Pergamon

Tetrahedron Vol. 51, No. 15, pp. 4507-4518, 1995

0040-4020/95 $9.50+0.00

0040-4020(94)01137-0

Generation of Allylic and Related Organozirconiums Through A Highly Effective Zirconium—β-Alkoxide Elimination Reaction

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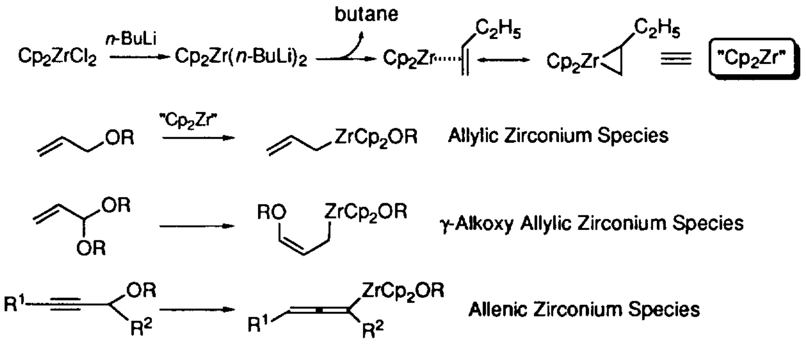
Abstract: Reactions and characterization of allylic and related zirconium reagents (allenic and γ-alkoxyallylic zirconiums) generated by treatment of allylic and/or propargylic ethers with a zirconocene-butene complex ("Cp_2Zr") are described.

Introduction

Allylic and related organometals are the important reagents in the current organic synthesis.[1-3] While many procedures for generating allylic metals have been reported, the benefits of preparation for allylic metal species from easily accessible and stable starting materials under mild conditions is significant.[4]

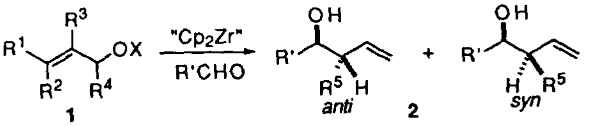
Recently low-valent zirconium species have been attracting a great deal of attention owing to its wide applicability to organic synthesis.[5] Since the discovery of a convenient method for generating low-valent zirconium species as a zirconocene equivalent ("Cp_2Zr") (Cp = cyclopentadienyl), organic synthesis by using "Cp_2Zr" has been extensively developed.[6] This reagent generated *in situ* from zirconocene dichloride (Cp_2ZrCl_2) and two equiv of n-butyllithium (-78 °C – ambient temperature) has been known to exist as a zirconocene-butene complex and reacts with unsaturated compounds to form corresponding zirconacycles.[5] It is also known that the oxophilic nature of zirconium metal causes the β-elimination of the alkoxyl group at β-position of the zirconium metal to form an unsaturated compound.[7] By applying these characters of zirconium compounds to organic reactions, we have reported effective preparations of allylic and related organozirconium species through reactions of "Cp_2Zr" with allylic ethers, α,β-unsaturated aldehyde acetals and propargylic ethers (Scheme 1).[8] We disclose herein a full account on those preparations.

Scheme I



Results and Discussion

Allylic Zirconium Species. Although the generation of the allylic zirconium species through transmetalation[9] of allylmagnesium bromide with zirconium complex or hydrozirconation[10] of allenyl compound has been reported, the synthetic significance of these species would be greatly enhanced if the allylic zirconium species could be prepared from chemically stable allylic ethers under mild conditions. We found that the reaction of allyl silyl ether with "Cp_2Zr" generated *in situ* (-78 °C – ambient temperature) in THF followed by addition of benzaldehyde gave an allylated product (eq 1). A survey of other allylic ethers by the present procedure and the following reactions with aldehydes are summarized in Table I. In all cases examined, homoallylic alcohols were obtained regio and *anti* selectively. The diastereoselectivities of the products showed a similar tendency to previous results of allylic zirconium species.[9a,b,10] Therefore, in the present procedure, the generation of allylic zirconium species in a reaction media is considered (*vide infra*). It is noteworthy that the diastereoselectivity of the product was increased with the bulkier leaving alkoxyl group. Thus, higher diastereoselectivities were observed with benzyloxyl and t-butyldimethylsiloxyl derivatives (**1c**, **1d**) (15-23 : 1) compared to that of the methoxyl derivative (**1b**) (10 : 1) (entries 2, 3, 4). Cinnamyl ether derivatives (**1b**-**1d**) and its regioisomer, α-alkoxyallylbenzene (**1e**, entry 5), gave an identical product **2b** in a similar diastereomeric ratio. Aliphatic and α,β-unsaturated aldehydes also gave 1,2-adduct (entries 6, 7). The diastereomeric ratio was not affected by the olefinic geometry of the starting allylic ethers (entries 8, 9). Tri-substituted olefin **1l** required a higher temperature (50 °C) and a longer reaction time (10 h) to obtain a fair amount of product **3**, also a significant amount of **1l** was recovered (entry 14).[11] An examination of the enantioselective allylation of carbonyl compounds by treating optically pure allyl ethers (e.g., allyl (D)-menthyl ether, etc.) with "Cp_2Zr" followed by addition of carbonyl compounds failed to yield optically enriched product.[12]

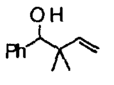


(1)

