Dependence of the Lewis Acid-Induced Reaction of β-Stannyl Ketones upon Substitution Pattern: Cyclopropanation versus 1,2-Alkyl Migration †

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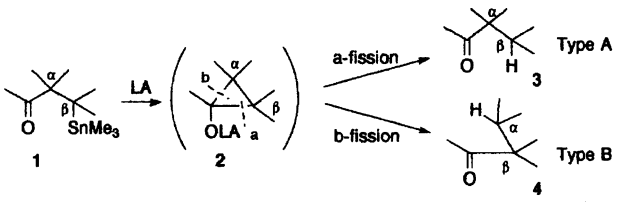
3-Stannylcyclohexanones fully substituted at 2 and 3 positions underwent a 1,2-alkyl migration, along with the cyclopropanation. The balance of the reactions depended upon the steric environment and migratory aptitude of the alkyl groups.

Due to the latent carbanionic character of the carbon–tin bond, the tin compounds containing cationic center within the same molecule undergo various types of reaction.[1] Typical types of the reaction are cyclization and hydride shift, and the reaction types depend upon the relative position of the cationic center to the carbon–tin bond, the number of the substituents at the tin-bearing carbon, and the activation methods. In case of β-stannyl ketones, the reaction usually proceeds with cyclopropanation.[2] In the present study, we found that a 1,2-alkyl migration competed with the cyclopropanation under specific conditions.

So far, we have investigated the Lewis acid-induced reaction of β-stannyl ketones having at least one hydrogen atom at α-position in **1**. In every cases, the reaction proceeded via cyclopropanol intermediates **2**, which afforded saturated ketones **3** or **4**, according to the position of the bond cleavage of the cyclopropanol ring of **2**, a or b (Scheme 1). The general trend is that, (1) the ring cleavage of the cyclopropanol intermediates **2** occurs at bond leading to the less substituted carbon, (2) in cases both α and β-carbons have the same number of substituents, trimethylsilyl trifluoromethanesulfonate (TMSOTf) facilitated the Type B reaction, while $TiCl_4$ induced both reactions unselectively, and (3) the introduction of hydroxyl group into the α-substituent induces the Type B reaction, irrespective of the substitution pattern or the nature of Lewis acid.[2]

In order to find the limitation of the trend, we extended our investigation to the reaction of 3-stannylcyclohexanones having various types of substituents at 2 and/or 3-positions. First we chose the stannyl ketones fully substituted at 2-position by alkyl groups. The starting materials **5a** and **5b** were prepared from



Scheme 1.

†Preliminary paper: J. Fujiwara, T. Yamamoto, and T. Sato, *Chem. Lett.*, **1992**, 1775.

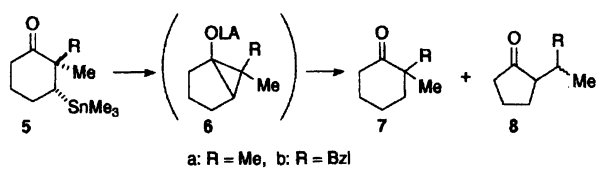
2-methyl-2-cyclohexen-1-one by conjugate addition of Me_3SnLi, followed by quenching the enolate with methyl iodide and benzyl bromide, respectively. When **5a** and **5b** were treated with $TiCl_4$ or TMSOTf, the type A products **7a** and **7b** were obtained as major products, although **7b** contained a trace amount of impurity which could be assigned as **8b** in view of the small doublet at δ=0.80 in the NMR spectrum (Table 1 Runs a—d). The preferential formation of the Type A products is consistent with the general trend that the ring cleavage of the cyclopropanol intermediate **6** occurs at bond leading to the less substituted carbon (Scheme 2).

In contrast with the exclusive cyclopropanation of **5a**

Table 1. Lewis Acid-Induced Reaction of 2,2-Dialkyl-3-stannylcyclohexanones

Run	Substrate	Lewis[a] acid	React time min	Product (yield/%) 7	8			
a	**5a**	A	60	96				0
b	**5a**	B	60	98				0
c	**5b**	A	30	79				tr
d	**5b**	B	30	41				tr
				10	**11**	**12**	**13**	**14**
e	**9a**	A	10	0	0	0	30	16
f	**9a**	B	10	11	23	10	Tr	0
g	**9a**	C	10	17	46	16	0	10
h	**9b**	A	10	0	0	0	33	23
i	**9b**	B	10	0	0	39	Tr	24
j	**9b**	C	10	Tr	Tr	78	Tr	0
k	**9c**	A	10	0	0	0	43	54
l	**9c**	B	10	0	0	23	24	37
m	**9c**	C	10	0	0	73	8	16
				21	**22**	**23**	**24**	
n	**19**	A	10	11	6	0	27	
o	**19**	C	10	0	33	0	34	
p	**19**	D	10	61	Tr	0	0	
				29				
q	**25**	A	180	85				
r	**25**	B	90	80[b]				
				32				
s	**30**	B	240	46				

