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Highly Regioselective Allylation of α-Enones and Epoxides with Lithium Tetraallyllanthanoid Ate Complex

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Tetraallyllanthanoid ate complex (**1**), which was readily prepared in situ from tetraallyltin, lanthanoid trichloride, and butyllithium in tetrahydrofuran (THF), reacts smoothly with α-enones (**3**—**11**) with a high degree of 1,2-regioselectivity ($1,2:1,4={>}99:1$) to give 1,5-diene-3-ols in good to excellent yields. The mechanistic study with 4,4-(ethylenedioxy)-2,6-dimethyl-2,5-cyclohexadienone (**29**) as a probe suggests that single electron transfer (SET) may be involved in this carbonyl allylation reaction with **1**. Allylative ring opening of styrene oxide with **1** occurs at the more subsituted carbon (α-attack) in higher selectivity ($\alpha:\beta=85:15$) than with allyllithium and allylmagnesium bromide in diethyl ether. The complex **1** reacts with 3,4-epoxy-1-butene (**35**) in diethyl ether predominantly at the most substituted carbon of the oxirane to give 3-hydroxymethyl-1,5-hexadiene (**36**) together with 1,6-heptadien-3-ol (**37**), (*E*) and (*Z*)-2,6-heptadienols (**38**) (**36**:**37**:**38**=87:9:4)

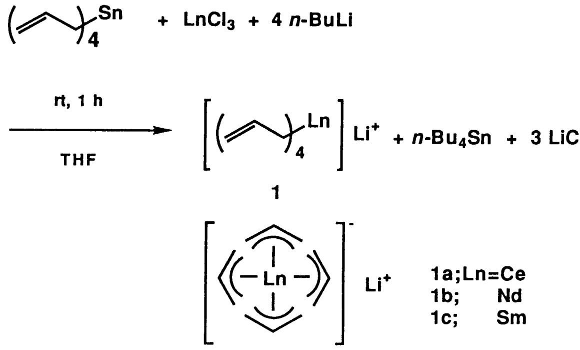
Allyl metal compounds have been recognized as important allyl-transfer agents which transform carbonyl compounds to synthetically useful homoallylic alcohols. Various kinds of allyl metal compounds have been developed and the nucleophilicity of those compounds depends on the nature of the metallic species.[1)] Therefore choice of the metallic species is important to achieve high degree of stereo-, regio-, or chemoselective allylation of organic substrates. Thus, allyltrimethylsilane undergoes 1,4-addition to α-enones in the presence of titanium tetrachloride,[2)] while crotyltributyltin allows its use for highly diastereoselective addition to aldehydes,[3)]and allylchromium compounds add to aldehydes chemoselectively.[4)] Recently, Yanagisawa et al. reported that allylbarium compounds undergo regioselective and stereospecific allylation of carbonyl compounds.[5)] Allyltitanium compounds are also very useful as chemo-, stereo-, and regioselective allyl-transfer reagents.[6)]

There is much current interests in the use of organolanthanoid compounds in organic synthesis.[7)] These compounds exhibit some distinct reactivities as compared with conventional reagents such as Grignard reagents and organolithium reagents; the characteristics, such as strong oxophilicity but weak Lewis acidity of lanthanoid elements, reflect well their potential in on organic synthesis. Alkyllanthanoid halides have been shown to function as mild and efficient nucleophiles in addition to carbonyl compounds in a regio- and stereoselective manner.[8)] Allyllanthanoid π-complexes are expected to be synthetically as important as the alkyllanthanoid halides for allylation of organic substrates.[9)] We were interested in the easily preparable tetraallyllanthanoid ate complex (**1**), and have reported[10)] that **1** is a promising allyl-transfer reagent and especially effective for the 1,2-regioselective allylation of α-enones. We have further applied this reagent to the regioselective ring opening of oxiranes. We now wish to report the details of the regioselectivity in the reaction with α-enones and epoxides in comparison with allyllithium[11)] and allylmagnesium reagents.

Results and Discussion

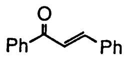
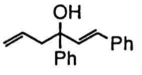
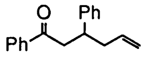
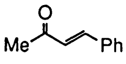
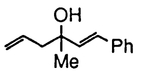
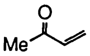
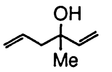
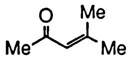
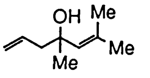
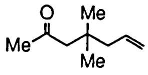
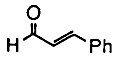
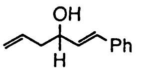
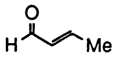
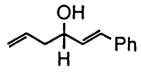
Reactions with α-Enones. As **1** is highly air- and moisture sensitive and pyrophoric, we used it in tetrahydrofuran (THF) or in diethyl ether solution without isolation. It was readily prepared in THF or diethyl ether at ambient temperature under nitrogen by a transmetalation reaction, utilizing tetraallyltin, anhydrous lanthanoid trichloride, and 4 equiv of butyllithium (Scheme 1).[9a)] The reaction was usually carried out at 0 °C or room temperature by adding an organic substrate to the colored, homogeneous solution which contained **1**, tetrabutyltin, and lithium chloride.

1,2-Regioselective allylation of α-enones with allylic metal compounds is an important process to obtain 1,5-hexadien-3-ols.[12)] However, the 1,2-adduct, is often contaminated with unwanted 1,4-adduct. Indeed, the reaction of 1,3-diphenyl-2-propen-1-one (**2**) with allyllithium in THF gave a mixture of 1,2- (**12**) and 1,4-adducts (**13**) in a ratio of 40:60, showing that there was



Scheme 1.

