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THE REACTION OF TRIALKYLSTANNYLMETHYLLITHIUM WITH α,β-EPOXY KETONES AND α-CHLORO KETONES[1]

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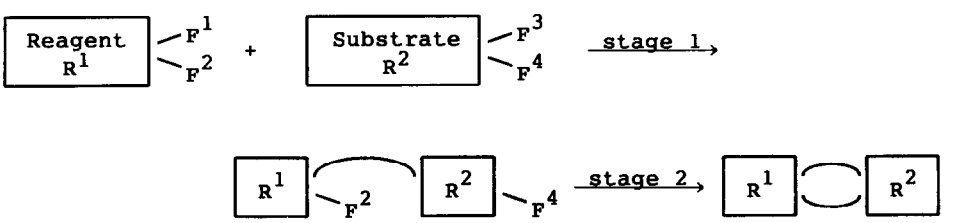
The reactions of trialkylstannylmethyllithium with α,β-epoxy ketones afforded mainly cyclopropanols, while α-chloro ketones afforded allyl alcohols and/or cyclopropanols, in varying amounts depending upon the molar ratio of the reagent to the substrate.

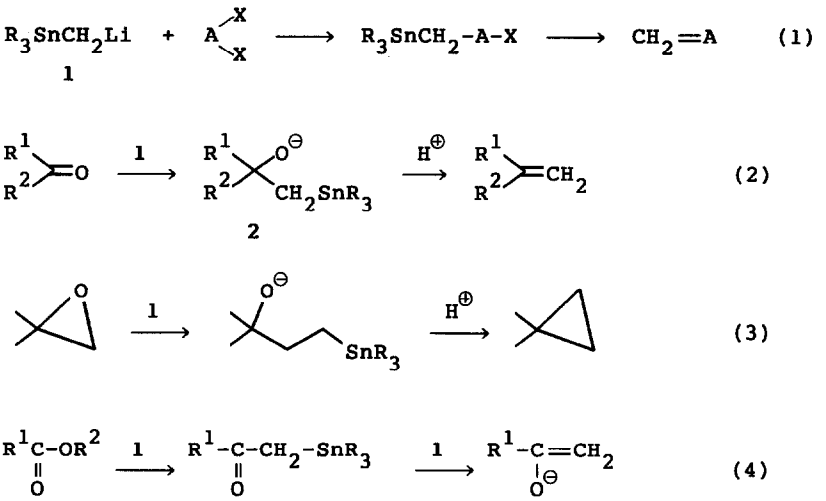
In the recent review,[2] we characterized trialkylstannylmethyllithium **1** as a reagent having multifunctioning property. The characteristic point is that the reagent can be represented as the one having two functionalities F^1 (C–Li) and F^2 (C–Sn), and reacts with the substrate having two functionalities F^3 and F^4 in two consecutive stages as shown in Scheme 1. Although both F^1 and F^2 behave as carbanion due to the electropositive character of the metal atoms as compared with carbon atom, the reactivity of F^1 is far greater than that of F^2 due to the weak polarity of the carbon–tin bond as compared with that of the carbon–lithium bond. Therefore, no obvious interference of F^2 is involved during the reaction of F^1 with F^3, thus allowing us to choose a wide variety of functionalities for F^3 and F^4 in the substrates. Furthermore, the mode of the second stage reaction can be diversified by introducing an auxiliary functional group in the



Scheme 1

substrate, which could modify the reaction between F^2 and F^4, thus furnishing the reagent with multifunctioning property.

In our previous paper,[3] we reported the reaction of trialkylstannylmethyllithium **1** with several electrophiles: the synthetic utility has been shown in the preparation of α-olefins from carbonyl compounds (eq 2), cyclopropanes from oxiranes (eq 3), and enolates from esters (eq 4). Since each of the functional groups in the starting materials (carbonyl, oxirane, or ester) are assumed to contain two leaving functions in a



(1)

(2)

(3)

(4)

single group, these reactions could be depicted as replacing two C–X bonds with methylene group. Evidently, as shown in eq 1, the reagent **1** could be viewed as methylene double anion equivalent **3**, having one explicit carbanion and one latent carbanion characters.

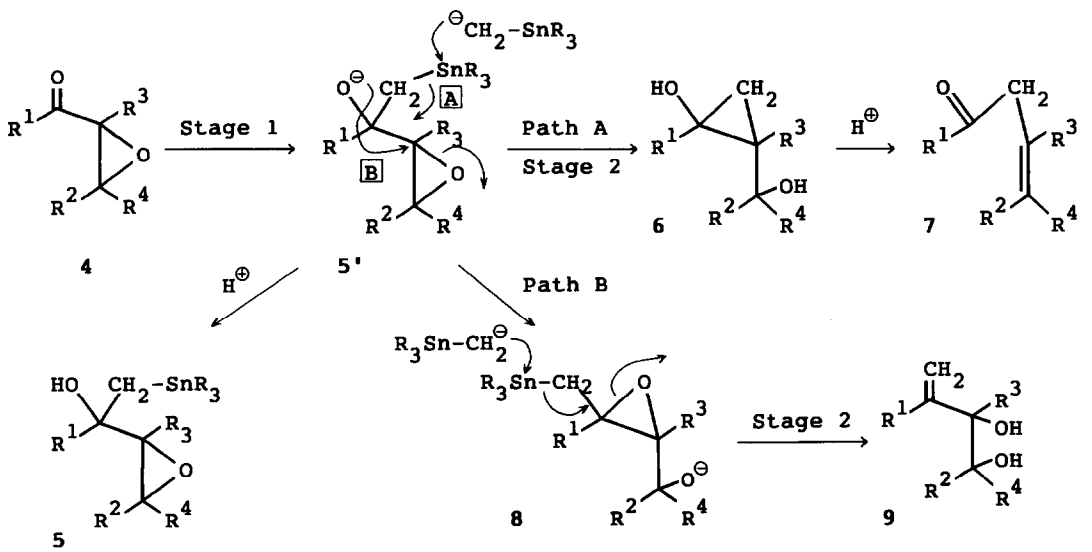
In the reaction with carbonyl compounds (eq 2), the anionic oxygen in the intermediate **2** has no leaving ability under basic conditions, and hence, it does not function as F^4 until it has been protonated. With an expectation that the presence of an independent leaving group as an auxiliary group might influence the overall reaction pattern, we investigated the reaction of α,β-epoxy ketones and α-chloro ketones with the reagent **1**. In these cases, the epoxy oxygen or chlorine atom could serve as a good leaving group.

Epoxy ketones **4a–4c** and **4g–4l** in Table 1 were prepared from the corresponding

α,β-enones by treating with hydrogen peroxide and sodium hydroxide (Method A). Epoxy ketones **4d**, **4e**, **4f** were prepared from the corresponding allyl alcohols by treating with t-butyl hydroperoxide to give epoxy alcohols, followed by CrO_3 or Swern oxidation (Method B). It has been well known that the cis,trans structure of the epoxy ketones is controlled thermodynamically to afford the more stable product with the Method A, while it corresponds to the E,Z-geometry of the double bond of the starting allyl alcohols with the latter method. In runs a–e, the epoxy ketones were trans isomer, while the epoxy ketones in run f and run l were cis,trans mixtures. The epoxy ketone in run j was a single isomer, with 5-methyl group in trans position to the oxirane ring.

The following conditions were used for the reaction of epoxy ketones with the reagent **1**, the preparative method of the reagent and the reaction conditions being shown. Condition I : $Me_3SnCH_2SnMe_3$ + n-BuLi (or MeLi) (each, two equivalents) at −78 to 0 °C; Condition II : $(n\text{-}Bu)_3SnCH_2I$ + n-BuLi (each, two equivalents) at −78 to 0 °C; Condition III :same as Condition I, but only one equivalent of the reagent was used; Condition IV : same as Condition I, but the whole reaction was carried out at −78 °C.

Under the Conditions I, III, and IV, part of the methyl groups on the tin atom are replaced by n-butyl group when n-butyllithium was used as a base.[1] In case the isolation

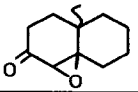


Scheme 2

of the tin-containing compounds is intended, therefore, methyllithium was used, instead of n-butyllithium.