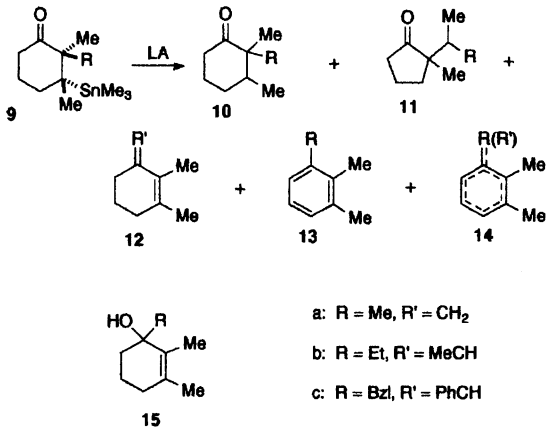
a) A: TMSOTf; B: $TiCl_4$; C: $TiCl_4$/BzlEt$_3$NBr; D: (*n*-Bu)$_2$BOTf. b) Overall yield via **28**.



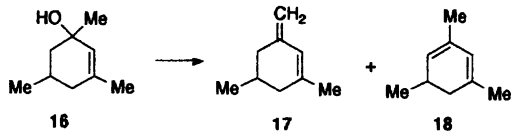
Scheme 2.

and **5b**, 1,2-alkyl migration competed with the cyclization, when both 2 and 3-positions were fully substituted by alkyl groups. The starting materials **9a**—**9c** were prepared from 2,3-dimethyl-2-cyclohexen-1-one in the same way as mentioned above, by conjugate addition of Me_3SnLi, followed by quenching the enolate with methyl iodide, ethyl iodide, and benzyl bromide, respectively. It has been established that the introduction of the alkyl groups takes place at *trans* position to the stannyl group.[3] When **9a**—**9c** were treated with Lewis acids (A: TMSOTf; B: $TiCl_4$; C: $TiCl_4$/$BzlEt_3NBr$), the corresponding **10**—**14** were obtained (Table 1, Runs e—m). The products **14a**—**14c** were mixtures of regioisomers of monoenes. The structure assignment of the products will be discussed below. Evidently **12**—**14** are the products involving a 1,2-alkyl migration, while **10** and **11** are the Type A and Type B products mentioned above, respectively (Scheme 3). Probably, the primary 1,2-alkyl migration product **15** was dehydrated to **12**, which disproportionated to aromatic compounds **13** and monoenes **14**.[4] Although the dehydration of **16** is known to produce a mixture of *exo* and *endo* dienes **17** and **18** in 3:2 ratio, respectively,[5] no *endo* diene was identified in the present reaction (Scheme 4). Probably the presence of three consecutive substituents would destabilize the planar ring structure required for the endocyclic diene.

In the 1,2-alkyl migration reactions, the migrating group was always R, which had been introduced after the stannylation, and occupied *trans* position to the stannyl group. No products involving the methyl migration were identified in the reactions of **9b** and **9c**. As evident from Table 1, Runs e—m, the alkyl migration



Scheme 3.



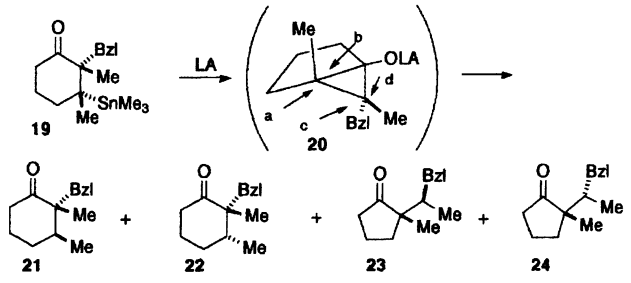
Scheme 4.

(leading to **12**—**14**) became more facilitated than the cyclopropanation (leading to **10** and **11**), as R changed from methyl to ethyl, and then to benzyl group.

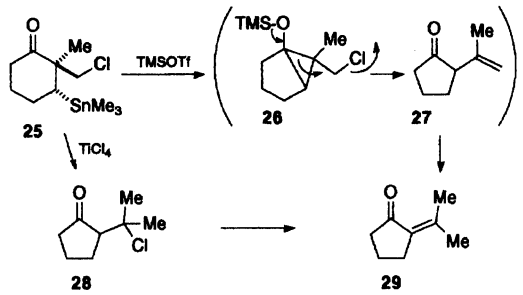
In order to verify whether the absence of the methyl migration products in the reactions of **9b** and **9c** is due to the low migratory aptitude of the methyl group, or to the steric requirement imposed by the *cis*-relation of the methyl versus stannyl group, we examined the reaction of **19**, which is a stereoisomer of **9c**. The starting material was prepared from 2-benzyl-3-methyl-2-cyclohexen-1-one by the addition of Me_3SnLi followed by quenching the enolate with methyl iodide. In contrast to the exclusive 1,2-alkyl migration observed with **9c**, **19** gave only the Type A (**21** and **22**) and Type B products (**24**), as shown in Table 1, Runs n—p (Scheme 5). Neither of the another possible Type B product **23** nor alkyl migration products were identified. Evidently **21** and **23** are the products resulted from the protonative opening of the cyclopropane ring of the intermediate **20** with inversion (a and c-proton attacks, respectively), while **22** and **24** are the products through the ring opening with retention (b and d-attacks, respectively). The results indicate that even benzyl group, which has an ample migrating ability, can not migrate when it occupies *cis* position to the stannyl group.