Table 1. Reaction of Acyclic α-Enones with Lithium Tetraallyllanthanoid Ate Complex[a)]

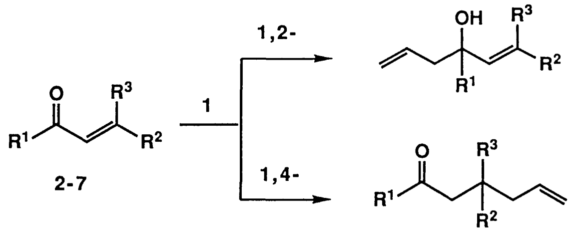
Run	α-Enone	Ln in **1**	Products	Yield (%) and isomer ratio[b)]
1	 **2**	[c)]	 **12** +  **13**	99, **12**:**13**=40:60
2		Ce		90, **12**:**13**=75:25
3		Nd		95, **12**:**13**=80:20
4		Sm		97, **12**:**13**=85:15
5	 **3**	[c)]	 **14**	80, **14** only
6		Ce		84, **14** only
7	 **4**	[c)]	 **15**	47, **15** only
8		Ce		64, **15** only
9	 **5**	[c)]	 **16** +  **17**	90, **16**:**17**=95:5
10		Ce		95, **16**:**17**=100:0
11[d)]	 **6**	Ce	 **18**	99, **18** only
12[d)]	 **7**	Ce	 **19**	99, **19** only

a) α-Enone (1.6 mmol), tetraallyltin (0.4 mmol), n-BuLi (1.6 mol dm^{-1}, 1 cm^3), lanthanoid trichloride (0.4 mmol), and THF (10 ml); 0 °C—room temperature, 1 h. b) Isolated total yield of 1,2- and 1,4-adducts and isomer ratio was determined by GLC. c) Allyllithium was used. d) The reaction was carried out at −78—0 °C.

almost no regioselectivity. When the reaction was carried out by using tetraallylcerium ate complex (**1a**), the regioselectivity for 1,2- vs. 1,4-adduct was dramatically improved (75:25). The use of neodymium (**1b**) and samarium (**1c**) complexes further upgraded the selectivity to 80:20 and to 85:15, respectively. The results are shown in Table 1. As a control experiment, tetrabutyltin and lithium chloride were eliminated from the reaction,[9a)] a high 1,2-regioselectivity still remained, showing that the presence of these compounds was not essential for the regioselectivity and we may use the allyllanthanoid complex in solution without isolation.

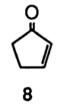
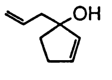
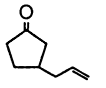
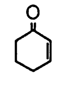
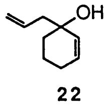
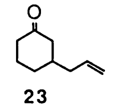
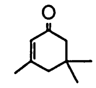
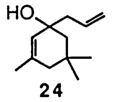
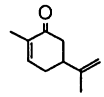
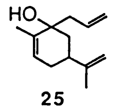
With other acyclic α-enones such as 4-phenyl-3-buten-2-one (**3**), 3-buten-2-one (**4**), 4-methyl-3-penten-2-one (**5**), **1** was superior not only in higher 1,2- regioselectivity but also in a higher yield to allyllithium. The results are also included in Table 1. The complex **1** added also to α-enals like cinnamaldehyde (**6**) and crotonaldehyde (**7**) in exclusive 1,2-selectivity without contamination of any side reactions at −78 to 0 °C.

Table 2 summarizes the results of the reaction of **1** with various cyclic α-enones (**8**—**11**). Complex **1** was also effective for high regioselective 1,2-allylation of cyclic α-enones such as 2-cyclopenten-1-one (**8**) and 2-cyclohexen-1-one (**9**). The neodymium and samarium complexes produced exclusively the 1,2-adducts in excellent yields. For example, allyllithium gave a mixture of 1,2- (**22**) and 1,4-adduct (**23**) in the reaction with **9** in a ratio of 89:11, whereas the reaction of **9** with the neodymium complex afforded only the 1,2-adduct. It should be noted that the regioselectivity depends on the reaction temperature. Excellent 1,2-regioselectivity was observed at higher temperature (0 °C—room temperature), while the selectivity decreased at lower temperature (−78 °C).

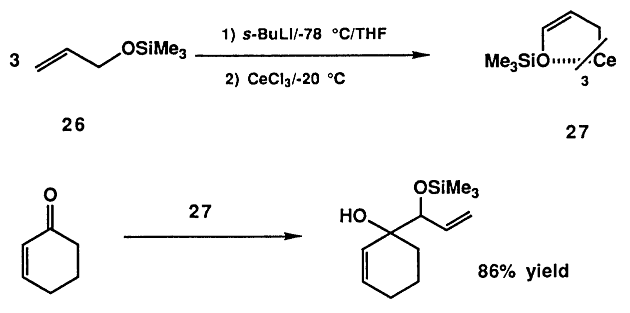


Scheme 2.

Table 2. Reaction of Cyclic α-Enones with Lithium Tetraallyllanthanoid Ate Complex[a)]

Run	α-Enone	Ln in 1	Products	Yield (%) and isomer ratio[b)]
1	 **8**	c)	 **20** +  **21**	72, **20**:**21**=89:11
2		Ce		82, **20**:**21**=97:3
3		Nd		77, **20**:**21**=100:0
4	 **9**	c)	 **22** +  **23**	64, **22**:**23**=84:16
5		Ce		96, **22**:**23**=99:1
6		Nd		93, **22**:**23**=100:0
7		Sm		98, **22**:**23**=100:0
8	 **10**	Ce	 **24**	94, **24** only
9		Nd		99, **24** only
10	 **11**	Ce	 **25**	95, **25** only

a) See footnotes in Table 1. b) Isolated total yield of 1,2- and 1,4-adducts and isomer ratio was determined by GLC. c) Allyllithium was used.



26 27 9 28

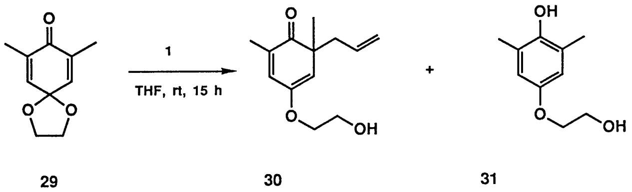
Scheme 3.