When acyclic α,β-epoxy ketones **4a–4f** were reacted with trimethylstannyl reagent **1** under the Condition I, cyclopropanols **6** were obtained as major product (Scheme 2 and Table 1). The structures of **6** were confirmed by spectroscopic evidence and by deriving them to β,γ-enones **7**.[4] The reaction leading to **7** will be described in detail in the later part of the present paper. We schemed the reaction as shown in Scheme 2; firstly the reagent **1** attacked the carbonyl group (stage 1) to produce **5'**, and secondly, another

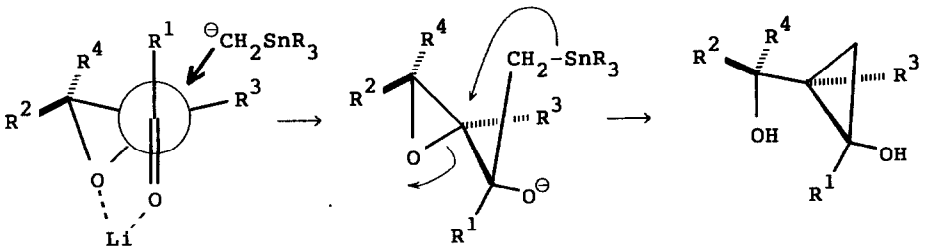
Table 1. Reaction of **1** with α,β-Epoxy Ketones.

Run	4				Cond	Yield (%)			Yield(%) of 7 from 6
	R^1	R^2	R^3	R^4		5[a]	6	9	
a	Me	Me	H	Me	I	0	51	0	98
b	Me	H	H	C_3H_7	I	0	75	0	80
c	Me	H	H	Ph	I	0	16	0	94
d	Me	H	Me	Et	I	0	83[b]	0	89
e	Me	H	Et	Me	I				c)
f	Me	$Me_2C{=}CH(CH_2)_2$-	H	Me[d]	I	0	75[e]	0	
g		$-(CH_2)_3-$	H	H	I	0	24[f]	0	
h		$-(CH_2)_3-$	Me	H	I	57	0	0	
i		$-(CH_2)_3-$	H	Me	I	0	40	0	80
					II	53	0	0	
					III	23	0	0	
j	$-CH_2CH(Me)CH_2-$		H	Me	I	tr	39	0	83
					II	38	0	0	
					III	44	0	0	
k	$-CH_2C(Me)_2CH_2-$		H	Me	I	0	20	50	
					II	0	6	61	
					III	46	0	0	
					IV	50	0	0	
l					I	0	24	0	

a) R = n-Bu (Condition II), R = Me (Conditions III and IV).
b) Diastereomer mixture (1 : 1.2). c) See Table 3. d) cis,trans-mixture. e) Two diastereomers; see text. f) Very unstable.

molecule of 1 attacked the tin atom of 5' enhancing the nucleophilicity of the neighboring carbon to produce 6 through 1,3-elimination (Stage 2, Path A). The formation of bis(trimethylstannyl)methane was confirmed by NMR analysis of the crude reaction mixture.

The epoxy ketones in which R^3 is hydrogen (4a–4c) gave 6 as a single stereoisomer, while that having alkyl group at this position (4d) gave a 1 : 1.2 mixture of two diastereomers. Although most of the protons in the products were assignable with 400 MHz ^{1}H-NMR, the exact assignment of the stereochemistry was not attained from these data. Unambiguous stereostructures were not obtained from NOE experiment either. Therefore, we assigned the structures by making a couple of assumptions as follows. Since it has been known that the nucleophilic attack at the carbonyl group of α,β-epoxy ketones proceeds with high stereoselectivity via cyclic model,[5] we schemed the reaction as shown in Scheme 3. The loss of the selectivity in case of run d could be an evidence for the model, because the α-alkyl group (R^3) might reduce the diastereofacial selection during the attack of the reagent to the carbonyl group. It could thus be concluded that the diastereoisomerism in run d concerns with the cis,trans substitution pattern on the cyclopropane ring. In case of run f, where the reaction was carried out with a cis,trans

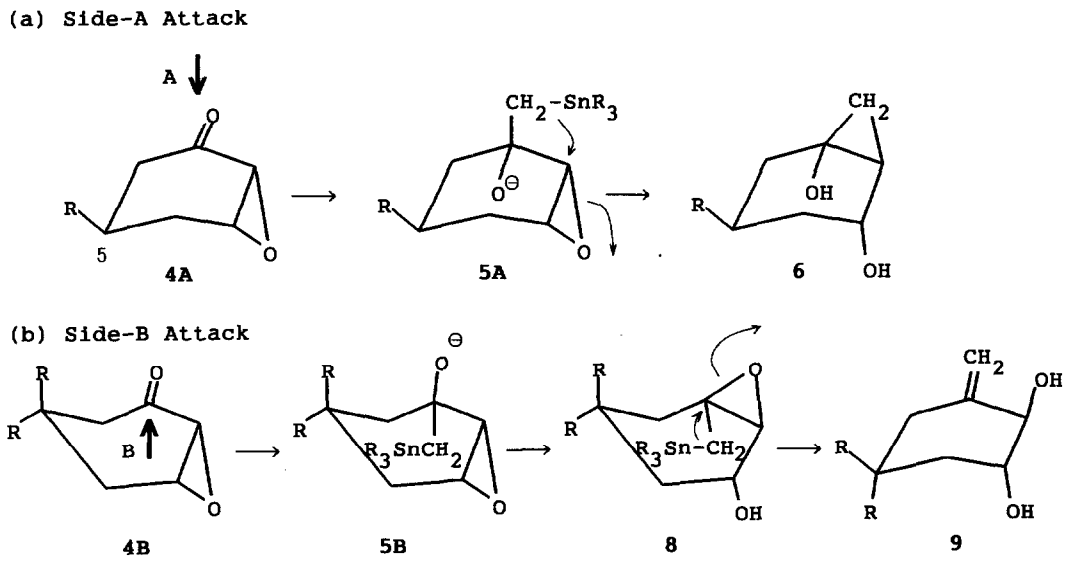


Scheme 3

mixture of 4f, 6 was obtained as a mixture of two diasteromers. Notably the diastereomeric ratios of 6 were exactly same as the cis,trans ratios of 4 in the range of 2 : 1 to 1 : 5. In view of these observations, we concluded that the reaction itself is stereoselective in run f, and the diastereoisomerism concerns with the different configuration of the carbinol carbon in the side chain.

The reaction with cyclic system **4g–4l** was studied next. The substrates **4g**, **4i**, **4j**, and **4l** gave only the corresponding cyclopropanols **6** as products, while **4k** having two methyl groups at 5-position gave a methylene 1,2-diol **9k** as a major product, as well as a minor product of **6k**.

Remarkably, all the products were also stereochemically pure in referring to the ^{1}H-(400 MHz) and ^{13}C-NMR spectra, and the stereochemistry was assigned by assuming a reaction route shown in Scheme 4. The reagent **1** could attack the carbonyl group from the side either opposite (side-A) or same (side-B) to the oxirane ring. Apparently from the stereochemical requirement, the side-A attack would give cyclopropanols **6** as above, while the side-B attack would give methylene 1,2-diols **9** through 1,2-elimination of the intermediate epoxy stannane **8**. Thus, the most plausible stereostructures of the products could be assigned as shown. In view of the fact that the formation of **6** was generally a major reaction pathway, it seems that the side-A attack is preferable. The situation does not change very much upon introducing one methyl group in the trans position at C5 (**4j**), because the methyl group could occupy a pseudoequatorial position as shown in **4A**. However, the introduction of another methyl group to the same carbon (**4k**) might force the



Scheme 4

conformation to take the form of 4B, thus favoring the side-B attack leading to 9. Although 4l was a diastereomeric mixture, only one stereoisomer 6l was identified in the product, but further investigation on the stereochemistry was not pursued.

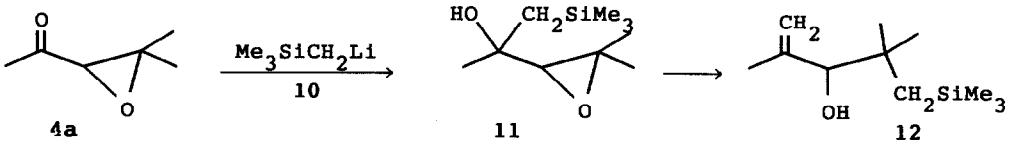
Although the stage 2 reaction was generally induced smoothly by the second molecule of the reagent 1 in one pot, the reaction of 4h terminated at the stage 1 affording 5h. This is probably because of the steric hindrance of the 2-methyl group (R^3) for the cyclization. It seems that the difference in the reactivities of the stage 1 and stage 2 is large, and some intermediate tin compounds 5 were isolated when only one equivalent of the reagent was used (Condition III), or the reaction was carried out at −78 °C (Condition IV). The stage 2 reaction was also induced by treating the isolated stannyl alcohol 5 with a base such as n-Butyllithium.

When tributylstannyl reagent 1 was used (Condition II) with 4i and 4j, the reaction also terminated at the stage 1 to give 5i and 5j (both with Bu_3Sn group), respectively. However, with 4k, the stage 2 reaction proceeded along Path B even under the Condition II to give 9k. Apparently the reactivity is diminished with tributystannyl reagent, particularly for the 1,3-elimination (Path A), while the 1,2-elimination still proceeds readily in the tributylstannyl compound.