Table I. Preparation and Reaction of Allylic Zirconium Species with Aldehyde

entry	substrate no.	R^1	R^2	R^3	R^4	X	R'CHO	product no.	R^5	yield (%)[a]	*anti* : *syn*[b]
1	**1a**	H	H	H	H	TBDMS	PhCHO	**2a**	H	60	——
2	**1b**	Ph	H	H	H	Me	PhCHO	**2b**	Ph	79	10 : 1
3	**1c**	Ph	H	H	H	Bn	PhCHO	**2b**	Ph	89	15 : 1
4	**1d**	Ph	H	H	H	TBDMS	PhCHO	**2b**	Ph	96	23 : 1
5	**1e**	H	H	H	Ph	TBDMS	PhCHO	**2b**	Ph	93	19 : 1
6	**1d**	Ph	H	H	H	TBDMS	iPrCHO	**2c**	Ph	96	49 : 1
7	**1d**	Ph	H	H	H	TBDMS	Ph⁀CHO	**2d**	Ph	92	15 : 1
8	**1f**[c]	Me	H	H	H	Bn	PhCHO	**2e**	Me	76	1.8 : 1
9	**1g**[d]	H	Me	H	H	Bn	PhCHO	**2e**	Me	67	1.9 : 1
10	**1h**[e]	Me	H	H	H	TBDMS	PhCHO	**2e**	Me	77	2.0 : 1
11	**1i**	H	H	H	Me	TBDMS	PhCHO	**2e**	Me	70	2.1 : 1
12	**1j**[f]	c-Hex	H	H	H	TBDMS	PhCHO	**2f**	c-Hex	90	10 : 1
13	**1k**[f]	H	H	H	c-Hex	TBDMS	PhCHO	**2f**	c-Hex	84	16 : 1
14	**1l**[f]	Me	Me	H	H	TBDMS	PhCHO	**3**	see below	41[g]	——
15	**1m**[f]	H	H	Me	H	TBDMS	PhCHO	**4**	see below	84	——

[a] Isolated yield. [b] The ratio was determined by GLC or ^1H NMR. [c] *E* : *Z* = 15 : 1. [d] *E* : *Z* = 1 : 13. [e] *E* : *Z* = 21 : 1. [f] 1.5 equiv of "Cp_2Zr" was employed. The allylic zirconium species was formed at 50 °C. [g] Starting allylic ether **1l** was recovered.



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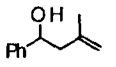

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In the present procedure, the formation of an allylic zirconium species can be explained in terms of the initial formation of zirconacyclopropane followed by elimination of the β-alkoxyl group (Scheme 2) from the following facts. (1) The addition of "Cp_2Zr" to allylic ether was greatly influenced by the substituent of olefin. (2) The geometrical isomers (**1d**, **1e**) and regioisomers of the allylic alcohol gave identical product with similar diastereoselectivities. (3) The organozirconium compound prepared by the reaction of **1c** with "Cp_2Zr" was characterized spectroscopically and converted to **2b** by addition of benzaldehyde. The NMR data of the organozirconium intermediate showed that the reactive species exists as an (*E*)-allylic zirconium (Figure 1). Thus, we conclude that the formation of the (*E*)-allylic zirconium species was initiated by the reaction of "Cp_2Zr" with the double bond of allylic ethers **1** to form zirconacyclopropane followed by elimination of the β-alkoxyl group. When a steric repulsion between α-substituent and the ligands of zirconium metal is notable in the initially formed allylic zirconium species, zirconium metal is shifted to a less hindered site of the allyl moiety through 1,3-metallotropic rearrangement to give a thermodynamically more stable allylic zirconium derivative (Scheme 2).[9b]

Scheme 2

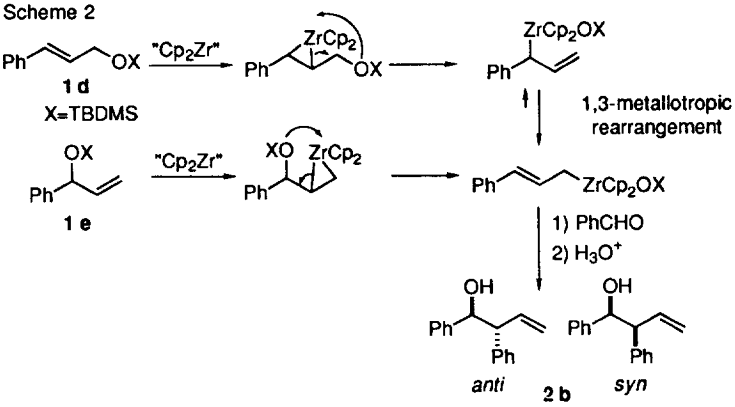
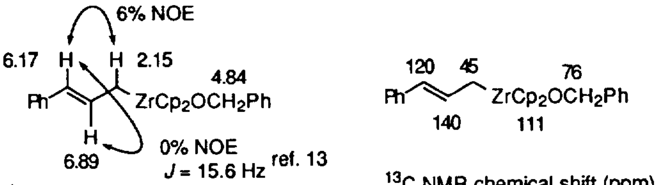


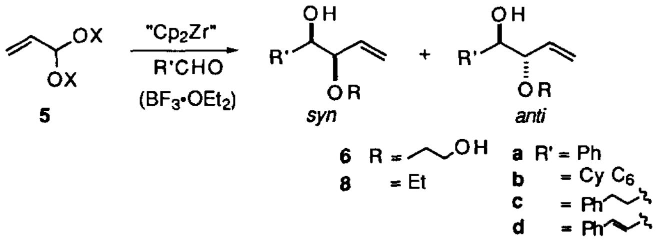
Figure 1



^1H NMR chemical shift (ppm)

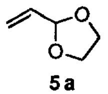
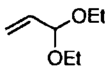
^{13}C NMR chemical shift (ppm)

γ-Alkoxy Allylic Zirconium Species. Application of our "Cp_2Zr"-tactics to α,β-unsaturated aldehyde acetals should make it possible to generate α- or γ-alkoxy allylic zirconium derivatives. γ-Alkoxy allylic zirconium species could be generated from acrolein ethylene acetal (**5a**) and acrolein diethyl acetal (**5b**) with "Cp_2Zr" in toluene. Although the reaction of the γ-alkoxy allylic zirconium species with aldehydes proceeded smoothly to give a mixture of diastereoisomers **6** and/or **8** (eq 2), the ratio of the diastereoselectivity was low. Addition of $BF_3{\bullet}OEt_2$ to the reaction mixture improved the yields and changed to a slight *syn*-selectivity (Table II). In γ-alkoxy allylic zirconium species prepared by transmetalation of the corresponding lithium species with zirconocene dichloride, a similar changing of diastereoselectivity in the reaction with aldehyde under $BF_3{\bullet}OEt_2$ conditions has been reported by Yamamoto et al.[14]