The oxy allylic anion, which is readily prepared by allyloxytrimethylsilane (**26**) and *s*-BuLi, is an important synthetic equivalent of homoenolate anion (*β*-acyl carbanion).[13)] Some alkoxyallylmetal reagents are designed for 1,2-regioselective addition to α-enones with α-selective attack.[14)] We were also able to achieve exclusive 1,2-carbonyl addition with the allyllanthanoid reagent (**27**). Addition of **27** to 2-cyclohexen-1-one (**9**) afforded dienol (**28**) in good yield (Scheme 3).

In conclusion, allyllanthanoid complexes offer a broad synthetic versatility and are particulaly useful for the 1,2-regioselective addition to α-unsaturated carbonyl compounds providing an easy access to 1,5-hexadien-3-ols.[15)]

Mechanistic Aspect of Allyl Transfer from Allyllanthanoid Complex to Carbonyl. High degree of 1,2-regioselectivity in the reaction of **1** with α-enones is consistent with the alkylation by alkyllanthanoid σ-complexes[8a)] and reduction by the combination of NaBH$_4$[16)] or LiAlH$_4$[17)] with lanthanoid trichloride. The 1,2-regioselective allylation may be rationalized by strong oxophilicity and hardness of lanthanoid metal species. The activation of a carbonyl group by a lanthanoid ion should be the essential factor for the high 1,2-regioselectivity.[18)]

Allylation of α-enones is supposed to proceed through a single-electron-transfer (SET) pathway in analogy with organolithium and magnesium reagents. Liotta et al. first proposed that 4,4-(ethylenedioxy)-2,6-dimethyl-2,5-cyclohexadienone (**29**) was a useful probe for detecting SET processes in carbonyl additions[19)] and some other research groups have used this compound to prove the reaction mechanism to be SET.[8a,20)] When the tetraallylcerium complex was allowed to react with **29**, the compound (**30**) was obtained in 40% yield, which may be produced through carbonyl allylation followed



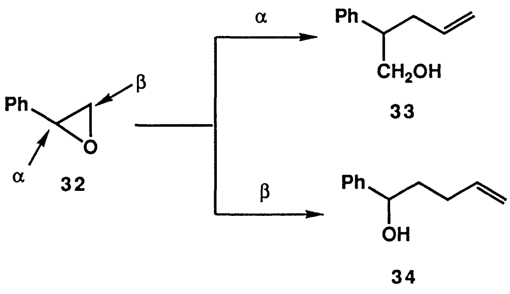
29 30 31

40% 11%

Scheme 4.

by allylic rearrangement. Phenol derivative (**31**) was also formed in 11% yield probably via the ketyl intermediate. These experimental data are consistent to that SET is involved in this allyl-transfer reaction.

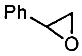
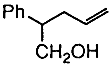
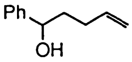
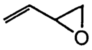
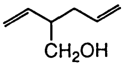
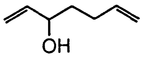
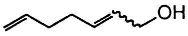
Reactions with Epoxides. Oxirane ring opening by organometallic reagents is a useful route for a carbon–carbon bond formation.[21] The regioselectivity of the nucleophilic attack is of major concern. Regioselective cleavage of oxirane ring at the more substituted carbon atom (α-attack) as well as at the less substituted carbon (β-attack) has been observed. Organocuprates including allylic cuprates exhibit a strong preference for attack the less substituted carbon.[22] On the other hand, Reetz[6] as well as Iwata[23] reported that the reaction of epoxides, such as styrene oxide (**32**), with allyltitanium reagents occurred in 99% α-selectivity. We are interested in the allylative ring opening of epoxides with **1** and expecting a predominant α-attack. The prediction is based on the previously reported fact that methyllanthanoid reagents selectively attacks at the more substituted carbon of styrene oxide.[24]



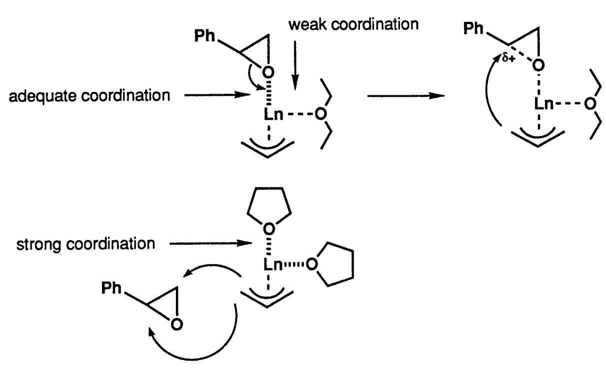
Scheme 5.

In our initial trials we investigated the reaction of **32** with the allyllithium and allyllanthanoid reagents (Table 3). Treatment of **32** with allyllithium in diethyl ether at room temperature for 5 h yielded an almost 1 : 1 mixture of primary (**33**) (α-attack) and secondary (**34**) (β-attack) alcohols. When the allylcerium complex (**1a**) was employed under the same conditions, allylation occurred selectively with a ratio of 85 to 15 in favor of α-attack. This result is compatible with the epoxide opening by methyllanthanoid reagents. It is noteworthy that the regioselectivity appears to be quite sensitive to the solvent used. Use of either THF or 1,2-dimethoxyethane (DME) instead of diethyl ether in the reaction of **1a** with **32** resulted in a loss of regioselectivity (Table 3, Runs 6,7).[25] Solvent dependance of the regioselectivity is not fully understood yet, but one explanation is the strength of the metal-solvent complex formation.[26] The oxygen atom of the epoxide adequately coordinates to the metal moiety in diethyl ether generating an oxonium ion species; then the benzylic carbon becomes cationic (S_N1-mechanism) and therefore α-attack predominates.[22] On the other hand, coordination of the oxirane to the metal is discouraged by a strongly coordinating solvent such as THF leading to a nucleophilic attack of the allyl metal species at the less substituted carbon atom (S_N2-mechanism). In