It was also found that ^{1}H-NMR spectrum of 5i (with Me_3Sn group) obtained under the Condition III showed only one set of signals for methyl and hydrogen atom on the oxirane ring at δ 1.29 and 2.71, respectively, while the spectrum of 5k (with Me_3Sn group) showed two sets of signals for these protons, as well as for those of geminal methyl groups. Evidently 5i is a single isomer, while 5k is a mixture of diastereomers. Reasonably, upon further treatment under Condition I, 5i gave 6i in 44% yield, while 5k gave 6k and 9k in 21% and 41% yields, respectively. The stannyl compound 5h did not react under the same conditions. Upon treatment with trifluoroborane-etherate, 5k gave vinyl oxirane 21k.

With a view to compare the reactivities of the stannyl reagent 1 with those of the corresponding silyl compound, the reaction of trimethylsilylmethyllithium[6] 10 with 4a was investigated. When the reaction was carried out at −78 °C, only one equivalent of the reagent was consumed to produce an epoxy silane 11, even when excess amount of the reagent was used. Only when the reaction was carried out at room temperature for 2 h, the second molecule of the reagent reacted to produce a vinyl silane 12 in 31% yield, along with 39% of 11. Evidently, the reactivity for the stage 2 reaction is greatly

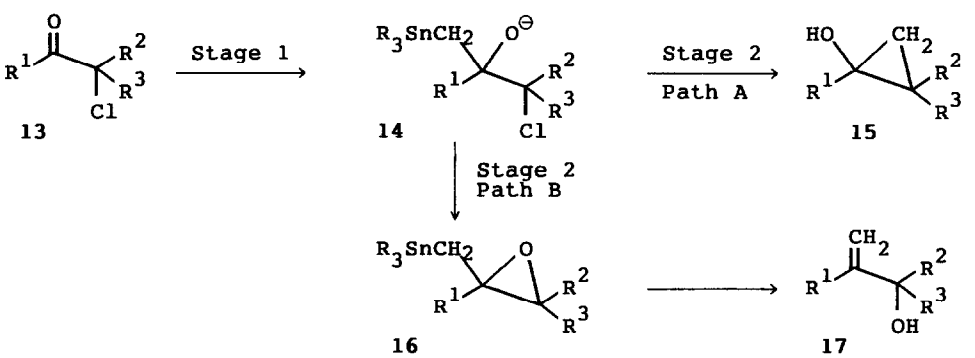
diminished with the silyl reagent, and, if the reaction proceeds at all, the reagent attacks the oxirane ring rather than silicon atom of 11, in contrast to the case of the



stannyl counterpart. It has been reported that silyl or phosphoryl carbanions react with α,β-epoxy ketones to afford vinyl oxiranes 21, which might be produced through an intermediate corresponding to 11.[7]

In contrast to the almost exclusive cyclopropanol formation from the epoxy ketones, a different situation was observed with α-chloro ketones. Although we described the exclusive formation of allyl alcohols 17 from α-chloro ketones 13 in our preliminary report,[1b] we found now that cyclopropanols 15 were also produced depending upon the types of the substrates and molar ratio of the reagent used (Scheme 5).

As shown in Table 2, 17 were the major product in acyclic system (runs m–r), when one equivalent of the reagent was used (Condition III), while 15 were also produced when two equivalents of the reagent were applied (Condition I). The general trend is that the cyclopropanol formation is the more facilitated with compounds having the less sub-



Scheme 5

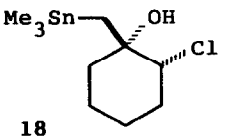
stituents on the chlorine-bearing carbon. In cyclic system (run s), the products from 13s with one equivalent of the reagent were tin-containing compound 18 in 39% yield, as well as 15s in 15% yield. However, the reaction with two equivalents of the reagent gave 15s as a sole product in 75% yield.

The results could be rationalized by assuming a reaction route shown in Scheme 5, which is quite similar to that of epoxy ketones (Scheme 2). It seems that the superficial difference between the reactions of epoxy ketones and chloro ketones originates from the different reactivities of the primary intermediates 5 and 14. Unless any stereochemical environment causes otherwise, the oxirane formation along Path B proceeds spontaneously from 14, while the intermediates 5 from the epoxy ketones are stable. The intermediates 5 react only with the assistance of the second molecule of the reagent 1, but the reaction, under these conditions, proceeds along Path A producing cyclopropanol 6. The cyclopropanation from 14 is also induced in the presence of excess

Table 2. Reaction of 1 with α-Chloro Ketones.

Run	13			Condition	Yield (%)	
	R^1	R^2	R^3		15	17
m	Ph	H	H	III	0	67
				I	58	11
n	Ph	Me	H	III	0	70
				I	23[a]	50
o	Ph	Me	Me	III	0	82
				I	0	83
p	C_6H_{13}	H	H	III	0	71
				I	54	9
q	Me	C_5H_{11}	H	III[b]	0[a]	58
				I	26	31
r	C_4H_9	C_3H_7	H	III	0	80
s	$-(CH_2)_4-$		H	III[c]	15	0
				I	75	0

a) Stereochemistry was not examined. b) Not separated.

c) 

39%

18

amount of the reagent **1**, but it competes with the oxirane formation, thus giving the product as a mixture of **15** and **17**. In cyclic system, the first molecule of the reagent **1** attacked the carbonyl carbon from the side opposite to the chlorine atom to give **18**, which was incapable of cyclizing to **16**, due to the steric requirement.

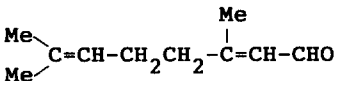
The present reaction proceeds most satisfactorily with α-chloro ketones. With α-bromo ketones, the major reaction is the reductive elimination of bromine atom, as revealed by the reaction of 2-bromo-1-phenyl-1-propanone with **1**, which gave 1-phenyl-1-propanone in 60% yield, accompanied by allyl alcohol **17n** in only 32% yield.

It has been reported that α-chloro ketones undergo complicated reaction with Wittig reagent.[8] While the epoxy stannane **16** was not detected, it has been proposed as an intermediate in the allyl alcohol formation from allyl stannane by m-chloroperoxybenzoic acid oxidation.[9] The formation of cyclopropanols from α-halo ketones using samarium reagent was reported,[10] where the reaction has been schemed as involving radical species resulted from electron transfer.

When the cyclopropanols **6** were treated with trifluoroborane-etherate or hydrochloric acid, β,γ-enones **7** were obtained in good yields as shown in Table 1. Notably the reaction proceeded without any formation of α,β-enones. It was also found that the acidic treatment of the reaction mixture of **1** and **4** gave **7** directly in fair yields in one pot. Since cyclopropylcarbinyl rearrangement has been widely documented,[11] we focused our attention on the stereochemical correlation between **4** and **7**. In order to prepare the epoxy ketone **4f** of definite cis,trans structure by the Method B, we tried to isolate the respective enals **19** in pure states. Although trans-**19** (geranial) was isolated in almost pure state by the known method,[12] the enrichment of cis-isomer (neral) was not accomplished above 2 : 1 ratio. Therefore the preparation of cis-epoxy ketone was undertaken starting from the cis-rich enal, and the final product **4f** was isolated as a cis-rich mixture (22 : 1) by a column chromatography at the last stage.

The product **7b** was identical with the authentic sample prepared by the known method.[13] The (E)-geometry was assigned for **7c**, since it is known that the (Z)-enone isomerizes easily to (E)-isomer upon standing, and the reported data for the (Z)-isomer did not coincide with our product.[14] Both (E) and (Z)-isomers were obtained for **7e**, whose geometry of the double bond was determined by comparing the NMR data with those reported.[15] Both (E) and (Z)-isomers were also obtained in run f. Although they were not separated, they were discernible on GLC analysis, and we concluded that the fraction

having shorter retention time on GLC as having (E)-geometry, because it was identical with the sample prepared from (E)-acid **20** by the reaction with the reagent **1** on its



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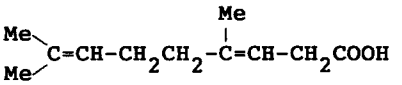

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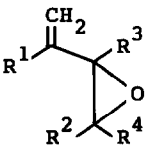

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ester.[3] The fraction having longer retention time was, therefore, assigned as (Z)-isomer. The NMR spectrum of the mixture was identical with that of the (E)-isomer. Mass spectra of both fractions were almost identical. The E,Z ratio determined from GLC analysis and yields are shown in Table 3.