The introduction of a leaving group (Cl) into the 1′-position of the C2-substituent induced the reaction to proceed exclusively in the Type B manner, irrespective of the substitution pattern. Namely, upon treatment with TMSOTf, **25** underwent a ring contraction exclusively to give **29**. Apparently the reaction proceeded via **26** and **27**. Presumably the double bond migration from **27** was induced by the Lewis acid, because **27**, obtainable by the photoreaction of **25** under neutral conditions[6] afforded **29** with acid treatment (Scheme 6). When $TiCl_4$ was used as a Lewis acid, **25** gave **28** as an unstable product, which was dehydrochlorinated to **29** by $NaHCO_3$.

In contrast to the smooth ring contraction of the



Scheme 5.

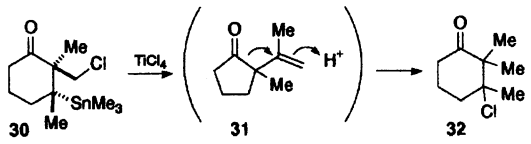


Scheme 6.

secondary tin compound **25**, a tertiary tin compound **30** gave **32** as major product when treated with $TiCl_4$ (Scheme 7). Although the reaction type seems quite different from that of **25**, we believe that a similar reaction pattern involving the Type B reaction proceeds to afford **31**, which subsequently undergoes a 1,2-acyl migration to give the final product. We have recently found a similar acid-induced 1,2-acyl migration in 2,2-disubstituted cyclopentanone system.[7]

Product Identification The spectroscopic data of **7a**[8] and **7b**[9] coincided with those reported. The products **12a** and **13a** were confirmed by comparing with the authentic samples. Since the Type A and Type B products from **9a** were obtained only as a mixture of **10a/11a**, we prepared the authentic sample of **11a** for reference (See Experimental). The NMR spectrum of the mixture was identical with the sum of those of **10a**[10] and **11a**. The mass spectra of each components were also identical with those of **10a**[10] and **11a**. The fractions corresponding to **14a—14c** showed single peaks on a GC machine equipped with a packed column, but they were split into a couple of peaks on GC machine equipped with a capillary column. They were not completely freed from the corresponding **12** and **13**, and therefore we were obliged to speculate the structures only from the spectroscopic data of the mixtures. The mass spectra of these components showed parent peaks two mass units higher than those of the corresponding dienes **12**, indicating that the product might be a mixture of positional isomers of monoenes, but no further structure elucidation was undertaken because of the difficulty in isolation of the components.

The Type A product **21** was assigned by comparing with the sample prepared by the conjugate addition of methylcopper to 2-methyl-2-cyclohexen-1-one, followed by quenching the intermediate enolate with benzyl bromide. Since it has been established[11] that the both alkyl groups are introduced so as to occupy mainly *trans* position with each other, we assigned the structure **21** for the product. The *cis* isomer **22** showed identical mass spectrum as that of **21**. With a view to prepare the Type B products **23** and **24** independently, we carried out the conjugate addition of benzylcopper to 2-ethylidenecyclopentanone, followed by quenching the enolate with methyl iodide. The reaction was sluggish,



Scheme 7.

and afforded the product only in ca. 5% yield with a diasteromer ratio of 3/2. The Type B product obtained as a single isomer from **19** was identical with the major product of the independent synthesis. Although there remains much ambiguity concerning with the stereochemistry due to the low yield and poor stereoselectivity of the independent synthesis, we tentatively assigned the structure **24** for the major product, since it has been established that this type of reaction proceeds through a conformation minimizing the allylic strain to afford an isomer corresponding to **24** as major product.[12] The other products were assigned in view of the spectroscopic data on samples isolated in pure states.

Discussion

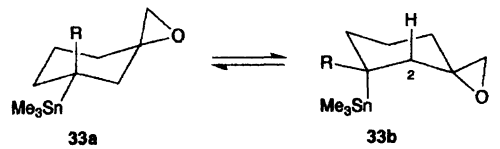
Typical reaction types of the stannyl and silyl compounds having cationic carbon at γ-position are cyclopropanation and 1,2-alkyl or hydride shift, and it has been observed that the stannyl compounds undergo the cyclopropanation preferably to the 1,2-shift, while the silyl compounds favor the 1,2-shift over the cyclization, when respective compounds having the same carbon skeleton were compared under the same conditions.[13] Even with silyl compounds, however, the 1,2-alkyl migration is observed only in special case of norbornane system,[14] or it is competed with the hydride shift,[15] even though diphenylphosphinoyl,[16] phenylthio,[17] phenyl or hydride[15] migrates smoothly.