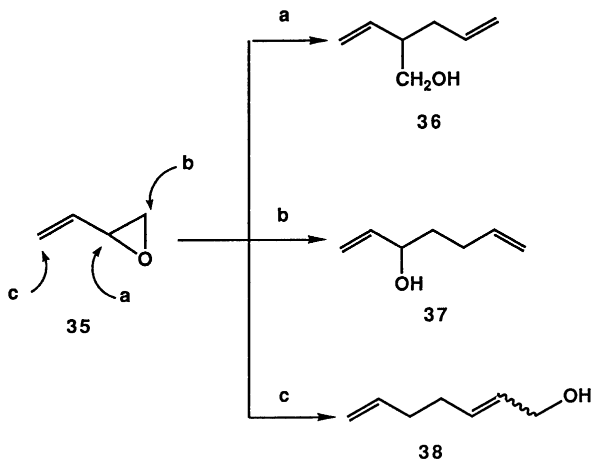
Table 3. Reaction of Epoxide with Lithium Tetraallylcerium Ate Complex[a]

Run	Epoxide	Solvent	Products	Yield (%) and isomer ratio[b]
1[c]	 **32**	Et_2O	 **33** +  **34**	95, **33**:**34**=55:45
2[d]		Et_2O		90, **33**:**34**=70:30
3		Et_2O		97, **33**:**34**=85:15
4[e]		Et_2O		91, **33**:**34**=75:25
5[c]		THF		75, **33**:**34**=50:50
6		THF		90, **33**:**34**=44:56
7		DME		50, **33**:**34**=45:55
8		Et_2O–HMPA		70, **33**:**34**=40:60
9[c]	 **35**	Et_2O	 **36** +  **37**	85, **36**:**37**:**38**=74:21:5
10		Et_2O		90, **36**:**37**:**38**=87:9:4
11[e]		Et_2O	+  **38**	90, **36**:**37**:**38**=83:13:4
12		THF		60, **36**:**37**:**38**=67:29:4
13[c]		THF		65, **36**:**37**:**38**=63:20:17

a) Epoxide (1.6 mmol), tetraallyltin (0.4 mmol), *n*-BuLi (1.6 mol dm^{-1} cm^3), cerium trichloride (0.4 mmol), and solvent (10 cm^3); room temperature, 5 h. b) Isolated total yield of adducts and isomer ratio was determined by GLC. c) Allyllithium was used. d) Allylmagnesium bromide was used. e) Allylsamarium complex was used instead of allylcerium complex.



Scheme 6.



Scheme 7.

agreement with this hypothesis is the fact that addition of hexamethylphosphoric triamide (HMPA) (2%) to diethyl ether dramatically decreased the selectivity for **33** ($\alpha:\beta$=40:60), suggesting that coordination of the solvent affects the regioselectivity.

There are three potential sites of nucleophilic allylation in 3,4-epoxy-1-butene (**35**); allylation could occur at the most substituted carbon to give 3-hydroxymethyl-1,5-hexadiene (**36**), at the less substituted carbon to give 1,6-heptadien-3-ol (**37**), or at the allylic carbon to give (*E*) and (*Z*)-2,6-heptadienols (**38**). Treatment of **35** with the allyllanthanoid complex in diethyl ether yielded **36** mainly, along with traces of **37** and **38** (**36**:**37**:**38**=87:9:4). For comparison: treatment of **35** with allyllithium yielded **36**, **37**, and **38** in a ratio of 74:21:5. Here again, the organocerium reagent is more selective than the organolithium reagent (Table 3). In this case, the selectivity was essentially the same in either diethyl ether or THF; the attack at the more substituted carbon was most favored.

Experimental

General. ^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM EX-90 (90 MHz), and JEOL JNM A-400 (400 MHz) spectrometers in $CDCl_3$. Chemical shifts are reported in δ units downfield from the internal Me_4Si. Assignment of ^{13}C resonance was aided by use of the DEPT spectra. Infrared spectra were obtained from solutions in chloroform with Shimadzu IR 410 spectrometer. GLC analyses were carried out on a Shimadzu 8A gas chromatograph equipped with EGSS-X(3%)-Chromosorb-W(2 m), Silicone DC QF-1(5%)-Chromosorb-W(2 m), and PEG-20M(5%)-Chromosorb-W(2 m) columns (N_2 as carrier gas). Elemental analyses were carried out at Microanalytical Center of Kyoto University, Kyoto, Japan. Flash column chromatography was performed by EYELA EF-10 apparatus equipped with UV detector by using Wakogel C-300. Preparative TLC separation was conducted using 20×20 cm glass plates coated with a 2.0 mm thick layer of Merck Kieselgel PF_{254} gipshaltig.

Materials. Anhydrous $CeCl_3$, $NdCl_3$, and $SmCl_3$ were obtained by drying the commercial hydrates with $SOCl_2$,[27] and further heated at 150 °C in vacuo for 2 h over KOH. Tetrahydrofuran (THF) and diethyl ether were distilled under nitrogen from sodium diphenylketyl prior to use. Tetraallyltin was prepared from the reaction of allylmagnesium bromide with anhydrous tin tetrachloride in over 70% yield by the reported method.[28] Butyllithium in hexane solution (1.6 mol dm^{-3}) was purchased from Kanto Chemical. Authentic 1,4-allylation products of α-enones for GLC analyses were prepared by the reaction with allyltrimethylsilane catalyzed by titanium tetrachloride.[2] 3,4-Epoxy-1-butene was purchased from Aldrich. All organic compounds were commercially available and used without further purification unless otherwise noted.

Caution: Anhydrous lanthanoid trichloride is very moisture-sensitive. Even a slight contamination of the lanthanoid trichloride with moisture prevents the correct formation of the tetraallyllanthanoid complex. The authors recomend a microwave heating of lanthanoid trichloride for 5—10 min just before use.