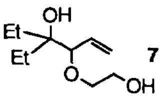


(2)

Table II. Reactions of γ-Alkoxy Allylic Zirconium Reagents with Carbonyl Compounds

entry	substrate	carbonyl compound	Lewis acid[a]	product	yield (%)[b]	*syn* : *anti*[c]
1	 **5a**	PhCHO	A	**6a**	70	35 : 65
2			B		82	71 : 29
3		cy-HexylCHO	A	**6b**	40	13 : 87
4			B		61	67 : 33
5		β-Phenylpropionaldehyde	A	**6c**	—	——
6			B		59	67 : 33
7		Cinnamaldehyde	A	**6d**	52	40 : 60
8			B		71	69 : 31
9		Diethylketone	A	**7** see below	—	——
10			B		60	——
11	 **5b**	PhCHO	A	**8a**	80	57 : 43
12			B		72	78 : 22
13		cy-HexylCHO	A	**8b**	59	14 : 86
14			B		85	77 : 23
15		β-Phenylpropionaldehyde	A	**8c**	—	——
16			B		84	68 : 32
17		Diethylketone	A	**9** see below	—	——
18			B		43	——

[a] A: No Lewis acid was used. B: 1.3 eq. of $BF_3{\cdot}OEt_2$ was used. [b] Isolated yield.
[c] Ratio was determined by 300 MHz ^1H NMR.



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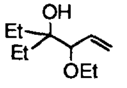

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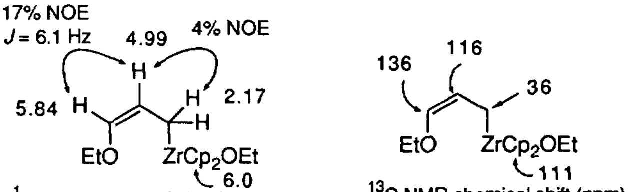
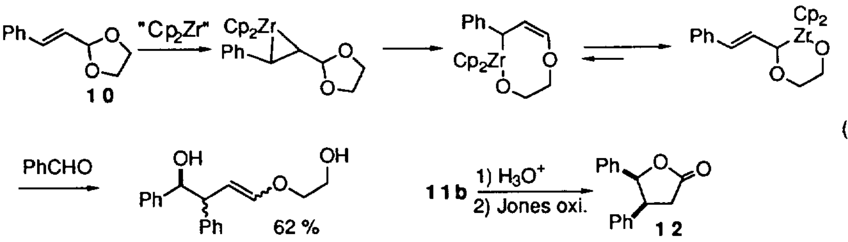
The intermediate generated from **5b** was confirmed to be γ-ethoxy (*Z*)-allylic zirconium species by the NMR experiments (^1H, ^{13}C and NOE experiment) (Figure 2). It is probable that the oxygen of the γ-alkoxyl group coordinates to zirconium metal due to the oxophilicity of zirconium and the proper proximity.[15]

Figure 2



^1H NMR chemical shift (ppm) ^{13}C NMR chemical shift (ppm)

The reaction of cinnamaldehyde ethylene acetal (**10**) with "Cp_2Zr" followed by addition of benzaldehyde gave compound **11** in 62 % yield. This observation implies that the allylic zirconium species reacted as a homoenolate anion of aldehyde. The primarily formed allylic zirconium intermediate rearranged to the less hindered α-alkoxy allylic zirconium species, which then reacted as a homoenolate anion equivalent (eq 3). The relative stereochemistry of the unstable enol ether **11** was determined by converting to the known compound **12**[16] in two steps. The geometry of the double bond of **11** was determined by the coupling constants and the NOE correlations of olefinic protons.

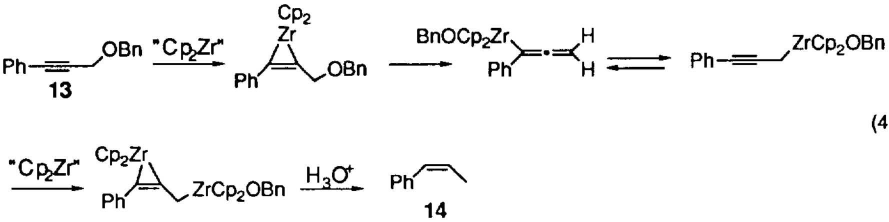


(3)

11a *anti Z* 42.4 % *anti E* 3.8 %

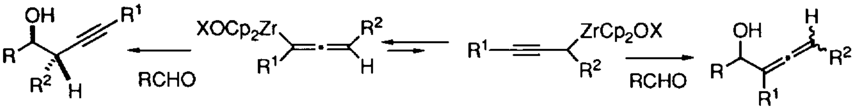
11b *syn Z* 8.8 % *syn E* 45.0 %

Allenic Zirconium Species. The allenic zirconium species is one of the promising candidates in the reaction of propargylic ether with "Cp_2Zr". Since the acetylenic proton disturbs the reaction of "Cp_2Zr" with triple bond, propargylic ether that has terminal acetylene can not be used as substrate.[17] In the reaction of propargylic ether derivative **13** with an equimolar amount of "Cp_2Zr", (*Z*)-β-methylstyrene (**14**) along with the recovered starting substrate could be obtained after acidic quenching (1N HCl). Two equimolar amounts of "Cp_2Zr" are required for the consumption of the starting propargylic ether **13**. Under these conditions, **14** was obtained as a sole product and no starting substrate was detected by ^1H NMR spectrum of the crude reaction mixture. It is thus suggested that the addition rate of "Cp_2Zr" to propargylic ether **13** must be slower than the addition of second "Cp_2Zr" to the propargyl zirconium species to explain the result of the equimolar experiment (eq 4).