The results in the Table 3 are characteristic in the following points : (1) All the products **7** from **4b–4d** were exclusively (E)-isomer, irrespective of whether the intermediate **6** is a single isomer (runs b and c) or a cis,trans mixture (run d). (2) The poduct **7** from **4d** was only (E)-isomer, while that from **4e** was an E,Z mixture, despite the similar substitution pattern on the double bond in both cases. (3) The product **7** from cis-**4f** was only (E)-isomer, while that from trans-**4f** was an E,Z mixture. These points

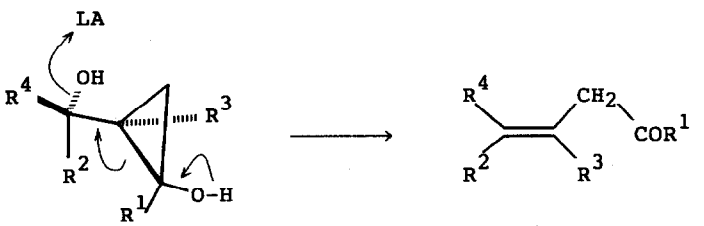
Table 3 Stereochemical Relationship Between the Starting Epoxy Ketones and the Product β,γ-Enones.

Epoxy Ketone	trans:cis	β,γ-Enone	E : Z	Yield(%)
4a	-	**7a**	-	78
4b	1 : 0	**7b**	1 : 0	76
4c	1 : 0	**7c**	1 : 0	94[a)]
4d	1 : 0	**7d**	1 : 0	64
4e	1 : 0	**7e**	7 : 3	76
4f	1 : 0	**7f**	1 : 1	75
4f	1 : 22	**7f**	1 : 0	68

a) From **6c**.

could be interpreted most satisfactorily as follows.

If we assume that the formation of 7 proceeds in concerted way from the cyclopropanol intermediate 22, which was formed from 4 through the reaction sequence shown in Scheme 3, the products from trans-epoxy ketones should be (Z)-β,γ-enones (R^4 is superior to R^2), as shown in Scheme 7. Evidently the present results are not consistent with this scheme, and so we thought that the reaction from trans-epoxy ketones proceeded in stepwise manner, involving cationic species to produce more stable isomer. Probably the steric repulsion between R^4 and cyclopropane ring inhibits the cyclopropanol to take the conformation 22, which is favorable for the concerted process. In case the reaction proceeds stepwise, the E,Z ratios of the enones would be determined by the relative stability of the products. Expectedly, the stability difference between E,Z geometry is



22 7

Scheme 7

large with disubstituted olefins (7b and 7c), which would give (E)-isomer selectively. On the other hand, the difference would be smaller with trisubstituted compounds (7d, 7e, and 7f), and the isomer ratio would be quite sensitive to the minor effects of the alkyl groups, and range from 1 : 0 with 7d to 7 : 3 with 7e, and finally to 1 : 1 with 7f. In case of the cyclopropanol from cis-epoxy ketone 4f, however, the R^4 group is smaller, thus favoring the concerted reaction from 22 producing only (E)-enones 7f. Similar interpretation has been submitted in other cases.[16]

Since α,β-epoxy ketones can be prepared easily from the corresponding α,β-enones, the present reaction could be a convenient method for the preparation of β,γ-enones by inserting methylene group between olefinic and carbonyl groups of the α,β-enones. We can prepare seven-membered ring system quite easily by this method. The present cyclopropanol formation is complementary to that via Simmons-Smith reaction upon enol ethers.[17]

Experimental Section

General. GLC experiments were carried out on a 2.5 m × 3 mm stainless steel column packed with silicon SE 30 or Carbowax 20 M on silanized Chromosorb W. Preparative TLC was carried out on DC-Alufolien Kieselgel 60 F_{254}, Art. 5554, using solvents as indicated. 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 a pure sample obtained by either distillation, preparative TLC, or column chromatography. Due to the unavailability of enough amounts of pure sample, elemental analyses of **6b**, **6j**, **6l**, and **9k** indicatated errors of 0.4–0.9% in carbon, but the purities and the structures were guaranteed by either ^{1}H, ^{13}C-NMR, TLC, and/or GLC analyses even with these compounds. Exact masses could not be determined either with these compounds, because of the lack of parent peaks on mass spectra. All products except those with melting point description are oil. ^{1}H-NMR spectra (60 MHz) were recorded on a Hitachi R-24 or JEOL PMX 60 SI spectrometer. ^{1}H-NMR (90 MHz) and ^{13}C-NMR (22.5 MHz) spectra were measured on a Hitachi JNM-PMX 60S R-90 H spectrometer, and ^{1}H-NMR (400 MHz) spectra on a JEOL GSX-400 spectrometer. Unless otherwise stated, the data shown below are those obtained on the 60 MHz machines with CCl_4 or $CDCl_3$ solutions using TMS as an internal reference. With tin-containing compounds, $CHCl_3$ or CH_2Cl_2 was used as a reference. All of the ^{1}H-NMR signal of the methyl group on tin atom at $\delta \sim 0$ ppm accompanied splitting signals by ^{117}Sn (7.54% abundance, J = 51 Hz) and ^{119}Sn (8.62% abundance, J = 53 Hz). GC-MS spectra were taken on a Shimadzu QP-1000 mass spectrometer, and high resolution mass spectra on a JEOL DX-300 mass spectrometer. IR spectra were recorded on a Shimadzu IR-400 spectrometer.

Bis(trimethylstannyl)methane was prepared as follows, by modifying the reported procedure.[18] To 60.3 g (0.225 mol) of CH_2I_2 in a four-mouth flask, 125.4 g (0.4 mol) of $SnBr_2$ and 1.5 ml of Et_3Sb (Et_3Sb can be replaced by Et_3N) were alternatively added in three portions, making sure that the reactants are thoroughly mixed. The mixture was heated under nitrogen atmosphere at 140 °C for 15 h, and then, methyl Grignard solution, prepared from 281 g of CH_3I and 43.8 g of Mg in 450 ml of diethyl ether was added. The solution was refluxed for 1 h, poured onto crashed ice, and acidified with HCl. The product was extracted with hexane, washed with NaCl aqueous solution, and dried over Na_2SO_4. The product was purified by distillation to give 40.5 g (53%) of pure sample. bp 80 °C/16 mmHg.

(Trimethylsilyl)(tributylstannyl)methane was prepared according to the reported method.[6b]

Starting Materials. The following epoxy ketones were prepared from the corresponding α,β-enones with H_2O_2 and NaOH according to the method reported for the preparation of **4k**.[19] **3,4-Epoxy-4-methyl-2-pentanone (4a)**, bp 71–73 °C/27 mmHg, Lit,[20] bp 61–62 °C/20 mmHg.; **trans-3,4-Epoxy-2-heptanone (4b)**, bp 77–78 °C/14 mmHg. Lit,[21] bp 54.5–55 °C/5 mmHg. **trans-3,4-Epoxy-4-phenyl-2-butanone (4c)**, bp 89.5–90 °C/0.8 mmHg, mp 52–53 °C. Lit,[22] mp 52–53 °C, mp 54–54.5 °C.[23] **2,3-Epoxy-1-cyclohexanone (4g)**, purified by Kugelrohr distillation. Lit,[24] bp 70 °C/9 mmHg. **2,3-Epoxy-2-methyl-1-cyclohexanone (4h)**, bp 73–74 °C/13 mmHg. **2,3-Epoxy-3-methyl-1-cyclohexanone (4i)**, bp 95–97 °C/28 mmHg. **2,3-Epoxy-3r,5c-dimethyl-1-cyclohexanone (4j)**, Lit,[24] bp 65 °C/5 mmHg. **2,3-Epoxy-3,5,5-trimethyl-1-cyclohexanone (4k)**, bp, 70–70.5 °C/5 mmHg, Lit,[19] bp 70–73 °C/5 mmHg. **1,8a-Epoxy-4a-methyl-3,4,4a,5,6,7,8,8a-octahydro-2(1H)-naphthalenone (4l)**, purified by a column chromatography (hexane : ether = 8 : 1). In view of two pairs of singlets of methyl and oxirane protons, the product must be a mixture (6 : 4) of two diastereomers. ^{1}H-NMR, δ 1.12 and 1.22 (two singlets, 3H), 1.48–2.45 (m, 12 H), 2.80 and 2.90 (two singlets, 1H).

The epoxy ketones **4d**, **4e**, and **4f** were prepared from the corresponding α,β-enals by a sequence of reactions (1) with methyl Grignard reagent to allyl alcohols, (2) epoxidation with t-butyl hydroperoxide or mCPBA to α,β-epoxy alcohols, and (3) CrO_3 or Swern oxidation to the α,β-epoxy ketones. Typical procedures are given below for the preparation of **trans-4f**.