Reaction of α-Enones with the Tetraallyllanthanoid Complex (1). All reactions were carried out under nitrogen by standard techniques for air-sensitive materials. The following example provides a general procedure for the reaction of **1** with α-enones. A hexane solution of butyllithium (1.6 mol dm^{-1}, 1 cm^3) was added slowly at room temperature to a suspension of anhydrous lanthanoid trichloride (0.4 mmol) and tetraallyltin (0.4 mmol) in THF (5 cm^3) under nitrogen. The solution became homogeneous and colored (Ce: violet, Nd: yellow, Sm: orange) within 10 min and was stirred for 1 h.[8] To the resulting solution was added a THF solution (5 cm^3) of 2-cyclohexen-1-one (**9**) (1.6 mmol) at 0 °C by a syringe. The color of the solution faded out and the solution was stirred at 0°C for 1 h. The solution was poured into an aqueous solution of NH_4Cl, extracted with diethyl ether (25 cm^3×3), and then dried over $MgSO_4$. GLC analysis showed the presence of the corresponding 1,2-adduct (**22**) as a major product together with tetrabutyltin and a slight amount of 1,4-adduct (**23**). The isomer ratio of **22** to **23** was determined by GLC. Evaporation of the solvent left a pale yellow oil and the product was isolated by column chromatography on silica gel; hexane eluted tetrabutyltin and then hexane–diethyl ether (5:1) eluted **22**. Kugelrohr distillation (oven temperature 180 °C/5 mmHg, 1 mmHg=133.322 Pa) gave pure products.

1,3-Diphenyl-1,5-hexadien-3-ol (12): ^{1}H NMR ($CDCl_3$, 90 MHz) δ=2.81 (2H, d, *J*=7.0 Hz), 5.1—5.3 (2H, m), 5.6-5.9 (1H, m), 6.43 (1H, d, *J*=17 Hz), 6.84 (1H, d, *J*=17 Hz), and 7.0—8.0 (5H, m, Ph). IR 3420 (ν_{OH}), 1664, and 1638 ($\nu_{C=C}$)

cm^{-3}. The title compund was analyzed as its trimethylsilyl ether. Found: C, 77.92; H, 8.00%. Calcd for $C_{21}H_{26}OSi$: C, 78.21 ; H, 8.13%.

1,4-Diphenyl-5-hexen-1-one (13): ^{1}H NMR ($CDCl_3$, 90 MHz) δ=2.45 (2H, t), 3.2—3.7 (3H, m), 2.39 (2H, d, *J*=7.6 Hz), 4.8—5.1 (2H, m), 5.5—5.9 (1H, m), 6.62 (1H, d, *J*=16 Hz), and 7.0—7.9 (10H, m, Ph). IR 1730 ($\nu_{C=O}$) cm^{-1}. Found: C, 86.10 ; H, 7.31%. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25%.

1-Phenyl-3-methyl-1,5-hexadien-3-ol (14): ^{1}H NMR ($CDCl_3$, 90 MHz) δ=1.39 (3H, s), 2.0 (1H, br s, OH), 2.39 (2H, d, *J*=7.6 Hz), 5.0—5.2 (2H, m), 5.8 (1H, m), 6.27 (1H, d, *J*=16 Hz), 6.62 (1H, d, *J*=16 Hz), and 7.3 (5H, br s, Ph). ^{13}C NMR δ=27.9, 47.3, 72.3 (C–O), 119.2 (*CH*$_2$=CH), 125.6 (*CH*=CH$_2$), 126.4, 127.4, 128.5 (Ph), 133.5, 136.2 (*CH*=*CH*), and 136.9. IR 3370 (ν_{OH}) and 1635 ($\nu_{C=C}$) cm^{-1}. Found: C, 83.14; H, 8.68. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57%.

3-Methyl-1,5-hexadien-3-ol (15): ^{1}H NMR ($CDCl_3$, 90 MHz) δ=1.27 (3H, s), 2.28 (2H, d, *J*=7.0 Hz), and 4.8—6.2 (6H, m). ^{13}C NMR δ=27.4, 46.8, 60.4 (C–O), 111.9 (*CH*$_2$=CH), 118.6 (*CH*$_2$=CH), 133.6 (CH$_2$=*CH*), and 144.7 (CH$_2$=*CH*). IR 3500 (ν_{OH}) cm^{-1}. Found: C, 74.92; H, 10.75%. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78%.

2,4-Dimethyl-2,6-heptadien-4-ol (16): ^{1}H NMR ($CDCl_3$, 90 MHz) δ=1.26 (3H, s), 1.65 (3H, s), 1.80 (3H, s), 2.27 (2H, d, *J*=7.7 Hz), and 4.9—6.2 (4H, m). ^{13}C NMR δ=18.8, 27.2, 28.7, 48.4, 72.2 (C–O), 118.6 (*CH*$_2$=CH), 130.6 (CH$_2$=*CH*), 134.2 (*CH*=CMe$_2$), and 134.4 (CH=*CMe*$_2$). IR 3420 (ν_{OH}) cm^{-1}. Found: C, 77.09; H, 11.50%. Calcd for $C_9H_{16}O$: C, 76.56; H, 11.65%.

1-Allyl-2-cyclopenten-1-ol (20): ^{1}H NMR ($CDCl_3$, 90 MHz) δ=1.8—2.17 (5H including OH, m), 2.40 (2H, d, *J*=7.2 Hz), 5.10—5.30 (2H, m), and 5.60—6.10 (3H, m). IR 3350 (ν_{OH}) and 1640 ($\nu_{C=C}$) cm^{-1}. Found: C, 77.33; H, 9.83%. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74%.