The 1,2-alkyl shift driven by stannyl group has been observed in norbornane system by Hartman and Traylor.[18] They speculated from kinetic data that the reaction proceeded through a transition state in which the Sn–C–C–R bonds are coplanar, although their system lacked in the requirement for the stereochemical discussions. A definite stereochemical environment for the 1,2-shift, albeit hydride shift, was provided by Plamondon and Wuest, who carried out a Lewis acid-induced reaction of stereochemically defined spirocyclic (3,4-epoxybutyl)stannanes **33**.[19] They found that the cyclopropanation proceeded when R was hydrogen, while 1,2-hydride shift proceeded when R was alkyl, and concluded that the reaction types were dependent critically upon the relative orientations of tin, oxygen and the three connecting carbon atoms, and a concerted 1,3-eliminative cyclization involving inversion of configuration at both carbon centers proceeded only when a W-arrangement of these atoms was possible. Obviously the reaction proceeds from the conformer **33a** when R is hydrogen, in which the bulky stannyl group occupies equatorial orientation to fulfil the W-requirement, while

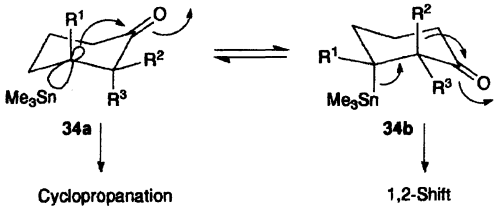
the reaction proceeds from the conformer **33b** when R is methyl, which is better suited to a 1,2-shift of the axial C2-hydrogen, driven by the antiperiplanar carbon–tin bond (Scheme 8).

Referring to the fact that the cyclopropanation proceeds with inversion of the configuration of the tin-bearing carbon,[20] while the *anti* configuration of the stannyl and the migrating group is requisite for the alkyl migration, we assume that the cyclopropanation proceeds from the conformer **34a**, while the alkyl migration proceeds from the conformer **34b** (Scheme 9). The reaction types could be balanced by the relative stability of the conformers and migratory aptitude of the alkyl groups. Although there are some superficial differences in the reaction pattern among the compounds mentioned above, most of the reactions (except the case of **9**) are essentially the Type A or B reactions, somewhat modified by the secondary reactions. The 1,2-alkyl migration proceeded only with compounds in which R^1 and R^3 are alkyl groups, and R^2 has sufficient migratory aptitude. Presumably the introduction of the alkyl groups into R^1 and R^3 would shift the conformation in favor of **34b**, thus facilitating the alkyl migration. Even under these circumstances, however, the chloromethyl group in **25** and **30** has too small migratory aptitude to undergo the alkyl shift.

In view of these considerations, it is conceivable that **35** would fulfil the requirement for the 1,2-shift, because hydrogen atom as R^2 is a good migrant, and the absence of the bulkiness for R^2 would favor the conformer **34b**. Actually however, the TMSOTf treatment of **35** gave only an unidentifiable product which was neither volatile enough to permit the GC analysis, nor showed any IR and NMR signal consistent with typical functional groups, suggesting that it might be a hydrocarbon polymer. The results are in sharp contrast to the reaction of its epimer **37**, which afforded the Type B product exclusively under the same conditions.[21] We assume that the 1,2-hydride shift from the conformer **34b** proceeded to produce an allyl alcohol **36**, which underwent dehydration-polymerization upon TMSOTf treatment. Supporting this speculation, **36**, which had been synthesized independently, actually afforded similar hydrocarbon polymer under the same conditions (Scheme 10).



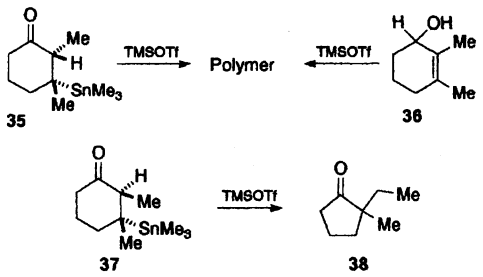
Scheme 8.



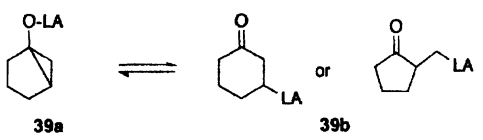
Scheme 9.