(E)-4,8-Dimethyl-3,7-nonadien-2-ol. Commercial citral was purified by deriving to the bisulfite adduct in accordance with the known method[12] to afford (E)-rich aldehyde (E : Z = 95 : 1, on GLC). To a Grignard solution prepared from methyl iodide (2.58 g, 18.2 mmol) in ether (18 ml) was added a solution of (E)-rich aldehyde obtained above (2.123 g, 13.9 mmol) in ether (3 ml), and refluxed for 30 min. The mixture was quenched with NH_4Cl aqueous solution, and distillation under reduced pressure gave (E)-rich dienol (1.585 g, 67.8%, E : Z = 95 : 1 on GLC). bp 60–64 °C/0.5 mmHg. ^{1}H-NMR, δ 1.20 (d, J = 8 Hz, 3H), 1.60 (s, 3H), 1.65 (s, 6H), 2.00 (br.s, 4H), 3,10 (br.s, 1H), 4.30 (q, J = 8Hz, 1H), 4.8–5.2 (m, 2H).

trans-3,4-Epoxy-4,8-dimethyl-7-nonen-2-ol. To a solution of $VO(acac)_2$ (40 mg, 0.144 mmol) in benzene (18 ml) was added (E)-4,8-dimethyl-3,7-nonadien-2-ol obtained above

(1.585 g, 9.42 mmol). While heating the solution under reflux, an aqueous solution (70%) of t-butyl hydroperoxide (1.500 g, 11.7 mmol) was added during the period of 20 min, and refluxed for another 4 h. The reaction mixture was poured into saturated NaCl aqueous solution, and extracted with ether. The product was purified on a column (AcOEt : hexane = 2 : 3) to give 1.546 g (90%) of pure sample. ^{1}H-NMR, δ 1.20 (s, 3H), 1.55 (s, 3H), 1.60 (s, 3H), 1.8–2.2 (m, 4H), 2.50 (d, J = 8Hz, 1H), 3.20 (br.s, 1H), 3.40 (br, 1H), 5.00 (t, J = 8Hz, 1H).

trans-3,4-Epoxy-4,8-dimethyl-7-nonen-2-one (trans-4f). To a cooled (0 ^{o}C) solution of N-chlorosuccinimide (1.2 g, 9.0 mmol) in dry toluene (16 ml), was added dimethyl sulfide (0.97 g, 15.6 mmol), and cooled to −25 ^{o}C. A solution of trans-3,4-epoxy-4,8-dimethyl-7-nonen-2-ol obtained above (1.54 g, 8.5 mmol) in toluene (3 ml) was added during the period of 2 h at −25 ^{o}C. A solution of triethylamine (1.2 g, 12 mmol) in toluene (1 ml) was added, and the reaction mixture was warmed up to room temperature. After 5 min, the solution was poured into saturated NH_4Cl aqueous solution, and extracted with ether. The product was purified on a silica gel column (AcOEt : hexane = 2 : 3). A pure sample of **trans-4f** (512 mg) and a sample containing **cis-4f** (trans : cis = 5 : 1, on GLC) (373 mg) were obtained. For **trans-4f** : ^{1}H-NMR, δ 1.21 (s, 3H), 1.58 (s, 3H), 1.64 (s, 3H), 1.9–2.3 (m, 4H), 2.08 (s, 3H), 3.22 (s, 1H), 4.9–5.25 (m, 1H).

cis-3,4-Epoxy-4,8-dimethyl-7-nonen-2-one (cis-4f). While the separation of almost pure (E)-aldehyde (geranial) was accomplished by the method mentioned above, the enrichment of (Z)-isomer (neral) was not achieved above 2 : 1 ratio even after repeated separation of the bisulfite adducts. Therefore, cis,trans mixture of the epoxy ketone was prepared from the (Z)-rich aldehyde (2 : 1) through the same reaction sequence as mentioned above. The epoxy ketone (trans : cis = 1 : 22, on GLC) was obtained by purifying the mixture on a preparative TLC, which was used for the further reaction. For **cis-4f** : ^{1}H-NMR, δ 1.32 (s, 3H), 1.58 (s, 3H), 1.64 (s, 3H), 1.9–2.3 (m, 4H), 2.08 (s, 3H), 3.03 (s, 1H), 4.85–5.25 (m, 1H).

trans-3,4-Epoxy-3-methyl-2-hexanone (trans-4d). (E)-3-Methyl-3-hexen-2-ol was prepared from (E)-2-methyl-2-pentenal, obtained by aldol condensation of propanal, with methylmagnesium iodide. bp 71 ^{o}C/25 mmHg. ^{1}H-NMR, δ 0.95 (dist.t, 3H), 1.10 (d, J = 7 Hz, 3H), 1.55 (s, 3H), 1.65 (s, 1H), 1.90 (m, 2H), 4.00 (q, J = 7 Hz, 1H), 5.25 (t, J = 7 Hz, 1H). The allyl alcohol was epoxidized with t-butyl hydroperoxide/$VO(acac)_2$ in the same way as above to afford 3,4-epoxy-3-methyl-2-hexanol. bp 70.5–71 ^{o}C/18 mmHg.

^{1}H-NMR, δ 1.19 (t, J = 8 Hz, 3H), 1.25 (d, J = 7 Hz, 3H), 1.30 (s, 3H), 1.65 (m, 2H), 3.00 (t, J = 7 Hz, 1H), 3.70 (q, J = 7 Hz, 1H). Swern oxidation of the epoxy alcohol afforded **4d**. bp 88–93 ^{o}C/70 mmHg. MS, m/z 99 (M^+–Et), 85, 71, 43. ^{1}H-NMR, δ 1.07 (t, J = 8 Hz, 3H), 1.35 (s, 3H), 1.45–1.75 (m, 2H), 1.92 (s, 3H), 2.94 (t, J = 6 Hz, 1H). ^{13}C-NMR, δ 9.60, 11.5, 21.1, 22.4, 61.6, 62.9, 207.4.

trans-3,4-Epoxy-3-ethyl-2-pentanone (4e). (E)-3-Ethyl-3-penten-2-ol was prepared from a commercial (E)-2-ethyl-2-butenal. The product was almost pure without any purification. ^{1}H-NMR, δ 0.97 (t, J = 8 Hz, 3H), 1.15 (d, J = 6 Hz, 3H), 1.60 (d, J = 8 Hz, 3H), 2.03 (q, J = 8 Hz, 2H), 3.36 (bs, 1H), 4.05 (q, J = 6 Hz, 1H), 5.32 (q, J = 8 Hz, 1H). The allyl alcohol was epoxidized with t-butyl hydroperoxide/$VO(acac)_2$ to afford 3,4-epoxy-3-ethyl-2-pentanol. bp 90–95 ^{o}C/50 mmHg. ^{1}H-NMR, δ 0.98 (t, J = 7 Hz, 3H), 1.10 (d, J = 6 Hz, 3H), 1.26 (d, J = 6 Hz, 3H), 1.61 (q, J = 7 Hz, 2H), 2.30 (bs, 1H), 3.1 (q, J = 6 Hz, 1H), 3.87 (q, J = 6 Hz, 1H). Swern oxidation of the epoxy alcohol in the same way as above afforded **4e**. The product was purified on a column chromatography (Wako gel, C-200, $CHCl_3$). ^{1}H-NMR, δ 0.88 (t, J = 8 Hz, 3H), 1.28 (d, J = 5 Hz, 3H), 1.89 (s, 3H), 2.08 (q, J = 8 Hz, 2H), 3.09 (q, J = 5 Hz, 1H).

The following chloro ketones were prepared by the methods reported. **2-Chloro-2-methyl-1-phenyl-1-propanone (13o).**[25] **1-Chloro-2-octanone (13p).**[26] **3-Chloro-2-octanone (13q).**[27] **4-Chloro-5-nonanone (13r).**[28]

General Procedure for the Reaction of Epoxy Ketones 4 with 1. Condition I : To a THF solution of $Me_3SnCH_2SnMe_3$ (0.7 M, 2 eq) was added a hexane solution of n-BuLi (1.45 M, 2 eq) at –78 ^{o}C under N_2. After 10 min, a THF solution of the epoxy ketone 4 (0.7 M, 1 eq) was added dropwise, and the solution was allowed to warm up to room temperature during the period of 1 h. After the solution was stirred for another 2 h at room temp, it was cooled to 0 ^{o}C, and quenched with brine. The product was extracted with $CHCl_3$, and then with ethyl acetate. The products were purified on column chromatography, or by recrystallization if the products were solid. Condition II : same as Condition I, except that $(n\text{-}Bu)_3SnCH_2I$ and ether, instead of $Me_3SnCH_2SnMe_3$ and THF, respectively, were used. Condition III : same as Condition I, except that only one equivalent of the reagent was used. Condition IV : same as Condition I, except that the whole reaction was carried out at –78 ^{o}C for 3 h. Unless otherwise stated, the reaction was carried out under the Condition I. Due to the methyl/n-butyl exchange on tin atom (see text), MeLi was used as a base, instead of n-BuLi, when the isolation of tin-containing product such

as 5 was aimed under Conditions I, III, and IV.