1-Allyl-2-cyclohexen-1-ol (22): ^{1}H NMR ($CDCl_3$, 90 MHz) δ=1.64-2.15 (6H, m), 1.90 (1H, s, OH), 2.30 (2H, d, *J*=7.2 Hz), 4.92—5.29 (2H, m), and 5.50—6.12 (3H, m). ^{13}C NMR δ=18.9, 25.1, 35.5, 46.7, 69.1 (C–O), 118.4 (*CH*$_2$=CH), 130.0 (*CH*=CH$_2$), 132.2, and 133.7 (cyclohexene C=C). IR 3360 (ν_{OH}) and 1639 ($\nu_{C=C}$) cm^{-1}. Found: C, 78.63; H, 10.37%. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21%.

1-Allyl-3,5,5-trimethyl-2-cyclohexen-1-ol (24): ^{1}H NMR ($CDCl_3$, 90 MHz) δ=0.93 (3H, s), 1.01 (3H, s), 1.47 (3H, s), 158 (1H, s, OH), 1.62 (4H, br s), 2.20 (2H, d, *J*=7.2 Hz), and 4.9—6.1 (4H, m). ^{13}C NMR δ=25.4, 28.9, 31.4, 32.9, 45.9, 49.2, 49.9, 72.2 (C=O), 119.8 (*CH*$_2$=CH), 126.7 (*CH*=CH$_2$), 135.4, and 137.4 (cyclohexene C=O). IR 3420 (ν_{OH}) and 1660 ($\nu_{C=C}$) cm^{-1}. Found: C, 79.68; H, 11.41%. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18%.

1-Allyl-5-isopropenyl-2-methyl-2-cyclohexen-1-ol (25): ^{1}H NMR ($CDCl_3$, 90 MHz) δ=1.32—2.61 (5H, m), 1.71 (6H, s), 2.45, 2.50 (2H1, double d, *J*=7, 7 Hz), and 4.70—6.1 (6H including cyclohexene CH=C, m). ^{13}C NMR showed the presence of a diastereomer, δ=18.4, 19.0, 22.1, 22.3, 32.2, 32.5, 38.5, 40.6, 41.9, 42.4, 44.3, 45.8, 73.6, 74.9 (C–O), 110.3, 110.5 (*CH*$_2$=C), 120.0 (*CH*$_2$=CH), 125.2 (CH$_2$=*CH*) 128.2 (*CH*$_2$=C–CH$_3$), 135,1, 135.5 (CH$_2$=C–CH$_3$), 150.3, and 150.5 (CH$_2$=*C*). IR 3460 (ν_{OH}) and 1640 ($\nu_{C=C}$) cm^{-1}. Found: C, 81.79; H, 10.67%. Calcd for $C_{13}H_{20}O$: C, 81.62; H, 10.01%.

6-Allyl-4-(2-hydroxyethoxy)-2,6-Dimethyl-2,4-cyclohexadien-1-one (30): The title compound was obtained by the reaction with 4,4-(ethylenedioxy)-2,5-cyclohexadienone (**29**). ^{1}H NMR ($CDCl_3$, 90 MHz) δ=1.20 (3H, s), 1.88 (3H, s), 2.2—2.6 (2H, m), 2.4—2.5 (1H, m), 3.87 (4H, br s), 4.9—5.9 (3H, m), and 6.71 (1H, br s). ^{13}C NMR δ=15.1, 26.0, 45.9, 48.8, 61.1 (C–O), 68.5 (C–O), 117.7 (*CH*$_2$=CH), 133.5, 134.5, 136.7, 137.9, 148.6, and 204.9 (C=O). IR 3400 (ν_{OH}) and 1640 ($\nu_{C=O}$) cm^{-1}. Found: C, 68.51; H, 8.66%. Calcd for $C_{13}H_{18}O_3$: C, 68.54; H, 8.62%.

2,6-Dimethyl-4-(2-hydroxyethoxy)phenol (31): ^{1}H NMR ($CDCl_3$, 90 MHz) δ=2.24 (6H, s), 3.98 (4H, br s), and 6.6 (2H, m). ^{13}C NMR δ=16.2, 61.5 (C–O), 69.8 (C–O), 115.2, 124.5, 146.6, and 151.9. IR 3380 (ν_{OH}) cm^{-1}.

Reaction of 2-Cyclohexen-1-one with the Trimethylsiloxy Allylcerium Complex (27). The THF (10 cm^3) solution of allyloxytrimethylsilane (**26**) (0.29 g, 2.1 mmol) was added to 20 cm^3 of a two-neck round-bottom flask containing anhydrous $CeCl_3$ (0.18 g, 0.7 mmol) under nitrogen. The flask was cooled to −78 °C and 2.5 cm^3 o *s*-BuLi in hexane solution (1 mol dm^{-1}, 2.5 mmol) was injected. The mixture was stirred for 1 h during which time the temperature was warmed up to −20 °C. The enone **9** (0.20 g, 2 mmol) in 2 cm^3 of THF was added. The cooling bath was removed and the solution was warmed to room temperature. The solution was stirred for 20 min and worked up in the usual way. Flash column chromatography on silica gel gave 0.42 g (1.8 mmol, 90%) of the product **28**. ^{1}H NMR ($CDCl_3$, 400 MHz) δ=0.03 (9H, s), 1.0—2.5 (7H including OH, m), 3.95 (1H, broad peak), and 5.2—6.1 (5H, m). ^{13}C NMR spectrum shows the presence of the diastereomers: δ=0.0, 18.0, 18.4, 25.0, 26.8, 28.5, 30.9, 32.0, 79.7, 80.2, 116.6, 117.1, 128.5, 129.4, 130.7, 131.0, 136.6, and 137.0.

Reaction of Epoxides with Tetraallyllanthanoid Complex in Diethyl Ether. The following example provides a general procedure for the reaction of **1** with epoxides. Diethyl ether solution of **1a** was prepared by the reaction of cerium trichloride, *n*-BuLi and tetraallyltin in diethyl ether described above. Styrene oxide (**32**) (1.6 mmol) in diethyl ether (5 cm^3) was added to the homogeneous solution of **1a** by a 10 cm^3 syringe at room temperature. The solution was stirred at room temperature for 5 h during which time the color of the solution faded out. After usual workup, GLC analysis showed the presence of a mixure of **33** and **34** as products in a ratio of 85 : 15 together with tetrabutyltin. The product was isolated by column chromatography on silica gel; hexane eluted tetrabutyltin and then hexane–diethyl ether (5 : 1) eluted the olefinic alcohols; **34** eluted first and then **33** eluted later. Kugelrohr distillation (oven temperature 180 °C/5 mmHg) gave pure products.

