). MS, m/z: 126 (M^+), 98, 82, 70 (base peak), 53. ^1H NMR (CCl_4): δ 0.90 (t, J = 8 Hz, 3 H), 1.05 (s, 3 H), 1.25–2.50 (m, 8 H). Exact mass: calcd for $C_8H_{14}O$ (M) 126.1045, obsd 126.1023.

Reaction of 15. The product **15b** was obtained from **15** (0.200 g, 0.692 mmol) in 52% yield (0.045 g). MS, m/z: 126 (M^+), 111, 69, 56 (base peak). ^1H NMR (CCl_4): δ 0.97 (s, 3 H), 1.02 (s, 3 H), 1.12 (s, J = 6 Hz, 3 H) 1.30–2.70 (m, 5 H). Exact mass: calcd for $C_8H_{14}O$ 126.1045, obsd 126.1034. The NMR data are practically identical with those reported.[19]

Reaction of 16. The product **16b** was obtained from **16** (0.300 g, 0.990 mmol) in 51% yield (0.071 g). MS, m/z: 140 (M^+), 112, 96, 70 (base peak), 55. ^1H NMR (CCl_4): δ 0.80 (t, J = 8 Hz, 3 H), 0.90 (s, 3 H), 1.03 (d, J = 5.5 Hz, 3 H), 1.10–2.60 (m, 7 H). ^{13}C NMR ($CDCl_3$): δ 8.42, 20.89, 21.71, 27.38, 29.21, 44.73, 45.89, 50.06, 222.21. Exact mass: calcd for $C_9H_{16}O$ (M) 140.1201, obsd 140.1207.

Reaction of 17. The product **17b** was obtained from **17** (0.115 g, 0.38 mmol) at −78 °C in 54% yield (0.029 g). MS, m/z: 140 (M^+), 83 (base peak), 56. ^1H NMR (CCl_4): δ 1.05 (s, 6 H), 1.12 (s, 6 H), 1.76 (s, 2 H), 2.15 (s, 2 H). Exact mass: calcd for $C_9H_{16}O$ (M) 140.1201, obsd 140.1206. The NMR data are practically identical with those reported.[19]

General Procedure for the Preparation of β-Hydroxy β′-Trimethylstannyl Ketones 23–27b. To a cooled solution of (trimethylstannyl)lithium prepared as above (1.2–2.0 equiv) was added slowly a solution of α,β-enone (**23a**, **26a**, **27a**) in THF (0.7–1.0 M, 1.0 equiv) at −78 °C under N_2. After the reaction mixture was stirred for 5–10 min at this temperature, an aldehyde (1.1–2.0 equiv) was added dropwise and stirred for 10 min. The reaction was quenched with NH_4Cl (saturated aqueous), and the solution was allowed to warm up to room temperature. The solution was shaken with ether, and the extract was dried over Na_2SO_4. After removing the solvent in vacuo, the product was purified on a silica gel column or by TLC.

3-(1-Hydroxyethyl)-4-(trimethylstannyl)-2-pentanone (23b). The crude product obtained from **23a** and acetaldehyde was purified on a silica gel column ($CHCl_3$) to afford **23b** in 22% yield. ^1H NMR (CCl_4): δ 0.00 (s, 9 H), 0.90–1.40 (m, 7 H), 2.10 (s, 3 H), 2.30 (s, 1 H), 2.65 (dd, J = 4 and 8 Hz, 1 H), 3.75 (br s, 1 H).

4-Hydroxy-3-(1-(trimethylstannyl)ethyl)-2-hexanone (24b). The crude product obtained from **23a** and propanal was purified by TLC ($CHCl_3$, R_f 0.3) to afford **24b** in 45% yield. ^1H NMR (CCl_4): δ 0.00 (s, 9 H), 0.80–1.60 (m, 9 H), 2.15 (s, 3 H), 2.75 (dd, J = 4 and 8 Hz, 1 H), 2.40–2.70 (br s, 1 H), 3.40–3.90 (br s, 1 H).

4-Hydroxy-3-(1-(trimethylstannyl)ethyl)-2-octanone (25b). The crude product obtained from **23a** and pentanal (the reaction with the aldehyde was performed at −78 °C for 1 h) was purified on a silica gel column ($CHCl_3$) to afford **25b** in 58% yield. ^1H NMR (CCl_4): δ 0.10 (s, 9 H), 0.85–1.70 (m, 13 H), 2.10 (s, 3 H), 2.30 (br s, 1 H), 2.80 (dd, J = 4 and 8 Hz, 1 H), 3.55–4.00 (br 1 H).