From 3,4-Epoxy-4-methylpentan-2-one (4a). The solid obtained from **4a** (140 mg, 1.22 mmol) was recrystallized from hexane to give **6a** (81 mg, 51 %). mp 88.0–89.5 ^{o}C. IR, 3565, 3425 cm^{-1}. ^{1}H-NMR (400 MHz), δ 0.57 (dd, J = 7.3 and 5.2 Hz, 1H), 0.79 (dd, J = 10.7 and 5.2 Hz, 1H), 0.95 (br.s, 1H), 1.16 (dd, J = 10.7 and 7.3 Hz, 1H), 1.13 (s, 3H), 1.36 (s, 3H), 1.62 (s, 3H), 1.79 (br.s, 1H). ^{13}C-NMR, δ 14.6, 18.6, 26.9, 28.6, 32.7, 49.9, 62.5. Anal. Found, C, 64.60, H, 10.44. Calcd for $C_7H_{14}O_2$; C, 64.58 H, 10.84.

From 3,4-Epoxyheptan-2-one (4b). The product obtained from **4b** (140 mg, 1.09 mmol) was recrystallized from hexane to give **6b** (118 mg, 75%). mp 88.5–90.5 ^{o}C. ^{1}H-NMR (400 MHz,), δ 0.25 (t, J = 5.9 Hz, 1H), 0.91 (t, J = 7.3, 3H), 0.95 (dd, J = 10.3 and 5.9 Hz, 1H) 1.16 (dt, J = 10.3 and 5.9 Hz, 1H), 1.32–1.59 (m, 2H), 1.53 (s, 3H), 3.03 (dt, J = 10.3 and 6.4 Hz, 1H).

From 3,4-Epoxy-4-phenylbutan-2-one (4c). The solid obtained from **4c** (350 mg, 2.16 mmol) was recrystallized from CCl_4 to give **6c** (56 mg, 16 %). mp 120–122 ^{o}C. ^{1}H-NMR (d^6-acetone), δ 0.51 (dd, J = 11.5 and 5.8 Hz, 1H), 0.60 (dd, J = 10.8 and 5.8 Hz, 1H), 1.35 (ddd, J = 11.5, 10.8, and 10.7 Hz, 1H), 1.59 (s, 3H), 4.14 (d, J = 10.7 Hz, 1H).

From 3,4-Epoxy-3-methylhexan-2-one (4d). The oil obtained from **4d** (334 mg, 2.61 mmol) was separated into two diastereomers **6d$_1$** (170 mg, 45%) and **6d$_2$** (141 mg, 38%) on a column (Wako gel, AcOEt : hexane = 1 : 1). For **6d$_1$** : ^{1}H-NMR, δ 0.18 and 0.66 (ABq, J = 6 Hz, 2H), 0.93 (t, J = 8 Hz, 3H), 0.98 (s, 3H), 1.42 (s, 3H), 1.4–1.8 (m, 2H), 3,48 (t, J = 6 Hz, 1H), 3.81 (b, 2H). For **6d$_2$** : ^{1}H-NMR, δ 0.37 and 0.58 (ABq, J = 6 Hz, 2H), 0.94 (t, J = 8 Hz, 3H), 1.15 (s, 3H), 1.54 (s, 3H), 1.41–1.79 (m, 2H), 3.02 (t, J = 7 Hz, 1H), 3.00 (b, 2H). ^{13}C-NMR, δ 10.54, 10.83, 21.01, 24.73, 27.35, 29.46, 57.94, 77.63.

From 3,4-Epoxy-4,8-dimethyl-7-nonen-2-one (4f). The product obtained from **4f** (trans : cis = 2 : 1, 132 mg, 0.73 mmol) gave a mixture of two diastereomers (108 mg, 75%) in 2 : 1 ratio. The separation was not accomplished. ^{1}H-NMR, δ 0.4–1.1 (m, 3H), 1.12 and 1.20 (two singlets, 1 : 2, 3H), 1.45 (s, 3H), 1.55 (s, 3H), 1.60 (s, 3H), 1.8–2.3 (m, 4H), 2.9 (bs, 2H), 5.00 (bt, 1H). The relative intensity of the signals at δ 1.12 and 1.20 corresponded to the cis,trans ratio of **4f**.

From 2,3-Epoxycyclohexan-1-one (4g). The oil obtained from **4g** (105 mg, 0.94 mmol) was purified on column chromatography to give **6g** (28.4 mg, 24%). The product was unstable at room temperature. ^{1}H-NMR (400 MHz), δ 0.29 (t, J = 5.9 Hz, 1H), 0.92 (ddd, J = 11.2, 5.9, and 1.5 Hz, 1H), 1.2–2.2 (m, 10H), 1.71 (br. 2H), 3.86 (ddd, J = 7.3, 4.9,

and 1.0 Hz, 1H).

From 2,3-Epoxy-2-methylcyclohexan-1-one (4h). The reaction was carried out using MeLi under the Condition I, because the use of n-BuLi might complicate the product, due to the replacement of methyl group on the tin atom with butyl group.[1] The oil obtained from **4h** (132 mg, 1 mmol) was purified on a column ($AcOEt/CHCl_3$) to afford a tin-containing compound **5h** (175 mg, 57%). ^{1}H-NMR, δ 0.05 (s, 9H), 0.8–2.2 (m, 6H), 1.22 (s, 2H), 1.28 (s, 3H), 2.90 (m, 1H).

From 2,3-Epoxy-3-methylcyclohexan-1-one (4i). The solid obtained from **4i** (126 mg, 1 mmol) was recrystallized from hexane to give **6i** (57 mg, 40 %). mp 104–105 °C. ^{1}H-NMR (400 MHz), δ 0.16 (t, J = 5.9 Hz, 1H), 0.93 (ddd, J = 11.2, 5.9, and 0.09 Hz, 1H), 1.07 (ddd, J = 14.0, 12.0, and 3.4 Hz, 1H), 1.23 (s, 3H), 1.21–1.29 (m, 2H), 1.39 (ddd, J = 14.0, 5.4, and 3.4 Hz, 1H), 1.66–1.77 (m, 1H), 1.95–2.04 (m, 2H) 2.13 (br. 1H), 2.75 (br. 1H).

Under Condition II, the product was **5i** (R = n-Bu, 53%). ^{1}H-NMR, δ 0.8–1.1 (m, 17H), 1.1–2.0 (m, 22H), 2.70 (br.s, 1H). Under Condition III (using MeLi), the product was **5i** (R = Me, 23%). ^{1}H-NMR, δ 0.09 (s, 9H), 1.1–1.9 (m, 6H), 1.17 (s, 2H), 1.29 (s, 3H), 2.71 (s, 1H) 2.85 (br.s, 1H). The signal at δ 2.85 disappeared upon addition of D_2O.

From 2,3-Epoxy-3r,5c-dimethylcyclohexan-1-one (4j). The solid obtained from **4j** (140 mg, 1 mmol) was chromatographed on a silica gel column, and recrystallized from hexane to give **6j** (53 mg, 39 %). mp 109–110 °C. ^{1}H-NMR (400 MHz), δ 0.04 (t, J = 5.9 Hz, 1H), 0.67 (dd, J = 13.7 and 13.2 Hz, 1H), 0.84 (d, J = 6.8 Hz, 3H), 0.96 (ddd, J = 11.2, 5.9 an 0.09 Hz, 1H), 1.23 (s, 3H), 1.21–1.26 (m, 1H), 1.34 (dq, J = 13.4 and 1.0 Hz, 1H) 1.51 (dd, J = 14.4 and 12.0 Hz, 1H), 1.82 (br. 1H), 1.91–2.45 (m, 1H), 2.15 (dd, J = 14.4 and 6.35 Hz, 1H) 2.87 (br. 1H).

Some amounts of stannyl compound **5j** and vinyl oxirane **21j** were also identified. Under condition II, the products were **5j** (R = n-Bu, 38%). ^{1}H-NMR, δ 0.7–1.0 (m, 20H), 1.0–1.7 (m, 21H), 2.70 (s, 1H). Under Condition III (using MeLi), the product was **5j** (R = Me, 44%). ^{1}H-NMR, δ 0.09 (s, 9H), 0.86 (d, J = 6 Hz, 3H), 0.95–2.15 (m, 5H), 1.20 (s, 2H), 1.29 (s, 3H), 2.71 (s, 1H). For **21j** : ^{1}H-NMR, δ 0.85 (d, J = 8 Hz, 3H), 1.29 (s, 3H), 1.1–2.35 (m, 5H), 3.05 (s, 1H), 5.00 (br.s, 1H), 5.13 (br.s, 1H).