2-Phenyl-4-penten-1-ol (33): ^{1}H NMR ($CDCl_3$, 400 MHz) δ=2.35—2.53 (2H, m), 2.89 (1H, quint, *J*=7.0 Hz), 3.74 (1H, dd, *J*=7.0, 10.8 Hz, CH–OH), 3.81 (1H, dd, *J*=5.7, 10.8 Hz, CH–OH), 4.97 (1H, d, *J*=10.2 Hz), 5.03 (1H, d, *J*=17.1 Hz), 5.84 (1H, tdd, *J*=6.5, 10.8, 17.1 Hz), and 7.2—7.4 (5H, m). ^{13}C NMR δ=36.6, 48.1, 66.9 (C–O), 116.3 (*CH*$_2$=CH), 126.7, 128.0, 128.6, 136.3 (Ph), and 141.9 (CH$_2$=*CH*). IR 3420 (ν_{OH}) and 1620 ($\nu_{C=C}$) cm^{-1}. Found: C, 80.95; H, 8.85%. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70%.

1-Phenyl-4-penten-1-ol (34): ^{1}H NMR ($CDCl_3$, 400 MHz) δ=1.6—1.9 (2H, m), 2.0—2.2 (2H, m), 4.70 (1H, dd, *J*=5.4, 7.8 Hz, CH–OH), 4.99 (1H, dd, *J*=1.0, 10.0 Hz), 5.04 (1H, dd, *J*=1.0, 17.3 Hz), 5.82 (1H, tdd, *J*=6.6, 10.0, 17.3 Hz), and 7.3 (5H, s). ^{13}C NMR δ=29.9, 37.9, 73.8 (C–O), 114.8 (*CH*$_2$=CH), 125.8, 127.4, 128.3, 138.1 (Ph), and 144.6 (CH$_2$=*CH*). IR 3350 (ν_{OH}) and 1620 ($\nu_{C=C}$) cm^{-1}. Found: C, 81.52; H, 8.89%. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70%.

2-Vinyl-4-penten-1-ol (36): ^{1}H NMR ($CDCl_3$, 400 MHz) δ=1.62 (1H, br s, OH), 2.1—2.4 (3H, m), 3.47 (1H, dd, J=7.8, 10.7 Hz), 3.60 (1H, dd, J=4.9, 10.7 Hz), 4.9—5.1 (4H, m, $CH{=}\mathit{CH_2}$), and 5.6—6.0 (2H, m, $\mathit{CH}{=}CH_2$). ^{13}C NMR δ=35.3, 46.1, 65.1 (CH_2-O), 116.2, 116.9 ($\mathit{CH_2}{=}CH$), 136.1, and 139.2 ($CH_2{=}\mathit{CH}$). IR 3460 (ν_{OH}) and 1639 ($\nu_{C=C}$) cm^{-1}. Found: C, 74.82; H, 10.91%. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78%.

1,6-Heptadien-3-ol (37): ^{1}H NMR ($CDCl_3$, 400 MHz) δ=1.4—1.7 (3H including OH, m), 2.2 (3H, m), 4.14 (1H, dt, J=5.9, 6.3 Hz), 4.9—5.3 (4H, several peaks, $CH{=}\mathit{CH_2}$), and 5.8—5.9 (2H, several peaks, $CH_2{=}\mathit{CH}$). Found: C, 74.92; H, 10.80%. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78%.

(*E*)- and (*Z*)-2,6-Heptadien-1-ols (38): ^{1}H NMR ($CDCl_3$, 400 MHz) δ=1.3 (1H, br s, OH), 2.15 (4H, br s), 4.10 (1.6H, d, J=3.5 Hz, $\mathit{CH_2}$OH of E isomer), 4.19 (0.4H, d, J=7.0 Hz, $\mathit{CH_2}$OH of Z isomer), 4.97 (1H, d, J=10.2 Hz), 5.03 (1H, d, J=17.1 Hz), and 5.6—5.9 (3H, m).

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References

1) W. R. Roush, "Allyl Organometallics; Comprehensive Organic Synthesis," ed by B. M. Trost, Pergamon Press, Oxford (1991), Vol. 2, pp. 1—53.

2) a) A. Hosomi and H. Sakurai, *J. Am. Chem. Soc.*, **99**, 1673 (1977); b) R. Pardo, J.-P. Zahra, and M. Santelli, *Tetrahedron Lett.*, **1079**, 4557.

3) Y. Yamamoto, H. Yatagai, Y. Naruta, and K. Maruyama, *J. Am. Chem. Soc.*, **102**, 7107 (1980).

4) Y. Okude, S. Hirano, T. Hiyama, and H. Nozaki, *J. Am. Chem. Soc.*, **99**, 3179 (1977).

5) A. Yanagisawa, S. Habaue, and H. Yamamoto, *J. Am. Chem. Soc.*, **113**, 8955 (1991).

6) M. T. Reetz, "Organotitanium Reagents in Organic Synthesis," Springer Verlag, Berlin (1986).

7) For reviews, a) H. B. Kagan and J. L. Namy, *Tetrahedron*, **42**, 6573 (1986); b) T. Imamoto, "Organocerium Reagents," in "Comprehensive Organic Synthesis," ed by B. M. Trost, Pergamon Press, Oxford (1991), Vol. 1, pp. 231—250; c) G. A. Molander, "Samarium and Ytterbium Reagents," in "Comprehensive Organic Synthesis," Vol. 1, pp. 251—282.