Since the cyclopropane ring formation from (3-hydroxypropyl)stannane derivatives under acidic conditions was first reported by Davis in 1970,[22] many papers dealing with the 1,3-eliminative cyclization in stannyl compounds have appeared.[19] It has been established that the 1,3-eliminative cyclopropanation proceeds stereospecifically with inversion of configuration at both carbon atoms.[13] Since we have confirmed that the cyclopropanation in the β-stannyl ketone system also proceeds with inversion at the tin-bearing carbon,[20] the stereochemistries of the products from **19** should be determined at the stage of the protonative ring opening of the cyclopropanol intermediates **20**. It has been known that the protonative ring opening proceeds with retention under acidic conditions, while it proceeds with inversion under basic conditions.[23] Although the stereochemical assignment for **24** leaves ambiguity as mentioned above, it is definite that the Type B reaction affords a single isomer while the Type A reaction affords both diastereomers depending upon the nature of the Lewis acids. If we assume the stereochemistry of **24** as shown, we could conclude that the Type B reaction proceeded exclusively through protonation with retention, while the Type A reaction proceeded either with inversion producing **21**, or with retention producing **22**. We tentatively assume that the product distribution is determined by the character of the cyclopropanol intermediate at the protonation step, which lies on a wide range between cyclopropanolate **39a** and homoenolate extremes **39b** depending upon the Lewis acid (Scheme 11).

Some of the reactions mentioned above, particularly the formation of α,α-disubstituted cyclohexanone and cyclopentanones of definite stereochemistry, could be useful from the synthetic viewpoint. It has been known



Scheme 10.



Scheme 11.

that the α,α-dialkylation of cyclohexanone derivatives requires special precautions to prevent the possible regiochemical scrambling.[24] We are developing a couple of reactions from this novel system, which will be reported elsewhere.

Experimental

General Procedure and Instrumentation. GC experiments were carried out on a 2.5 m×3 mm stainless steel column packed with Silicone SE 30 on silanized Chromosorb W and 25 m×0.25 mm capillary column (SE 30). Column chromatography was carried out on Kieselgel 60, Art. 7734 (70—230 mesh ASTM) using solvents as indicated. Unless otherwise stated, all the spectroscopic data were determined on pure samples obtained by either distillation or column chromatography, checking the purity by TLC or GC analyses; the mass spectra were obtained by EI method at 70 eV, the ^{1}H NMR data on the 60 MHz machines with CCl_4 solutions, the ^{13}C NMR data (22.5 MHz) with $CDCl_3$ solutions, and IR spectra with neat samples.

All of the ^{1}H NMR signal of the methyl group on tin atom at δ=ca. 0 ppm accompanied splitting signals by ^{117}Sn (7.54% abundance, J=51 Hz) and ^{119}Sn (8.62% abundance, J=53 Hz). Mass spectral peaks of the tin-containing fragments showed isotope pattern typical to the tin atom, but only values corresponding to ^{120}Sn were shown.

General Procedure for the Preparation of β-Stannyl Ketones. To a THF solution Me_3SnLi (1.2 —3.3 equiv) prepared as described in our previous report[21] was added a solution of the corresponding α,β-enones (0.3—0.6 M, 1 equiv) in THF at 0 °C. After stirred for 1 h, the solution was quenched with water, or reacted with appropriate alkyl halides at room temperature for periods described below. The ether extracts, after dried over $MgSO_4$, were concentrated in vacuo. Column chromatography gave pure materials.

2,2-Dimethyl-3-(trimethylstannyl)cyclohexanone (5a): The product was obtained in 63% yield (0.55 g) from 2-methyl-2-cyclohexen-1-one[25] (0.33 g, 3.0 mmol), Me_3SnLi solution (4.5 mmol), and methyl iodide (0.87g, 6. 0 mmol), by stirring for 2 h. The product was purified by column chromatography (hexane : ether=4 : 1): ^{1}H NMR δ=0.04 (s, 9H), 1.01 (s, 3H), 1.04 (s, 3H), 1.4—2.0 (m, 5H), and 2.0—2.5 (m, 2H); MS (20 eV) m/z 290 (M^+), 275 (base), 247, 165, 151, 125, 107, 97, and 83. Exact mass: Found: m/z 290.0664. Calcd for $C_{11}H_{22}OSn$: M, 290.0693.

***r*-2-Benzyl-2-methyl-*t*-3-trimethylstannylcyclohexanone (5b):** The product was obtained in 33% yield (0.55 g) from 2-methyl-2-cyclohexen-1-one (0.5 g, 4.54 mmol), Me_3SnLi solution (6.81 mmol), and benzyl bromide (1.160 g, 6.81 mmol), by stirring for 3 h. The product was purified by column chromatography (hexane : ether=4 : 1); ^{1}H NMR δ=0.10 (s, 9H), 1.00 (s, 3H), 1.50—2.10 (m, 5H), 2.10—2.50 (m, 2H), 2.71 and 3.04 (each d, J=13.2 Hz, 2H), and 7.10 (bs, 5H)

2,2,3-Trimethyl-3-trimethylstannylcyclohexanone (9a): The product was obtained in 80% yield (0.79 g) from 2,3-dimethyl-2,3-dimethyl-2-cyclohexen-1-one[26] (0.40 g, 3.22 mmol), Me_3SnLi solution (4.84 mmol), and methyl iodide (0.921 g, 6.45 mmol), by stirring for 4 h. The product was purified by column chromatography (hexane : ether=4 : 1); ^{1}H NMR δ=0.01 (s, 9H), 0.97 (s, 3H), 1.05 (br. s, 3H), 1.11 (s, 3H), 1.4—1.95 (m, 4H), and 2.2—2.5 (m, 2H); MS (CI) m/z 303 (M^+-1) and 138. Exact mass: Found: m/z 304.0944. Calcd for $C_{12}H_{24}OSn$: M, 304.0849.