From 2,3-Epoxy-3,5,5-trimethylcyclohexan-1-one (4k) with 1. The solid obtained from **4k** (154 mg, 1 mmol) was a mixture of **6k** and **9k** (123 mg, 72%, **6k** : **9k** = 1 : 2) in view of

the ^{1}H-NMR spectra. Recrystallization from hexane or CCl_4 gave each components in pure states. For **6k** : mp 119–122 ^oC. ^{1}H-NMR, δ 0.07 (t, J = 6.2 Hz, 1H), 0.84 (s, 3H), 1.16 (s, 3H), 1.19 (s, 3H), 0.8–1.6 (m, 6H) 1.75 (br.s, 1H), 1.85 (br.s, 1H). For **9k** : mp 109.5–110 ^oC. IR, 3540, 3370 cm^{-1}. ^{1}H-NMR, δ 0.89 (s, 3H), 0.95 (s, 3H), 1.17 (s, 3H), 1.58 (m, 2H), 1.95–2.15 (m, 2H), 2.40 (br.s, 2H), 3.88 (s, 1H), 4.88 (br.s, 1H), 5.08 (br.s, 1H).

The methylene diol **9k** was the major product under the Condition II, while **5k** (R = Me) was the major product under the Conditions III and IV, in 46% and 50% yields, respectively. For **5k**: ^{1}H-NMR, δ 0.01 (s, 9H), 0.85 and 1.00 (two singlets, 3H), 0.90 and 0.96 (two singlets, 3H), 1.25 (s, 2H), 1.31 (s, 3H), 1.2–2.25 (m), 2.62 and 2.72 (two singlets, 1H).

Upon treating with BF_3-etherate, **5k** afforded vinyl oxirane **21k**. ^{1}H-NMR, δ 0.80 (s, 3H), 0.93 (s, 3H), 1.29 (s, 3H), 1.5–2.3 (m, 4H), 3.10 (s, 1H), 4.93 (br.s, 1H), 5.13 (br.s, 1H).

From 1,8a-Epoxy-4a-methyl-3,4,4a,5,6,7,8,8a-octahydro-2(1H)-naphthalenone (4l). The solid obtained from **4l** (181 mg, 1 mmol) was recrystallized from hexane–CCl_4 to afford a single isomer of **6l** (48 mg, 24%). mp 125–127 ^oC. ^{1}H-NMR (400 MHz), δ 0.39 (t, J = 6.4 Hz, 1H), 0.88 (ddd, J = 11.2, 6.4, and 2.0 Hz, 1H), 1.02 (s, 3H), 1.16 (dd, J = 11.2 and 6.4 Hz, 1H), 1.2–1.6 (m, 10H), 1.60 (br.s, 2H), 1.98 (tdd, J = 13.9, 6.4, and 1.5 Hz, 1H), 2.09 (ddd, J = 13.9, 6.4, and 1.5 Hz, 1H).

General Procedure for the Reaction of Cyclopropanol 6 with BF_3•OEt_2 or HCl. To a solution of cyclopropanol (0.1 M, 1.0 eq) in $CHCl_3$ was added dropwise BF_3•OEt_2 (2.0 eq) or 12M HCl/MeOH (1:1) at 0 ^oC under N_2. After stirring for 15 min at 0 ^oC, the reaction mixture was poured into a cooled solution of saturated $NaHCO_3$ aqueous solution, and the product was extracted with $CHCl_3$. After dried over Na_2SO_4, the extract was concentrated *in vacuo* to give almost pure sample of β,γ-enones **7**. Pure samples were obtained by column chromatography.

From 1-Methyl-2-(1'-hydroxy-1'-methylethyl)-1-cyclopropanol (6a). The product obtained from **6a** (50 mg, 0.385 mmol) and BF_3•OEt_3 was **7a** (43 mg, 98 %). IR, 1718 cm^{-1}. ^{1}H-NMR, δ 1.62 (br.s, 3H), 1.75 (br.s, 3H), 2.05 (bs, 3H), 3.04 (d, J = 7.0 Hz, 1H), 5.31 (t, J = 7.0 Hz, 1H). These data are practically identical with those reported.[29]

From 1-Methyl-2-(1'-hydroxybutyl)-1-cyclopropanol (6b). The product obtained from **6b** (118 mg, 0.82 mmol) and BF_3•OEt_3 was (E)-**7b** (82 mg, 80 %), which was identical with

the sample prepared by the known method.[13] MS, m/z 126 (M^+), 108, 97, 83, 69, 68, 67, 55, 54, 53, 43 (base peak). IR, 1700 cm^{-1}. ^{1}H-NMR, δ 0.98 (t, J = 6.0 Hz, 3H), 1.20–2.32 (m, 4H), 2.06 (s, 3H), 3.03 (dd, J = 4.2 and 1.0 Hz, 2H), 5.38–5.66 (m, 2H).

From 1-Methyl-2-(1'-hydroxybenzyl)-1-cyclopropanol (6c). The product obtained from **6c** (46 mg, 178 mmol) and BF_3•OEt_2 was (E)-isomer of **7c** (39 mg, 94 %). MS, m/z 160 (M^+), 118, 117, 116, 115, 91, 65, 63, 51, 43 (base peak). IR, 1710 cm^{-1}. ^{1}H-NMR, δ 2.10 (s, 3H), 3.22 (d, J = 5.6 Hz, 2H), 5.93–6.60 (m, 2H), 7.05–7.42 (m, 5H). The NMR data is different from that of (Z)-isomer reported.[14]

From 1-Methyl-2-methyl-2-(1-hydroxypropyl)-1-cyclopropanol (6d). The product obtained from **4d** (62 mg, 0.31 mmol) by treatment with HCl in ether (10 ml) was **7d** (50 mg, 89 %). MS, m/z 126 (M^+), 111, 97, 83, 69, 55, 43. ^{1}H-NMR, δ 0.94 (t, J = 8 Hz, 3H), 1.45–1.60 (m, 2H), 1.52 (s, 3H), 1.99 (s, 3H), 2.94 (s, 2H), 5.15 (t, 1H), ^{13}C-NMR, δ 14.0, 16.1, 21.4, 28.9, 54.8, 128.1, 130.9, 207.8.

From 1,5-Dihydroxy-5-methylbicyclo[4,1,0]heptane (6i). The product obtained from **6i** (56 mg, 0.40 mmol) and BF_3•OEt_2 was **7i** (39 mg, 80%). MS, m/z 124 (M^+), 96, 81, 68, 67, 55, 53, 41, 39. IR, 1712 cm^{-1}. ^{1}H-NMR, δ 1.68 (s, 3H), 1.80–2.62 (m, 6H), 3.03 (br.d, J = 6.0 Hz, 2H), 5.20 (t, J = 7.0 Hz, 1H). The data are practically identical with those reported.[29,30]

From 1,5-Dihydroxy-3,5-dimethylbicyclo[4,1,0]heptane (6j). The product from **6j** (26 mg, 0.17 mmol) and BF_3•OEt_2 was **7j**. ^{1}H-NMR, δ 0.96 (d, J = 6.0 Hz, 3H), 1.68 (s, 3H), 1.83–3.47 (m, 7H), 5.27 (t, J = 7.0 Hz, 1H).

General Procedure for the Reaction of Epoxy Ketones (4) with 1 and HCl. Epoxy ketones **4** were reacted with **1** under the Condition I as above. After stirred for 2 h at room temperature, the solution was again cooled down to 0 ^oC and treated with 12M HCl/MeOH (1 : 1). The solution was allowed to warm up to room temperature, stirred for 30 min, and the product was extracted with $CHCl_3$. Pure samples of β,γ-enones **7a**, **7b**, and **7d** were obtained by column chromatography in 78, 76, and 64% yields, respectively. For spectroscopic data, see above.

From trans-3,4-Epoxy-3-ethylpentan-2-one (4e). The product obtained from **trans-4e** (256 mg, 2.0 mmol) was a mixture of (E)-**7e** and (Z)-**7e** (192 mg, 76 %, E : Z = 7 : 3). For (E)-**7e** : ^{1}H-NMR, δ 0.92 (t, J = 8 Hz, 3H), 1.60 (d, J = 7 Hz, 3H), 2.00 (s, 3H), 2.04 (q, J = 8 Hz, 2H), 2.96 (s, 3H), 5.24 (q, J = 7 Hz, 1H). ^{13}C-NMR, δ 12.3, 13.3, 23.1, 30.8, 52.0, 123.4, 135.5, 207.8. For (Z)–**7e** : MS, m/z 126 (M^+), 111, 83, 69, 57, 55, 43.