8) For recent examples, a) T. Imamoto, T. Kusumoto, Y. Tawarayama, Y. Sugiura, T. Mita, Y. Hatanaka, and M. Yokoyama, *J. Org. Chem.*, **49**, 3904 (1984); b) T. Imamoto, N. Takiyama, K. Nakamura, T. Hatajima, and Y. Kamiya, *J. Am. Chem. Soc.*, **111**, 4392 (1989); c) L. A. Paquette and K. S. Learn, *J. Am. Chem. Soc.*, **108**, 7873 (1986); d) S. E. Denmark, T. Weber, and D. W. Piotrowski, *J. Am. Chem. Soc.*, **109**, 2224 (1987); e) L. A. Paquette, D. T. DeRussy, T. Vandenheste, and R. D. Rogers, *J. Am. Chem. Soc.*, **112**, 5562 (1990); f) G. A. Molander, E. R. Burkhardt, and P. Weinig, *J. Org. Chem.*, **55**, 4990 (1990); g) K. Utimoto, A. Nakamura, and S. Matsubara, *J. Am. Chem. Soc.*, **112**, 8189 (1990).

9) As examples of allyllanthanoid complexes, a) R. S. P. Coutts and P. C. Wailes, *J. Organomet. Chem.*, **25**, 117 (1970); b) M. Tsutsui and N. Ely, *J. Am. Chem. Soc.*, **97**, 3551 (1975); c) S. Fukuzawa, T. Fujinami, and S. Sakai, *J. Organomet. Chem.*, **299**, 179 (1986); d) M. Brunelli, S. Poggio, U. Pedretti, and G. Lugli, *Inorg. Chim. Acta*, **131**, 281 (1987); e) Z. Huang, M. Chen, W. Qui, and W. Wu, *Inorg. Chim. Acta*, **139**, 203 (1987); f) W. J. Evans, T. A. Ulibarri, and J. W. Ziller, *J. Am. Chem. Soc.*, **112**, 2314 (1990).

10) S. Fukuzawa, K. Sato, T. Fujinami, and S. Sakai, *J. Chem. Soc., Chem. Commun.*, **1990**, 939.

11) D. Seyferth and M. A. Weiner, *J. Org. Chem.*, **26**, 4797 (1961).

12) a) D. A. Evans, D. J. Baillargeon, and J. V. Nelson, *J. Am. Chem. Soc.*, **100**, 2242 (1978); b) L. Wartski and M. El Bouz, *Tetrahedron*, **38**, 3285 (1982).

13) N. H. Werstiuk, *Tetrahedron*, **39**, 205 (1982).

14) a) D. A. Evans, G. C. Andrews, and D. J. Baillargeon, *J. Am. Chem. Soc.*, **96**, 5560 (1974); b) W. C. Still and T. L. Macdonald, *J. Am. Chem. Soc.*, **96**, 5561 (1974); *idem*, *J. Org. Chem.*, **41**, 3620 (1976).

15) Cohen et al. applied 1,2-regioselective allylation of α-unsaturated carbonyl compounds with allylcerium reagents generated from allyl sulfides to synthesis of several pheromones. This work is consistent with our results. a) B.-S. Guo, W. Doubleday, and T. Cohen, *J. Am. Chem. Soc.*, **109**, 4710 (1987); b) W. D. Abraham and T. Cohen, *J. Am. Chem. Soc.*, **113**, 2313 (1991).

16) a) J.-L. Luche, *J. Am. Chem. Soc.*, **100**, 2226 (1978); b) J.-L. Luche, L. Rodriguez-Hahn, and P. Crabbe, *J. Chem. Soc., Chem. Common.*, **1978**, 601; c) A. L. Gemal and J.-L. Luche, *J. Am. Chem. Soc.*, **103**, 5454 (1981).

17) S. Fukuzawa, T. Fujinami, S. Yamauchi, and S. Sakai, *J. Chem. Soc., Perkin Trans. 1*, **1986**, 1929.

18) J.-M. Lefour and A. Loupy, *Tetrahedron*, **34**, 2597 (1978).

19) D. Liotta, M. Saindane, and L. Waykole, *J. Am. Chem. Soc.*, **105**, 2922 (1983).

20) K. S. Rein, Z.-H. Chen, P. T. Perumal, L. Echegoyen, and R. E. Gawley, *Tetrahedron Lett.*, **32**, 1941 (1991).

21) J. G. Smith, *Synthesis*, **1984**, 629.

22) a) B. H. Lipshutz, R. Crow, S. H. Dimock, E. L. Ellsworth, *J. Am. Chem. Soc.*, **112**, 4063 (1990); b) B. H. Lipshutz, C. Ung, T. R. Elworthy, and D. C. Reuter, *Tetrahedron Lett.*, **31**, 4539 (1990); c) B. H. Lipshutz, E. L. Ellsworth, S. H. Dimock, and R. A. J. Smith, *J. Am. Chem. Soc.*, **112**, 4404 (1990).

23) T. Tanaka, T. Inoue, K. Kamei, K. Murakami, and C. Iwata, *J. Chem. Soc., Chem. Common.*, **1990**, 906.

24) I. Mukerji, A. Wayda, G. Dabbagh, and S. H. Bertz, *Angew. Chem., Int. Ed. Engl.*, **25**, 760 (1986).

25) Regioselectivity is not observed in the reaction of butyllithium with **32** in THF. M. J. Eis, J. E. Wrobel, and B. Ganem, *J. Am. Chem. Soc.*, **106**, 3693 (1984).

26) V. Gutmann, "Coordination Chemistry in Non-Aqueous Solutions," Springer, Berlin (1968).

27) A. R. Pray, *Inorg. Synth.*, **5**, 153 (1957).

28) a) M. Fishwick and M. G. H. Wallbridge, *J. Organomet. Chem.*, **25**, 69 (1970); b) G. Daude and M. Pereyre, *J. Organomet. Chem.*, **190**, 43 (1980).