***r*-2-Ethyl-2,*c*-3-dimethyl-3-trimethylstannylcyclohexanone (9b) :** The product was obtained in 48% yield (0.30 g) from 2,3-dimethyl-2-cyclohexen-1-one (0.30 g, 2.44 mmol), Me_3SnLi solution (3.65 mmol), and ethyl iodide (1.95 g, 12.5 mmol), by stirring for 4 h. The product was purified by column chromatography (hexane : ether=4 : 1); ^{1}H NMR δ=−0.06 (s, 9H), 0.57 (t, J=6.8 Hz), 0.91 (s, 3H), 1.07 (s, 3H), and 1.3—2.4 (m, 8H); ^{13}C NMR δ=−8.30, 8.34, 19.57, 21.19, 23.95, 25.81, 33.43, 38.58, 42.09, 55.54, and 213.41; MS (20 eV) m/z 303 (M^+-15), 289 (base), 185, 165, and 135. Exact mass: Found: m/z 303.0803. Calcd for $C_{12}H_{23}OSn$: M−Me, 303.0771.

***r*-2-Benzyl-2,*c*-3-dimethyl-3-trimethylstannylcyclohexanone (9c):** The product was obtained in 67% yield (0.62 g) from 2,3-dimethyl-2-cyclohexen-1-one (0.30 g, 2.42 mmol), Me_3SnLi solution (3.63 mmol), and benzyl bromide (1.25 g, 7.31 mmol), by stirring for 16 h. The product was purified by column chromatography (hexane : ether=4 : 1); ^{1}H NMR δ=0.09 (s, 9H), 0.95 (s, 3H), 1.30 (s, 3H), 2.47 and 3.28 (each d, J=13.4 Hz, 2H), 1.8—2.9 (m, 6H), and 7.3—6.7 (m, 5H); ^{13}C NMR δ=−8.06, 21.13, 21.25, 26.16, 33.48, 37.67, 38.84, 42.99, 56.74, 125.98, 127.69, 129.72, 137.77, and 212.21; MS (CI) m/z 379 (M^+-1), 365, 289, and 199. Exact mass (CI): Found: m/z 380.1118. Calcd for $C_{18}H_{28}OSn$: M, 380.1162.

***r*-2-Benzyl-2,*t*-3-dimethyl-3-trimethylstannylcyclohexanone (19):** The product was obtained in 21% yield (0.12 g) from 2-benzyl-3-methyl-2-cyclohexen-1-one[27] (0.31 g, 1.55 mmol), Me_3SnLi solution (2.35 mmol), and methyl iodide (0.68 g, 4.82 mmol), by stirring for 8 h. The product was purified by column chromatography (hexane : ether=4 : 1); ^{1}H NMR δ=0.15 (s, 9H), 0.79 (s, 3H), 1.20 (s, 3H), 2.35 and 3.51 (each d, J=13.5 Hz, 2H), 1.50—2.60 (m, 6H), and 7.05 (bs, 5H).

***r*-2-Chloromethyl-2-methyl-*t*-3-trimethylstannylcyclohexanone (25) :** The product was obtained in 88% yield (0.65 g) from 2-methyl-2-cyclohexen-1-one (0.30 g, 2.72 mmol), Me_3SnLi solution (4.15 mmol), and chloroiodomethane (0.97 g, 5.49 mmol), by stirring for 16 h. The product was purified by column chromatography (hexane : ether=4 : 1); ^{1}H NMR δ=0.09 (s, 9H), 1.09 (s, 3H), 1.7—2.01 (m, 5H), 2.0—2.5 (m, 2H), 3.32 and 3.78 (each d, J=11.6 Hz, 2H); MS (20 eV) m/z 309 (M^+-15), 289, 273, 207, 185, 165, 149, 135, 124 (base), 109, 96, 81, and 68. Exact mass: Found: m/z 309.0085. Cacld for $C_{10}H_{18}OClSn$: M−Me, 309.0069.

***r*-2-Chloromethyl-2,*c*-3-dimethyl-3-trimethylstannylcyclohexanone (30) :** The product was obtained in 27% yield (0.22 g) from 2,3-dimethyl-2-cyclohexen-1-one (0.3 g, 2.42 mmol), Me_3SnLi solution (8.05 mmol), and chloroiodomethane (2.11 g, 11.9 mmol), by stirring for 8 h. The product was purified by column chromatography (hexane : ether=4 : 1); ^{1}H NMR δ=0.11 (s, 9H), 1.23 (s, 6H), 1.7—2.2 (m, 4H), 2.2—2.7 (m, 2H), and 3.46 and 4.08 (each d, J=11.8 Hz, 2H); ^{13}C NMR δ=−8.16, 19.25, 21.05, 25.82, 332.75, 38.14, 412.54, 47.94, 56.48, and 209.60; MS m/z 323 (M^+-15), 303, 185, 165, 138, 138, 123, 110 (base), 95, 82, 67, and 52. Exact mass (CI): Found: m/z 339.0506. Calcd

for $C_{12}H_{24}OClSn$: M^+-Me, 339.0538.