4-Hydroxy-3-(1-phenyl-1-(trimethylstannyl)methyl)-2-pentanone (26b). The crude product obtained from **26a** and acetaldehyde was purified on a silica gel column (hexane/ethyl acetate (1/1)) to afford **26b** in 49% yield. MS, m/z: 297 (M^+ − 59), 165 (base peak), 135, 120. ^1H NMR (CCl_4): δ 0.00 (s, 9 H), 1.10 (d, J = 6 Hz, 3 H), 2.30 (s, 3 H), 2.68 (d, J = 8 Hz, 1 H), 2.70 (br s, 1 H), 3.25 (dd, 1 H), 3.80 (m, 1 H), 6.75 (br d, 5 H).

2-(1-Hydroxyethyl)-3-(trimethylstannyl)-1-cyclohexanone (27b). The crude product obtained from **27a** and acetaldehyde was purified on a silica gel column ($CHCl_3$) to afford **27b** in 75% yield. MS, m/z: 247 (M^+ − 59), 165, 149, 135, 45, 41 (base peak). ^1H NMR (CCl_4): δ 0.10 (s, 9 H), 1.25 (d, J = 6 Hz, 3 H), 1.50–2.80 (m, 8 H), 3.20–3.60 (br, 1 H), 3.60–4.10 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ −9.92, 16.79–21.76 (quartet), 27.40–42.29 (multiplet), 57.33–59.89 (quartet), 65.81–67.90 (quartet), 209.75–214.62 (quartet).

General Procedure for the Reaction of β-Hydroxy β′-Trimethylstannyl Ketones 23–27b with Titanium(IV)

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(19) Rei, M.-H. *J. Org. Chem.* **1978**, *43*, 2173.

Chloride. To a cooled solution of the hydroxy trimethylstannyl ketone **23–27b** in CH_2Cl_2 (1.0 M, 1.0 equiv) was added a solution of $TiCl_4$ in CH_2Cl_2 (0.5 M, 2.0–4.0 equiv) at −78 °C under N_2. The reaction mixture was stirred for 2–4 h at this temperature, and the reaction was quenched by addition of water or a solution of $NaHCO_3$ (saturated aqueous). After the reaction mixture was extracted with CH_2Cl_2, the extract was dried over Na_2SO_4 and passed through a Florisil column to remove metal-containing byproducts. After removing the solvent in vacuo, the crude product was purified on a silica gel column or by TLC.

3-Methyl-4-hexen-2-one (23c). The crude product obtained from **23b** was purified on a silica gel column to afford **23c** in 21% yield. MS, *m/z*: 112 (M^+), 97, 94. 69 (base peak), 53. ^1H NMR (CCl_4): δ 1.13 (d, *J* = 8 Hz, 3 H), 1.72 (d, *J* = 5 Hz, 3 H), 2.10 (s, 3 H), 2.85–3.30 (m, 1 H), 5.45–5.75 (m, 2 H). IR (neat): 2940, 2910, 2840, 1720, 1450 cm^{-1}. Exact mass: calcd for $C_7H_{12}O$ (M) 112.0888, obsd 112.0896.

3-Methyl-4-hepten-2-one (24c). The crude product obtained from **24b** was purified by TLC ($CHCl_3$, R_f 0.7) to afford **24c** in 47% yield. MS, *m/z*: 126 (M^+), 97, 83, 55 (base peak), 43. ^1H NMR (CCl_4): δ 1.00 (t, *J* = 7 Hz, 3 H), 1.05 (d, *J* = 7 Hz, 3 H), 2.05 (s, 3 H), 1.80–2.30 (m, 2 H), 2.83–3.63 (m, 1 H), 4.95–5.75 (m, 2 H). The data are practically identical with those reported.[20]

3-Methyl-4-nonen-2-one (25c). The crude product obtained from **25b** was purified on a silica gel column to afford **25c** in 47% yield as a cis–trans mixture (7:2). MS, *m/z*: 154 (M^+), 139, 111, 69, 67, 53 (base peak). ^1H NMR (CCl_4): δ 0.80–1.60 (m, 10 H), 2.00 (s, 3 H), 2.00–2.30 (m, 2 H), 2.95–3.60 (m, 1 H), 5.98–6.70 (m, 2 H). ^{13}C NMR ($CDCl_3$):[21] δ 13.95, (16.14, 16.57*), (22.21, 22.39*), (27.36*, 27.82), (31.42, 31.69*, 32.24), (46.36*, 51.11), (128.62*, 128.89), (132.61*, 133.44), 209.69. Exact mass: calcd for $C_{10}H_{18}O$ (M) 154.1358, obsd 154.1399.