^{1}H-NMR, δ 0.93 (t, J = 8 Hz, 3H), 1.60 (d, J = 7 Hz, 3H), 2.00 (s, 3H), 2.04 (q, J = 8 Hz, 2H), 3.00 (s, 3H), 5.24 (q, J = 7 Hz, 1H). ^{13}C-NMR, δ 12.9, 13.9, 28.9, 30.6, 45.8, 121.2, 135.5, 207.8.

From trans-3,4-Epoxy-4,8-dimethyl-7-nonen-2-one (4f). The product obtained from **4f** (68 mg, 0.373 mmol) was a mixture of **(E)-7f** and **(Z)-7f** (50 mg, 75 %, 1 : 1 mixture by GLC analysis). ^{1}H-NMR (as a mixture), δ 1.50–1.60 (m, 9H), 1.95 (m, 4H), 2.00 (s, 3H), 3.00 (d, J = 7 Hz, 2H), 4.97 (m, 1H), 5.19 (t, J = 7 Hz, 1H).

From cis-3,4-Epoxy-4,8-dimethyl-7-nonen-2-one (4f). The product obtained from **cis-4f** (cis-rich material of 22/1) was purified on a column chromatography to give **(E)-7f** (38 mg, 68 %). The product showed identical retention time on GLC analysis with that of **(E)-7f**, prepared from **(E)-20**[31] with the reagent **1**, according to the method reported.[3]

General Procedure for the Reaction of α-Chloro Ketones 13 with 1. The reaction was carried out in the same way as with epoxy ketones under the Condition I and Condition III. Typical procedure is shown below with 2-Chloro-1-phenyl-1-ethanone (**13m**).

From 2-Chloro-1-phenyl-1-ethanone (13m). Condition I : To a solution of $Me_3SnCH_2SnMe_3$ (684 mg, 2 mmol) in THF (8 ml) was added a hexane solution of n-BuLi (1.33 ml, 2 mmol) at −78 °C. After 10 min, **13m** (155 mg, 1 mmol) was added, and the solution was allowed to warm up to room temperature. The solution was poured into an aqueous solution of NaCl, and extracted with ether. After the ether was evaporated, the residue was chromatographed on silica gel. The cyclopropanol **15m** (78 mg, 58%) and allyl alcohol **17m** (15 mg, 11%) were isolated. Condition III : Only allyl alcohol **17m** was isolated in 67% yield. For **15m** : ^{1}H-NMR, δ 3.67 (br, 1H), 4.30 (s, 2H), 5.20 (br, 1H), 5.35 (br, 1H), 7.17 (br.s, 5H). For **17m** : ^{1}H-NMR, δ 0.88 (m, 2H), 1.07 (m, 2H), 3.89 (br, 1H), 7.09 (m, 5H). Both data are practically identical with those reported.[32,33]

From 2-Chloro-1-phenyl-1-propanone (13n). Condition I : The products obtained from **13n** (168 mg, 1 mmol) were **15n** (35 mg, 23%) and **17n** (74 mg, 50%). Condition III : The product was only **17n** (118 mg, 70%). The starting material (**13n**, 33 mg) was also recovered. For **15n**[34] : ^{1}H-NMR, δ, 0.76 (m, 1H), 1.27 (m, 5H), 2.74 (bs, 1H), 7.24 (m, 5H). For **17n** : MS, m/z 148 (M^+), 133, 105, 104, 103, 78, 77, 73, 51, 45, 43. For **17n** : ^{1}H-NMR, δ 1.10 (d, J = 6.8 Hz, 1H), 3.30 (bs, 1H), 4.60 (q, J = 6.8 Hz, 1H), 5.05 (br.s, 1H), 5.23 (br.s, 1H), 7.10 (m, 5H).

From 2-Chloro-2-methyl-1-phenyl-1-propanone (13o). The product from **13o** was only **17o** under Conditions I and III. ^{1}H-NMR, δ 1.25 (s, 6H), 2.11 (bs, 1H), 4.79 (m, 1H),

5.27 (br.s, 1H), 7.09 (s, 5H). The data are practically identical with those reported.[35]

From 1-Chloro-2-octanone (13p). Condition I : The products obtained from **13p** (160 mg, 1 mmol) were a mixture of **15p** and **17p**. The yields were 54% and 9%, respectively by NMR analysis using TCE as an internal reference. Each components were obtained pure by column chromatography. Condition III : The product was only **17p** (101 mg, 71%). For **15p** : ^{1}H-NMR, δ 0.2–0.8 (m), 0.95 (t, 3H), 1.1–1.5 (b, 8H). For **17p** : MS, m/z 142 (M^+), 111, 95, 82, 81, 71, 57, 55, 43, 41. IR, 3300 cm^{-1}, ^{1}H-NMR, δ 0.90 (dist.t, 3H), 1.25 (br, 8H), 2.00 (br, 2H), 3.57 (br.s, 1H), 3.93 (br.s, 2H), 4.75 (br.s, 1H), 4.92 (br.s, 1H).

From 3-Chloro-2-octanone (13q). Condition I : The product obtained from **13q** (100 mg, 0.62 mmol) was a mixture of **15q** and **17q**. The separation was not accomplished, and the yields were estimated as 31% and 26%, respectively, by NMR analysis using endo-methylene and cyclopropane ring protons as probe signals. Condition III : The product from **13q** (162 mg, 1 mmol) was only **17q** (82 mg, 58%). For **17q** : MS, m/z 142 (M^+), 127, 113, 99, 86, 72, 71, 58, 43, 41. IR, 3300 cm^{-1}. ^{1}H-NMR, δ 0.92 (dist.t, 3H), 1.33 (br.s, 8H), 1.73 (s, 3H), 2.30 (br.s, 1H), 3.95 (dist.t, 1H), 4.73 (br.s, 1H), 4.85 (br.s, 1H).

From 4-Chloro-5-nonanone (13r). Condition III : The product from 13r (177 mg, 1 mmol) was only 17r (125 mg, 80%). MS, m/z 156 (M^+), 141, 127, 113, 99, 86, 71, 43. ^{1}H-NMR, δ 0.90 (dist.t, 6H), 1.1–1.7 (m, 8H), 1.8–2.2 (m, 2H), 3.95 (br.t, J = 8 Hz, 1H), 4.76 (br.s, 1H), 4.90 (br.s, 1H). ^{13}C-NMR, δ 13.84, 18.84, 22.156, 30.18, 30.93, 37.64, 74.96, 108.65, 152.10. Exact mass, Found, 156.1488, Calcd for $C_{10}H_{20}O$, 156.1514.

From 2-Chlorocyclohexanone (13s). Condition I : The products obtained from **13s** (133 mg, 1 mmol) were **15s** (15%, NMR analysis with TCE) and **18** (119 mg, 39%). Condition II : The product was only **15s** (84 mg, 75%). For **15s** : ^{1}H-NMR, δ 0.11 (t, J = 6 Hz, 1H), 0.51–2.72 (m, 10H), 3.70 (br.s, 1H). The data are practically identical with those reported.[34] For **18** : ^{1}H-NMR, δ 0.09 (s, 9H), 0.81 (br.t,), 1.0–2.1 (m), 2.35 (br.s, 1H), 3.87 (t, J = 7 Hz, 1H). The integration at δ 1.0–2.1 was not accurate, since the product contained a one-third amount of butyldimethylstannyl compound, as evident from the signal at δ 0.81.

The Reaction of 3,4-Epoxy-4-methylpentan-2-one (4a) with 10. To a solution of (trimethylsilyl)(tributylstannyl)methane (1.13 g, 3 mmol) in THF was added n-BuLi (3 mmol) at 0 °C, and the solution was stirred for 30 min. After the solution was cooled to −78 °C, **4a** (171 mg, 1.5 mmol) was added. After 5 min, the mixture was quenched with

water, and extracted with $CHCl_3$. The crude sample was purified on a column chromatography to afford **11** (246 mg, 82%). ^{1}H-NMR, δ 0.00 (s, 9H), 0.98 (s, 2H), 1.19 (s, 6H), 1.30 (s, 3H), 1.83 (br.s, 1H), 2.46 (s, 1H). When the reaction mixture after the addition of **4a** was warmed up to room temperature during the period of 1 h, and stirred for another 2 h at room temperature, the product was **12** (12.3 mg, 31%) along with **11** (11.8 mg, 39%). For **12** : ^{1}H-NMR, δ 0.00 (s, 9H), 0.88 (s, 1H), 0.96 (s, 1H), 1.05 (s, 3H), 1.20 (br.s, 3H), 1.74 (s, 3H), 2.48 (br.s, 1H), 3.72 (s, 1H), 4.84 (br.s, 1H).

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