General Procedure for the Reaction of β-Stannyl Ketones with Lewis Acids (runs a—p). For Reagents A, B, D: To a CH_2Cl_2 solution of β-stannyl ketones (0.2—0.5 M[#], 1 molar amount) was added a CH_2Cl_2 solution of Lewis acids (1.1—1.5 molar amounts; TMSOTf (A): neat; $TiCl_4$ (B): 0.3 M; $(n\text{-Bu})_2BOTf$ (D): 1.0 M) at 0 °C.

For Reagents C: To a CH_2Cl_2 solution of β-stannyl ketones (0.06—0.08 M, 1 molar amount) and $BzlEt_3NBr$ (2 molar amounts) was added a CH_2Cl_2 solution of $TiCl_4$ (0.17—0.20 M, 3 molar amounts) at 0 °C. After each solution was stirred for a period specified in Table 1, the reaction mixture was quenched with sat $NaHCO_3$ aq., the product was extracted with CH_2Cl_2. The extract was dried over $MgSO_4$, the solvent was removed in vacuo, and the product was directly subjected to the GC analyses to determine the product yields. Each component, unless otherwise stated, was isolated in pure state by column chromatography.

2,2,3-Trimethylcyclohexanone (10a) and 2-Isopropyl-2-methylcyclopentanone (11a): The products were obtained only as a mixture. The authentic **11a** was prepared from 2-methylcyclopentanone referring to the reported method.[28] MS *m/z* 140 (M^+), 98, 96, 84, 83, and 69 (base); ^1H NMR δ=0.79 (d, J=7.0 Hz, 3H), 0.86 (d, J=7.0 Hz, 3H), 0.92 (s, 3H), and 0.45—2.35 (m, 7H). The NMR spectrum of the mixture was identical with the sum of those of **10a**[10] and **11a**. The product mixture of **10a** and **11a** showed two peaks on GC, whose MS spectra were identical with the respective authentic data.[10]

1,2-Dimethyl-3-methylenecyclohexene (12a): The compound was identical with the authentic sample prepared from 2,3-dimethyl-2-cyclohexen-1-one by the reaction with $MePPh_3Br$/*n*-BuLi in ether at room temperature. ^1H NMR δ=1.81 (br.s, 6H), 1.8—2.5 (m, 6H), 4.65 (br.s, 1H), and 4.81 (br.s, 1H).

1,2,3-Trimethylbenzene (13a): The compound was identical with the authentic sample which is commercially available.

3-Ethylidene-1,2-dimethylcyclohexene (12b): ^1H NMR δ=1.71 (br.s, 6H), 1.62 (d, J=7.6 Hz, 3H), 1.4—2.5 (m, 6H), and 5.33 (br.q, J=7.6 Hz, 1H); MS *m/z* 136 (M^+), 121 (base), 107, 93, and 79. Exact mass: Found: *m/z* 136.1224. Calcd for $C_{10}H_{16}$: M, 136.1252.

3-Ethyl-1,2-dimethylbenzene (13b): ^1H NMR δ= 1.27 (t, J=7.6 Hz, 3H), 2.27 (s, 3H), 2.35 (s, 3H), 2.68, (q, J=7.6 Hz, 2H), and 6.95 (s, 3H); MS *m/s* 134 (M^+), 119 (base), 105, 91, 77, and 65. Exact mass: Found: *m/z* 134.1075. Calcd for $C_{10}H_{14}$: M, 134.1096.

Monoene Mixture 14b Ms *m/z* 138 (M^+), 109 (base), 81, and 67.

3-Benzylidene-1,2-dimethylcyclohexene (12c): MS *m/s* 198 (M^+, base), 183, 169, 155, 141, 129, 115, 107, 91, 77, and 65; ^1H NMR δ=1.50—2.73 (m, 6H), 1.83 (s, 3H), 1.86 (s, 3H), 6.33 (br.s, 1H), and 7.10 (s, 5H). Exact mass: Found: *m/z* 198.1388. Calcd for $C_{15}H_{18}$: M, 198.1409.

1-Benzyl-2,3-dimethylbenzene (13c): ^1H NMR δ= 2.08 (s, 3H), 2.30 (s, 3H), 3.99 (s, 2H), 6.94 (s, 3H), and 7.10 (br.s, 5H);[29] MS *m/z* 196 (M^+), 181 (base), 166, 153, 141, 128, 118, 105, 97, 91, 83, 77, and 65. Exact mass: Found: *m/z* 196.1223. Calcd for $C_{15}H_{16}$: M, 196. 1252.

Monoene Mixture (14c): MS *m/s* 200 (M^+), 157 (base), and 142.