3-Phenyl-4-hexen-2-one (26c).[11] The crude product obtained from **26b** was purified on a silica gel column ($CHCl_3$) to afford **26c** in 18% yield. MS, *m/z*: 174 (M^+), 131 (base peak), 129, 116, 115, 91, 77, 43. ^1H NMR (CCl_4): δ 1.70 (d, *J* = 6 Hz, 3 H), 2.00 (s, 3 H), 4.16 (d, *J* = 8 Hz, $^{12}/_{17}$ H), 4.51 (d, *J* = 8 Hz, $^{5}/_{17}$ H), 5.30–6.00 (m, 2 H), 7.10 (s, 5 H). Upon irradiation of the signal at δ 1.70, the multiplet at δ 5.30–6.00 became an AB quartet having *J* = 16 Hz, indicating that the major component has the trans geometry. ^{13}C NMR ($CDCl_3$):[21] δ (13.21, 18.04*), (28.21, 28.50*), (57.52, 62.89*), 126.78–129.23 (multiplet), (138.56*, 138.70), (206.39, 206.94*). IR (neat): 3030, 2920, 1710, 1600, 1500, 970 cm^{-1}. The ^1H NMR and IR spectra were practically identical with those reported.[11] Exact mass: calcd for $C_{12}H_{14}O$ (M) 174.1045, obsd 174.1063.

2-(1-Propenyl)-1-cyclopentanone (27c). The crude product obtained from **27b** was purified on a silica gel column ($CHCl_3$) to afford **27c** in 74% yield as a cis–trans mixture (1:3). MS, *m/z*: 124 (M^+), 96, 95, 81, 68 (base peak), 67, 56, 55, 53, 42, 41, 40, 39. ^1H NMR (CCl_4): δ 1.70–3.40 (m, 10 H), 4.90–6.00 (m, 2 H). IR (neat): 3030, 2970, 2890, 1730, 1650, 1150, 970, cm^{-1}. ^{13}C NMR ($CDCl_3$):[21] δ (13.41, 18.02*), (20.76*, 21.02), (29.95*, 30.79), (37.56, 37.74*), (48.35, 52.30*), (126.61, 127.13*), (127.89*, 128.00), (218.52, 218.63*). Exact mass: calcd for $C_8H_{12}O$ (M) 124.0888, obsd 124.0897.

General Procedure for the Preparation of Stannyl Silyl Enol Ethers 28a, 29a, and 31a. To a cooled solution of (trimethylstannyl)lithium (1.8–3.0 equiv) was added slowly a solution of the α,β-enone in THF (1.0 M, 1.0 equiv) at −78 °C under N_2. The reaction mixture was stirred for 10–15 min at this temperature, and triethylamine (1.8–3.0 equiv) and then trimethylsilyl chloride (1.8–3.0 equiv) were added dropwise. The reaction mixture was allowed to warm up to 0 °C and stirred for 1.5–3.0 h at this temperature. The reaction was quenched with water, and the product was extracted with ether. After being dried over Na_2SO_4, the extract was concentrated in vacuo. The crude product was purified by bulb-to-bulb distillation.

2-(Trimethylsiloxy)-4-(trimethylstannyl)-2-butene (28a). The crude product obtained from methyl vinyl ketone was purified by bulb-to-bulb distillation to afford **28a** in 81% yield, bp 60–90 °C (oven temperature, 9 mmHg). ^1H NMR (CCl_4): δ 0.10 (s, 9 H), 0.20 (s, 9 H), 1.65 (d, *J* = 8 Hz, 2 H), 1.75 (s, 3 H), 4.60–4.95 (t, *J* = 8 Hz, 1 H).