(4)

To prevent the addition of the second "Cp_2Zr", suppressing the 1,3-zirconium rearrangement to propargylic zirconium species is required. Thus, the substrate must possess the substituent at the propargylic position of starting propargylic ether to exist, preferably as an allenic zirconium, in an equilibrium between allenic and propargylic zirconium (eq 5). The reactions of propargylic ethers **15** with "Cp_2Zr" and the subsequent reaction of aldehyde in the presence of $BF_3•OEt_2$ (eq 6) are listed in Table III.



(5)

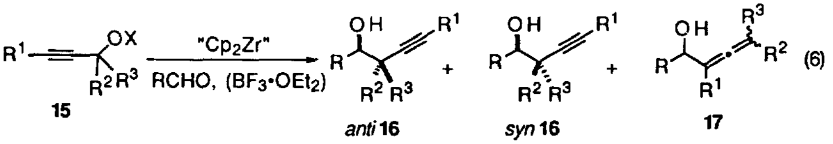


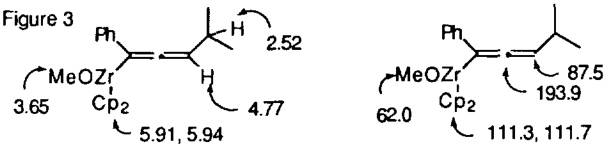
Table III. Preparation and Reactions of Allenic Zirconium Species with Aldehyde

entry	substrate	R^1	R^2	R^3	X	aldehyde	product series	16 : 17[a]	*anti* 16 : *syn* 16[a]	yield (%)[b]
1	**15a**	Ph	Me	H	Bn	PhCHO	**a**	79 : 21	3 : 1	19[c]
2	**15a**	Ph	Me	H	Bn	PhCHO	**a**	86 :14	3 : 1	80
3	**15a**	Ph	Me	H	Bn	c-HexCHO	**b**	97 : 3	31 : 1	23[c]
4	**15a**	Ph	Me	H	Bn	c-HexCHO	**b**	94 : 6	>49 : 1[d]	76
5	**15b**	Ph	Me	H	Me	c-HexCHO	**b**	95 : 5	29 : 1	65
6	**15c**	Ph	Me	H	TBDMS	PhCHO	**a**	58 : 42	3 : 1	49
7	**15c**	Ph	Me	H	TBDMS	c-HexCHO	**b**	>98 : 2[d]	22 : 1	73
8	**15d**[e]	Ph	Me	Me	Bn	PhCHO	**c**	>98 : 2[d]	——	51[c]
9	**15e**	Ph	i-Propyl	H	Bn	PhCHO	**d**	98 : 2	3 : 1	89
10	**15e**	Ph	i-Propyl	H	Bn	c-HexCHO	**e**	>98 : 2[d]	49 : 1	86
11	**15f**	TMS	Me	H	Bn	PhCHO	**f**	80 : 20	2 : 1	49
12	**15f**	TMS	Me	H	Bn	c-HexCHO	**g**	78 : 22	5 : 1	49
13	**15g**[e]	n-Hexyl	Me	H	Bn	PhCHO	**h**	>98 : 2[d]	——	68[c]

[a] Ratios of regio- and diastereoisomers were determined by ^{1}H NMR. [b] Isolated yield. [c] Reaction of allenic zirconium species with aldehyde in the absence of $BF_3{\bullet}OEt_2$ was carried out at 50 °C overnight. [d] None of the minor isomers could be detected. [e] The allenic zirconium species was formed at 50 °C.

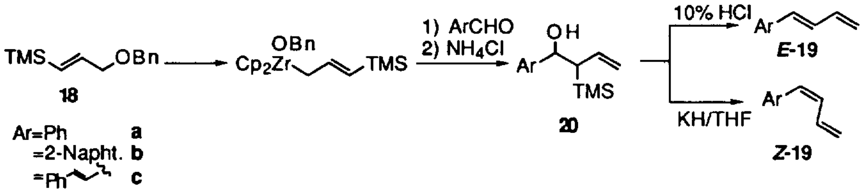
The existence of allenic zirconium species prepared from **15a** was proved by the typical IR absorption at 1900 cm^{-1}. Furthermore, the sole existence of the allenic zirconium species generated from **15h** (R^1=Ph, R^2=i-Pr, R^3=H, X=OMe) was confirmed by the ^{1}H and ^{13}C NMR spectra (Figure 3). In according to the allenic titanium reagent reported by Yamamoto et al.,[18] the regioselectivity of product was mainly influenced by substituents.

Figure 3



^{1}H NMR chemical shift (ppm) ^{13}C NMR chemical shift (ppm)

As a simple application of our present strategy to the organic synthesis, preparation of terminal diene derivatives was carried out by the reaction of a silylated allylic zirconium derivative with aldehydes (eq 7). Reaction of (*E*)-β-trimethylsilylallyl benzyl ether (**18**) with "$ZrCp_2$" at -78 ~ 50 °C and the subsequent reaction with aromatic aldehydes gave terminal *E*-diene compounds under the acidic (10 % HCl) workup in 63~87 % yields. Quenching of the reaction mixture with aqueous NH_4Cl gave silyl alcohol (**20a**) (86 %) as a single diastereoisomer that was directly converted to Z-diene upon treatment with potassium hydride in 40~60 % yields. Thus, it is possible to prepare *E*- or *Z*- terminal diene **19** by the standard Peterson olefination protocol. In the reaction of aliphatic aldehyde, however, we could not obtain a satisfiable yield of the product (less than 40 %). Recently, Suzuki et al. reported essentially the same procedure as ours for the preparation of terminal dienes, in which they used the hydrozirconation of tri-n-butylstannyl allene to generate a stannylallylic zirconium derivative as a bimetallic reagent.[19]



(7)

Conclusion

In summary, we showed that the β-elimination of the alkoxyl group from zirconacycle allows us to effectively prepare allylic, γ-alkoxy allylic and allenic zirconium species from the corresponding ethers or acetals under very mild conditions. The structure of each of the organometallics was characterized spectroscopically. Of particular interest is the *Z*-stereochemistry of γ-alkoxy allylic zirconium while the stereochemistry of the allylic zirconium is *E*-geometry. Allylic and other organozirconium species prepared by our strategy are of considerable synthetic utility.