***r*-2-Benzyl-2,*t*-3-dimethylcyclohexanone (21):** The compound was identical with the authentic sample prepared as follows. To a suspension of CuI (1.05 g, 5.51 mmol) in THF (10 cm^3) was added an ether solution of MeLi (1.05 M, 11 cm^3) at −78 °C over 10 min. After CuI had disssolved, the solution was stirred for another 30 min, and the temperature was raised gradually to −30 °C. Into the solution was added dropwise a THF solution (5 cm^3) of 2-methyl-2-cyclohexen-1-one (0.55 g, 5.0 mmol) over 10 min. After stirred for 3 h, benzyl bromide (0.94 g, 5.5 mmol) was added, and the solution was warmed up gradually to r.t. After stirred for 14 h, the reaction mixture was quenched by the addition of sat NH_4Cl aq, extracted with ethyl ether, dried over $MgSO_4$, and the solvent was removed in vacuo. Purification by column chromatography (hexane : ether=4 : 1) gave **21** (0.29 g, 27%) as a single isomer. ^1H NMR δ=0.97 (s, 3H), 0.99 (d, J=6.6 Hz, 3H), 1.5—2.1 (m, 5H), 2.1—2.5 (m, 2H), 2.56 and 3.22 (each d, J=13.2 Hz, 2H), and 7.06 (s, 5H); ^{13}C NMR δ=15.81, 19.45, 23.12, 28.80, 36.92, 38.38, 41.66, 53.58, 125.90, 127.73, 130.29, 138.19, and 214.95; MS *m/z* 216 (M^+) 159, 145, 91, 55, and 41. Exact mass: Found: *m/z* 216.1512. Calcd for $C_{15}H_{20}O$: M, 216.1514.

***r*-2-Benzyl-2,*c*-3-dimethylcyclohexanone (22):** The MS spectrum was identical with that of **21**.

2-Methyl-2-(α-methylphenethyl)cyclopentanone (24) : The compound was identical with the major fraction of the authentic sample prepared from 2-ethylidencyclopentanone[30] (0.90 g, 8.18 mmol) and benzyl cuprate (8.24 mmol), followed by quenching with methyl iodide (1.78 g, 12.5 mmol) in the same way as described above. The product obtained after the column chromatography (hexane : ether=4 : 1, 91.9 mg, combined yield, 5.2%) showed two peaks on GC (3:2). ^1H NMR (diastereomer mixture) δ=0.75 (br. d, J=6.0 Hz, 3H×2/5), 0.65 (br.d, J=6.0 Hz, 3H×3/5), 0.95 (s, 3H×3/5), 1.03 (s, 3H×2/5), 1.43—3.22 (br.t, J=10 Hz, 9H), and 7.07 (s, 5H); ^{13}C NMR δ=[13.54*, 14.40], 18.697, [21.33*, 20.84], [31.91*, 32.13], [38.84*, 39.35], [40.41*, 39.86], [52.81*, 51.64], 125.753, 128.058, 129.082, 141.010, and [223.04*, 222.66];[31] MS *m/z* 216 (M^+) 159, 145, 125, 115, 98, 91, 83, 69, 65, 55, and 41. Exact mass: Found: *m/z* 216.1512. Calcd for $C_{15}H_{20}O$: M, 216.1514.

Reaction of 25 with $TiCl_4$ The reaction of **25** (0.14 g, 0.43 mmol) and $TiCl_4$ (0.16 g, 0.86 mmol) in CH_2Cl_2 (5 cm^3) at 0 °C 1.5 h afforded **28** as an unsatable compound. ^1H NMR δ=1.67 (s, 6H), 1.8—2.5 (m, 7H). The product afforded **29**[32] readily by stirring with sat. $NaHCO_3$ aq (5 cm^3) for 2 h (43.0 mg, 80%).

Reaction of 25 with TMSOTf. The reaction of **25** (0.26 g, 0.65 mmol) and TMSOTf (0.166 g, 0.65 mmol) in CH_2Cl_2 (7 cm^3) at 0 °C for 3 h gave **29** (68.8 mg, 85%).

Reaction of 30 with $TiCl_4$ The reaction of **30** (0.22 g, 0.65 mmol) and $TiCl_4$ (0.124 g, 0.66 mmol) in CH_2Cl_2 (5 cm^3) at 0 °C for 4 h gave **32** (52.3 mg, 46%). ^1H NMR δ=1.08 (s, 3H), 1.18 (s, 3H), 1.48 (s, 3H), and 1.6—2.5 (m, 6H); MS *m/z* 176 (M^++2), 174 (M^+), 139, 138, 124, 110, 96 (base), 83, 69, and 55; IR 2944, 1713, 1458, 1390, 1314, 1280, 1134, 1072, and 788 cm^{-1}. Exact mass: Found: *m/z* 174.0851. Calcd for $C_9H_{15}ClO$: M, 174.0812.

[#] 1M=1 mol dm^{-3}.

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