2-(Trimethylsiloxy)-4-(trimethylstannyl)-2-pentene (29a). The crude product obtained from **23a** was purified by bulb-to-bulb distillation to afford **29a** in 69% yield, bp 100–150 °C (oven temperature, 20 mmHg). ^1H NMR (CCl_4): δ 0.08 (s, 9 H), 0.18 (s, 9 H), 1.25 (d, *J* = 7 Hz, 3 H), 1.70 (s, 3 H), 1.70–1.95 (m, 1 H), 4.65 (d, *J* = 11 Hz, 1 H).

1-(Trimethylsiloxy)-3-(trimethylstannyl)-1-cyclohexene (31a). The crude product obtained from **27a** was purified by bulb-to-bulb distillation to afford **31a** in 55% yield, bp 95 °C (oven temperature, 0.5 mmHg). ^1H NMR (CCl_4): δ 0.13 (s, 9 H), 0.21 (s, 9 H), 1.50–2.60 (m, 7 H), 4.85–4.95 (m, 1 H).

General Procedure for the Reaction of Stannyl Silyl Enol Ethers 28a, 29a, and 31a with Aldehydes in the Presence of Titanium(IV) Chloride. To a cooled solution of the stannyl silyl enol ether (**28a, 29a, 31a**) in CH_2Cl_2 (0.17 M, 1.0 equiv) was added an aldehyde (1.0–1.2 equiv) at −78 °C under N_2. After 1 min, a CH_2Cl_2 solution of $TiCl_4$ (0.5 M, 2.0 equiv) was added, and the reaction mixture was stirred for 2 h at this temperature. After the reaction was completed, water was added, and the solution was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4 and passed through a Florisil column to remove metal-containing byproducts. After removing the solvent in vacuo, the crude product was purified on a silica gel column or by TLC.

5-Phenyl-4-penten-2-one (28b).[12,13] The crude material obtained from **28a** and benzaldehyde was shaken with $NaHSO_3$ (saturated aqueous) and the crude product was purified on a silica gel column (hexane:ether = 1:1) to afford **28b** in 40% yield. MS, *m/z*: 160 (M^+), 117, 115, 91, 42 (base peak). ^1H NMR (CCl_4): δ 2.05 (s, 3 H), 3.20 (d, *J* = 6 Hz, 2 H), 5.95–6.70 (m, 2 H), 7.20 (br s, 5 H). Exact mass: calcd for $C_{11}H_{12}O$ (M) 160.0889, obsd 160.0879.

3-Methyl-4-hepten-2-one (29b). The crude product obtained from **29a** and propanal was purified on a silica gel column ($CHCl_3$) to afford **29b** in 47% yield. The product was identical with **24c**.

3-Methyl-5-phenyl-4-penten-2-one (30b). The crude material obtained from **29a** and benzaldehyde was shaken with $NaHSO_3$ (saturated aqueous), and the crude product was purified by preparative TLC ($CHCl_3$, R_f 0.7) to afford **30b** in 64% yield. MS, *m/z*: 174 (M^+), 131 (base peak), 116, 103, 91, 77, 65. ^1H NMR (CCl_4): δ 1.18 (d, *J* = 7 Hz, 3 H), 2.05 (s, 3 H), 3.20 (quintet, *J* = 7 Hz, 1 H), 6.00 and 6.29 (AB q, *J* = 16 Hz, 2 H, the upper half split further into doublets with *J* = 7 Hz), 7.00–7.45 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ 16.13, 28.02, 51.19, 126.14, 127.48, 128.42, 128.67, 131.99, 136.69, 208.76. Exact mass: calcd for $C_{12}H_{14}O$ (M) 174.1044, obsd 174.1072.

2-(1-Propenyl)-1-cyclopentanone (31b). The crude product obtained from **31a** and acetaldehyde was purified on a silica gel column ($CHCl_3$) to afford **31b** in 42% yield as a cis–trans mixture (3:4). The spectroscopic data were identical with those of **27c**, except the relative intensities of the ^{13}C NMR signals corresponded to the respective geometrical isomers.

(20) Dana, G.; Gharbi-Benarous, J.; Thuan, S. L. T. *Can. J. Chem.* **1980**, *58*, 1451.

(21) The figures in parentheses are chemical shifts of the same carbon in a set of diastereomers, with the major signal marked with an asterisk.