Experimental Section

All reactions were performed under an argon atmosphere using a standard Schlenk technique. THF was distilled from sodium benzophenone ketyl before use. Toluene and benzene-d_6 were distilled from calcium hydride and stored under an argon atmosphere. Zirconocene dichloride was purchased from Tokyo Kasei Kogyo and used without further purification. n-Butyllithium was purchased from Aldrich Chemical Co. as hexane solution. Proton (^1H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were measured in chloroform-d or benzene-d_6 on a Varian Gemini-300 or a Bruker AM-400. NMR chemical shifts are given in parts par million (ppm) in reference to the 7.26 ppm peak for $CDCl_3$. Infrared spectra (IR) were obtained on a Perkin-Elmer 1710 spectrometer. High-resolution mass spectra (HRMS) were obtained on VG Auto Spec. Melting points were uncorrected.

General Procedure for the Preparation of Allylic Zirconium Species and Reaction with aldehyde. To a solution of Cp_2ZrCl_2 (248 mg, 0.85 mmol) in THF (3 mL) was added a solution of n-butyllithium (1.45 M in hexane, 1.17 mL, 1.7 mmol) at -78 °C and the mixture was stirred at the same temperature for 1 h. A solution of **1** (0.65 mmol) in THF (2 mL) was added to the above reaction mixture at -78 °C and the temperature was raised to ambient temperature. After being stirred for 3 h, a solution of aldehyde (0.98 mmol) in THF (2 mL) at 0 °C was added to the reaction mixture, and the resulting mixture was stirred at ambient temperature for 2 h. 1N HCl was added to the reaction mixture and the resulting mixture was extracted with ether. The organic layer was washed with brine and dried over magnesium sulfate. Evaporation of the solvent under reduced pressure and purification of the residue by silica gel column chromatography (hexane : AcOEt) afforded **2**.

The structures of products **2b**,[20a] **2c**,[20b] **2d**,[20b] **2e**,[20c] **2f**[20d] were confirmed by comparing the spectroscopic data with the authentic samples in the literature.

General Procedure for the Preparation of γ-Alkoxy Allylic Zirconium Species and Reaction with aldehyde. To a solution of Cp_2ZrCl_2 (222 mg, 0.72 mmol) in toluene (4 mL) was added a solution of n-butyllithium (1.5 M in hexane, 0.96 mL, 1.44 mmol) at -78 °C and the mixture was stirred at the same temperature for 1 h. A solution of **5** (0.655 mmol) in toluene (2 mL) was added to the reaction mixture at -78 °C and the temperature was raised to ambient temperature. After being stirred for 3 h, a solution of aldehyde (0.8 mmol) in toluene (2 mL) (and 0.8 mmol of $BF_3{\bullet}OEt_2$) was added at -78 °C and the mixture was stirred at the same temperature for 3 h. 1N HCl was added to the reaction mixture, and the mixture was extracted with dichloromethane. The organic layer was washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure. Purification of crude material with silica gel column chromatography afforded a diastereomeric mixture of **6**.

The structure of products **6a**,[21a] **6c**,[21a] **8a**[21b] were confirmed by comparison to spectroscopic values of authentic samples in the literature.

1-Cyclohexyl-2-(2-hydroxyethoxy)but-3-en-1-ol (6b). (*syn* : *anti* = 67 : 33). *Syn* and *anti* isomers of the corresponding dibenzoate were separated by silica gel column chromatography (hexane : AcOEt, 5 : 1). Alkaline hydrolysis of the less polar fraction provided pure *syn*-**6b**. IR (neat) vcm^{-1}; 3363. ^{1}H NMR (400 MHz, $CDCl_3$) δ; 1.14-1.75 (m, 11 H), 2.67 (br s, 1 H), 3.31 (dd, J = 3.7, 7.0 Hz, 1 H), 3.40 (ddd, J = 3.2, 6.1, 9.4 Hz, 1 H), 3.65-3.75 (m, 4 H), 5.28 (d, J = 16.7Hz, 1 H), 5.29 (d, J = 10.9Hz, 1 H), 5.70 (ddd, J = 7.9, 10.9, 16.7 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ; 26.2, 26.3, 26.4, 26.5, 30.3, 39.3, 61.9, 69.9, 77.8, 83.0, 119.1, 135.4. Alkaline hydrolysis of the more polar fraction provided pure *anti*-**6b**. IR (neat) vcm^{-1}; 3418. ^{1}H NMR (400 MHz, $CDCl_3$) δ; 1.0-1.8 (m, 10 H), 1.99 (br d, J = 12.6 Hz, 1 H), 2.09 (br s, 2 H), 3.49 (dd, J = 4.0, 7.7 Hz, 1 H), 3.4-3.75 (m, 4 H), 3.79 (dd, J = 4.0, 8.1 Hz, 1 H), 5.30 (ddd, J = 0.8, 1.8, 17.3 Hz, 1 H), 5.38 (ddd, J = 0.4, 1.8, 10.4 Hz, 1 H), 5.85 (ddd, J = 8.1, 10.4, 17.3 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ; 25.9, 26.0, 26.5, 28.6, 29.0, 39.3, 62.0, 69.8, 76.8, 82.5, 120.0, 134.0. HRMS m/z calcd for $C_{12}H_{22}O_3$ (M^+) 214.1569, found 214.1590.

4-(2-Hydroxyethoxy)-1-phenylhexa-2,5-dien-3-ol (6d). (*syn* : *anti* = 69 : 31) *Syn* and *anti* isomers of the corresponding diaceate were separated by silica gel column chromatography (hexane : AcOEt, 6 : 1). Alkaline hydrolysis of the less polar fraction provided pure *anti*-**6d**. IR (neat) vcm^{-1}; 3316. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 3.48-3.76 (m, 6 H), 3.90 (dd, J = 3.3, 7.6 Hz, 1 H), 4.40 (ddd, J = 1.1, 3.3, 6.9 Hz, 1 H), 5.29 (br d, J = 16.8 Hz, 1 H), 5.31 (br d, J = 7.7 Hz, 1 H), 5.79 (ddd, J = 7.7, 10.9, 16.8 Hz, 1 H), 6.25 (dd, J = 6.9, 16.0 Hz, 1 H), 6.61 (d, J = 16.0 Hz, 1 H), 7.22-7.39 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 61.6, 70.2, 74.6, 84.6, 119.5, 126.5, 127.4, 127.6, 128.5, 132.2, 134.4, 136.6. Alkaline hydrolysis of the more polar fraction provided pure *syn*-**6d**. mp 81-83 °C. IR (KBr) vcm^{-1}; 3245. ^{1}HNMR (300 MHz, $CDCl_3$) δ; 3.46-3.81 (m, 5 H), 4.07 (br s, 2 H), 4.25 (ddd, J = 1.2, 6.5, 7.9 Hz, 1 H), 5.29 (d, J = 17.5 Hz, 1 H), 5.30 (d, J = 10.0 Hz, 1 H), 5.72 (ddd, J = 7.6, 10.0, 17.5 Hz, 1 H), 6.18 (dd, J = 6.5, 16.0 Hz, 1 H), 6.68 (d, J = 16.0 Hz, 1 H), 7.23-7.38 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 61.6, 70.1, 74.7, 85.3, 119.6, 126.5, 127.5, 127.6, 128.4, 132.0, 134.8, 136.6. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.65; H, 7.69.

2-Ethyl-4-(2-hydroxyethoxy)hex-5-en-3-ol (7). IR (neat) vcm^{-1}; 3377. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 0.85 (t, J = 7.6 Hz, 3 H), 0.88 (t, J = 7.5 Hz, 3 H), 1.3-1.67 (m, 4 H), 2.79 (br s, 2 H), 3.34-3.74 (m, 4 H), 3.60 (d, J = 8.1 Hz, 1 H), 5.25 (dd, J = 17.2, 1.7 Hz, 1 H), 5.32 (dd, J = 10.5, 1.7 Hz, 1 H), 5.77 (ddd, J = 17.2, 10.5, 8.1 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 7.3, 7.6, 26.7, 27.4, 61.9, 70.1, 75.9, 85.7, 119.4, 134.6. HRMS m/z calcd for $C_{10}H_{19}O_2$ (M^+ - OH) 171.1385, found 171.1368.

1-Cyclohexyl-2-ethoxybut-3-en-1-ol (8b). *Syn* and *anti* isomer were separated by silica gel column chromatography (hexane : AcOEt, 15 : 1), (*syn* : *anti* = 77 : 23). Less polar fraction: *syn*-**8b**, IR (neat) vcm^{-1}; 3461. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.16 (t, J = 7.0 Hz, 3 H), 1.13-1.73 (m, 11 H), 2.55 (br s, 1 H), 3.22 (dd, J = 3.5, 6.9 Hz, 1 H), 3.26-3.61 (m, 2 H), 3.63 (dd, J = 6.9, 7.9 Hz, 1 H), 5.23 (d, J = 16.4 Hz, 1 H), 5.25 (d, J = 11.1 Hz, 1 H), 5.66 (ddd, J = 7.9, 11.1, 16.4 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 15.2, 26.2, 26.3, 26.4, 26.5, 30.3, 39.2, 63.8, 77.5, 82.2, 118.6, 135.9. More polar fraction: *anti*-**8b**, IR (neat) vcm^{-1}; 3486. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.0-1.8 (m, 10 H), 1.18 (t, J = 7.0 Hz, 3 H), 2.0 (br d, J = 12.7 Hz, 1 H), 2.2 (br s, 1 H), 3.3-3.6 (m, 2 H), 3.44 (dd, J = 4.1, 7.7 Hz, 1 H), 3.72 (dd, J = 4.1, 8.1 Hz, 1 H), 5.26 (dd, J = 1.9, 17.3 Hz, 1 H), 5.33 (dd, J = 1.9, 10.5 Hz, 1 H), 5.82 (ddd, J = 8.1, 10.5, 17.3 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 15.3, 25.9, 26.0, 26.5, 28.6, 28.9, 39.1, 63.8, 76.9, 81.7, 119.3, 134.5. Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.55; H, 11.05.

4-Ethoxy-1-phenylhex-5-en-3-ol (8c). Syn and anti isomers were separated by silica gel column chromatography (hexane : AcOEt, 7 : 1) (*syn* : *anti* = 68 : 32). Less polar fraction: *syn*-**8c**, IR (neat) νcm^{-1}; 3469. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.22 (t, *J* = 7.0 Hz, 1 H), 1.68-1.82 (m, 2 H), 2.71 (ddd, *J* = 6.9, 9.9, 13.7 Hz, 1 H), 2.88 (br s, 1 H), 2.89 (ddd, *J* = 5.2, 10.2, 13.7 Hz, 1 H), 3.3-3.8 (m, 4 H), 5.28 (dd, *J* = 1.8, 16.9 Hz, 1 H), 5.31 (dd, *J* = 1.8, 10.6 Hz, 1 H), 5.64 (ddd, *J* = 7.1, 10.6, 16.9 Hz, 1 H), 7.16-7.32 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 15.2, 31.8, 34.3, 64.1, 72.5, 85.1, 119.6, 125.7, 128.3, 128.5, 135.5, 142.3. More polar fraction: *anti*-**8c**, IR (neat) νcm^{-1}; 3462. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.19 (t, *J* = 7.1 Hz, 3 H), 1.71-1.79 (m, 2 H), 2.26 (br d, *J* = 3.5 Hz, 1 H), 2.66 (dt, *J* = 8.5, 13.7 Hz, 1 H), 2.88 (dt, *J* = 7.4, 13.7 Hz, 1 H), 3.3-3.62 (m, 2 H), 3.63 (dd, *J* = 3.9, 7.0 Hz, 1 H), 3.71 (bs, 1 H), 5.27 (dd, *J* = 1.8, 17.2 Hz, 1 H), 5.33 (dd, *J* = 1.8, 10.5 Hz, 1 H), 5.80 (ddd, *J* = 8.3, 10.5, 17.2 Hz, 1 H), 7.18-7.32 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 15.3, 32.1, 34.0, 64.1, 72.4, 84.1, 119.5, 125.7, 128.3, 128.5, 134.9, 142.2. Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.19; H, 9.21.

4-Ethoxy-3-ethylhex-5-en-3-ol (9). IR (neat) νcm^{-1}; 3485. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 0.86 (t, *J* = 7.6 Hz, 3 H), 0.89 (t, *J* = 7.5 Hz, 3 H), 1.18 (t, *J* = 6.9 Hz, 3 H), 1.3-1.66 (m, 4 H), 2.26 (bs, 1 H), 3.26-3.62 (m, 2 H), 3.55 (d, *J* = 8.2 Hz, 1 H), 5.23 (dd, *J* = 17.1, 1.9 Hz, 1 H), 5.29 (dd, *J* = 10.4, 1.9 Hz, 1 H), 5.77 (ddd, *J* = 17.1, 10.4, 8.2 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 7.35, 7.66, 15.2, 26.8, 27.5, 64.2, 75.5, 85.1, 118.8, 135.1. HRMS m/z calcd for $C_{10}H_{20}O_2$ (M^+) 172.1463, found 172.1444.

1,2-Diphenyl-4-(2-hydroxyethoxy)but-3-en-1-ol (11). To a solution of Cp_2ZrCl_2 (491 mg, 1.68 mmol) in toluene (6 mL) was added a solution of n-butyllithium (1.45 M in hexane, 2.32 mL, 3.36 mmol) at -78 °C and the mixture was stirred at the same temperature for 1 h. A solution of cinnamaldehyde ethylene acetal (**10**) (246 mg, 1.4 mmol) in toluene (3 mL) was added to the reaction mixture at -78 °C and the temperature was raised to ambient temperature. After being stirred for 3 h, a solution of benzaldehyde (178 mg, 1.68 mmol) in toluene (3 mL) at -78 °C was added and the mixture was stirred at ambient temperature for 3 h. Aqueous NH_4Cl was added to the reaction mixture and the mixture was stirred for 1 h. The resulting gel was filtered through celite. The filtrate was diluted with dichloromethane, washed with brine, and dried over magnesium sulfate. The solvent was removed under reduced pressure. Purification of the residue by silica gel column chromatography (hexane-AcOEt, 1 : 1) afforded 245 mg (0.863 mmol, 62 %) of **11a** and **11b** (isomeric ratio E-**11a** : Z-**11a** : E-**11b** : Z-**11b** = 45.0 : 3.8 : 8.8 : 42.4). Less polar fraction: *anti* isomer **11a** (*E*, *Z* mixture) ^{1}H NMR (400 MHz, C_6D_6) δ; 3.22-3.39 (m, 4 H), {3.57 (dd, *J* = 9.1, 7.0 Hz), 4.53 (dd, *J* = 9.7, 6.9 Hz) 1 H}, {4.69 (dd, *J* = 9.7, 6.2 Hz), 5.08 (dd, *J* = 12.6, 9.1 Hz) 1 H}, {4.85 (d, *J* = 7.0 Hz), 4.90 (d, *J* = 6.9 Hz) 1 H}, {5.77 (d, *J* = 6.2 Hz), 6.12 (d, *J* = 12.6 Hz) 1 H}, 7.15-7.34 (m, 10 H). More polar fraction: *syn* isomer **11b** (*E*, *Z* mixture) ^{1}H NMR (400 MHz, C_6D_6) δ; {3.30-3.47 (m), 4.37 (dd, *J* = 9.5, 7.8 Hz) 5 H}, {4.71 (d, *J* = 7.2 Hz), 4.75 (d, *J* = 7.8 Hz) 1 H}, {4.88 (dd, *J* = 9.5, 6.2 Hz), 5.28 (dd, *J* = 12.5, 9.7 Hz) 1 H}, {5.92 (d, *J* = 6.2 Hz), 6.26 (d, *J* = 12.5 Hz) 1 H}, 7.15-7.34 (m, 10 H).

General Procedure for the Preparation of Allenic Zirconium Species and Reaction with aldehyde. To a solution of Cp_2ZrCl_2 (210 mg, 0.72 mmol) in THF (4 mL) was added a solution of n-butyllithium (1.5 M in hexane, 0.96 mL, 1.44 mmol) at -78 °C and the mixture was stirred at the same temperature for 1 h. A solution of **15** (0.6 mmol) in THF (2 mL) was added to the reaction mixture at -78 °C and the temperature was raised to ambient temperature. After being stirred for 3 h, a solution of aldehyde (0.9 mmol) containing 0.96 mmol of $BF_3{\bullet}OEt_2$ in THF (2 mL) was added and the mixture was stirred at ambient temperature. 10 % HCl was added to the reaction mixture and the mixture was extracted with ether. The organic layer was washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure to give crude material. Purification of the material by silica gel column chromatography using the indicated solvent system afforded a mixture of **16** and **17**.

The structure of products **16a, 16b, 16f, 16g** were confirmed by comparison to spectroscopic values of authentic samples in the literature.[18b]

2,2-Dimethyl-1,4-diphenylbut-3-yn-1-ol (16c). **16c** : **17c** = >98 : 2. IR (neat) νcm^{-1}; 3446, 2229. ^{1}H NMR (400 MHz, $CDCl_3$) δ; 1.22(s, 3 H), 1.38(s, 3 H), 2.46 (br s, 1 H), 4.60 (s, 1 H), 7.30-7.49 (m, 10 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ; 25.0, 26.2, 38.5, 80.6, 83.2, 94.5, 123.5, 127.7, 127.8, 127.9, 128.2, 131.6, 140.1. Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.33; H, 7.35.

1,4-diphenyl-2-iso-propylbut-3-yn-1-ol (16d). (Hexane : AcOEt, 10 : 1). **16d** : **17d** = 98 : 2. *anti* **13d** : *syn* **13d** = 3 : 1. Less polar fraction: *anti* **16d** mp = 63 °C. IR (KBr) νcm^{-1}; 3309, 2232. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.05 (d, J = 6.7 Hz, 3 H), 1.10 (d, J = 6.7 Hz, 3 H), 1.67 (dhep, J = 4.7, 6.7 Hz, 1 H), 2.85 (dd, J = 7.4, 4.7 Hz, 1 H), 4.77 (d, J = 7.4 Hz, 1 H), 7.31-7.48 (m, 10 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 18.3, 22.0, 28.6, 49.4, 74.4, 85.9, 87.5, 123.2, 126.5, 127.9, 128.0, 128.2, 128.4, 131.7, 142.0. More polar fraction: *syn* **16d** IR (neat) νcm^{-1}; 3398, 2228. ^{1}H NMR (400 MHz, $CDCl_3$) δ; 1.11 (d, J = 6.7 Hz, 3 H), 1.13 (d, J = 6.7 Hz, 3 H), 2.01 (br s, 1 H), 2.20 (dsep, J = 4.2, 6.7 Hz, 1 H), 2.91 (dd, J = 4.2, 8.6 Hz, 1 H), 4.76 (d, J = 8.6 Hz, 1 H), 7.23-7.50 (m, 10 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ; 17.6, 22.1, 27.4, 48.0, 74.8, 85.5, 87.9, 123.7, 126.9, 127.6, 127.7, 127.9, 128.1, 131.5, 143.0. Third fraction: **17d** IR (neat) νcm^{-1}; 3361, 1947. ^{1}H NMR (400 MHz, $CDCl_3$) δ; 0.98 (d, J = 6.8 Hz, 3 H), 0.99 (d, J = 6.8 Hz, 3 H), 2.35 (m, 1 H), 5.70-5.73 (m, 2 H), 7.18-7.45 (m, 10 H). Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.48; H, 7.83.

1-Cyclohexyl-4-phenyl-2-iso-propylbut-3-yn-1-ol (16e). (Hexane : AcOEt, 10 : 1). **16e** : **17e** = >98 : 2. Less polar fraction: *anti* **16e** : *syn* **16e** = 49 : 1. *anti* **16e** IR (neat) νcm^{-1}; 3456, 2224. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.03 (d, J = 6.7 Hz, 3 H), 1.12 (d, J = 6.7 Hz, 3 H), 1.02-2.02 (m, 12 H), 2.57 (dd, J = 7.3, 3.6 Hz, 1 H), 3.39 (dd, J = 7.0, 3.6 Hz, 1 H), 7.26-7.43 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ; 20.4, 21.2, 26.0, 26.3, 26.4, 28.3, 29.6, 42.4, 44.0, 75.2, 85.4, 88.3, 123.5, 127.8, 128.2, 131.6. More polar fraction: *syn* **16e** IR (neat) νcm^{-1}; 3386, 2224. ^{1}H NMR (400 MHz, $CDCl_3$) δ; 1.02 (d, J = 6.7 Hz, 3 H), 1.09 (d, J = 6.7 Hz, 3 H), 1.10-1.87 (m, 11 H), 2.17 (m, 1 H), 2.68 (dd, J = 9.2, 3.4 Hz, 1 H), 3.53 (dd, J = 9.2, 2.7 Hz, 1 H), 7.27-7.42 (m, 5 H). Anal. Calcd for $C_{19}H_{26}O$: C, 84.39; H, 9.69. Found: C, 84.18; H, 9.91.

2,2-Dimethyl-1-phenyldec-3-yn-1-ol (16h). **16h** : **17h** = >98 : 2. **16h** IR (neat) νcm^{-1}; 3467, 2240. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 0.91 (t, J = 7.0 Hz, 3 H), 1.05 (s, 3 H), 1.24 (s, 3 H), 1.27-1.49 (m, 8 H), 2.21 (t, J = 7.0 Hz, 2 H), 2.56 (br s, 1 H), 4.46 (s, 1 H), 7.27-7.41 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ; 14.0, 18.7, 22.5, 24.6, 26.8, 28.5, 28.9, 31.3, 38.0, 80.4, 83.4, 84.7, 127.5, 127.6, 127.7, 140.1.

General Procedure for the Preparation of Terminal Dienes (19).[22] To a suspension of Cp_2ZrCl_2 (380 mg, 1.3 mmol) in toluene (4 mL) was added a solution of n-butyllithium (1.40M in hexane, 1.86 mL, 2.6 mmol) at -78 °C and the mixture was stirred at the same temperature for 1 h. A solution of **18** (220 mg, 1 mmol) in toluene (3 mL) was added to the reaction mixture at -78 °C and the temperature was gradually raised to 50 °C. After being stirred at 50 °C for 2 h, a solution of aldehyde (2 mmol) in toluene (2 mL) was added at 0 °C and the mixture was stirred at the same temperature for 2 h. Quenching of the reaction mixture with 10 % HCl, extraction with ether and evaporation of the solvent gave *E*-diene derivatives (***E*-19a, b, c**) in 63, 87, and 65 % yields. Silylated alcohol **20a** from benzaldehyde was isolated in 86 % by quenching of the reaction mixture with saturated aq NH_4Cl instead of 10 % HCl. Thus, Z-diene derivatives (**Z-19b, c**) were obtained in 60 and 47 % yields by treating the crude silyl alcohol with an equiv amount of KH in THF at ambient temperature.

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(*Received* 25 *July* 1994)