

Regioselective Hydroalumination of Allenes and Their Synthetic Application

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The hydroalumination of a terminal allene, 1,2-nonadiene, with LiAlH_4 in THF using $[\text{TiCl}_2(\text{Cp})_2]$, TiCl_4 , TiCl_3 , ZrCl_4 , and $[\text{ZrCl}_2(\text{Cp})_2]$ catalysts afforded a wide variety of deuterated species by quenching hydroalumination products with D_2O , while $\text{PhB}(\text{OH})_2$ -catalyzed hydroalumination with AlHCl_2 in ether gave >95% pure 1-nonene-3-*d* as predominant product (92%) in high yield. The allylation of benzaldehyde using the $\text{PhB}(\text{OH})_2$ -catalyzed hydroalumination product suggested that the resulting hydroalumination product may be the allylaluminum compound, 2-nonenylaluminum dichloride. Allylation of *trans*-cinnamaldehyde using this allylaluminum compound proceeded with high regioselectivity, leaving the ketone functionality intact. Allylative ring-opening reaction of epoxides was less regioselective. The combination of catalytic $\text{PhB}(\text{OH})_2$ with AlHCl_2 also was effective for the regioselective hydroalumination of the disubstituted allenes, vinylidenecyclohexane and 1-trimethylsilyl-1,2-nonadiene, although the trisubstituted allene, 1-butenylidenecyclohexane, showed nonregioselective orientation results.

Although hydroalumination of allenes is a reasonably convenient method for the generation of allylaluminum compounds, only few studies have been made on this subject.¹⁾ One recent study includes the hydroalumination of allenes with diisobutylaluminum hydride (DIBAH) which gives excellent yields of allylaluminum compounds regioselectively, but this system is not employable for subsequent functionalization due to its inertness towards carbonyl compounds.^{1a)} In hydroalumination of alkenes, several successful examples have been reported which utilize transition metal catalysts²⁾ and organoborane catalysts³⁾ by combining use of inorganic aluminum hydride-type reagents such as LiAlH_4 and AlHCl_2 to effect the smooth hydroalumination. In this context, we have been interested in the development of the regioselective hydroalumination of allenes with inorganic aluminum hydride under the influence of a certain catalyst and its potential application to selective organic synthesis. Here we report the details of the regioselectivity in the hydroalumination of allenes with inorganic aluminum hydrides using various transition metal and organoborane catalysts and the reaction of the regioselectively generated allylaluminum compound with various electrophiles such as carbonyl compounds and epoxides.⁴⁾

Results and Discussion

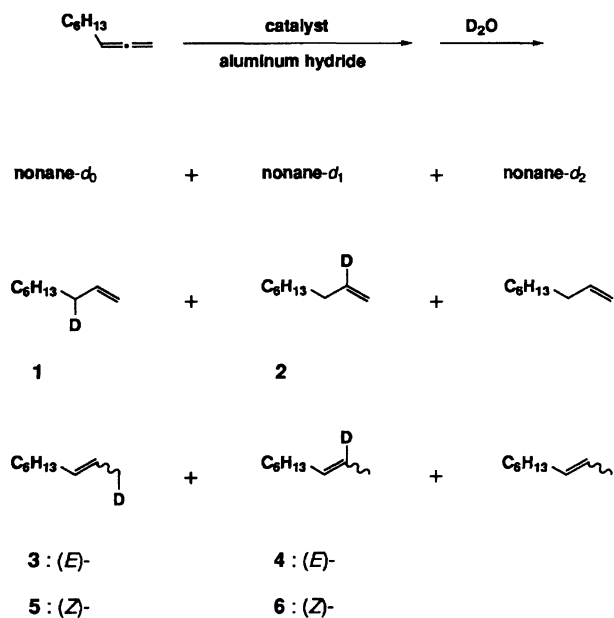
Initially, we studied the hydroalumination of a simple terminal allene, 1,2-nonadiene, with LiAlH_4 (0.25 equiv) in the presence of various transition metal catalysts (2.5 mol%). After the catalytic hydroalumination at 30 °C or under reflux conditions, the reaction was quenched with D_2O at 0 °C to monitor the regioselectivity of reaction under these conditions. As illustrated in Table 1 (Entries 1, 3—6, and 9—11), all of the transition metal catalysts provided a mixture of nonane, 1-nonene, and 2-nonenes. According to mass spectral analysis, the alkenes incorporated a high yield of deuterium

(>90%), but the nonane contained non-deuterated nonane (nonane- d_0), monodeuteriononane (nonane- d_1), and dideuteriononane (nonane- d_2). The ^{13}C NMR (inverse gated decoupling⁵⁾) study of the isolated alkenes indicated that Ti-catalysts and $[\text{ZrCl}_2(\text{Cp})_2]$ catalyst produced a wide variety of deuterated alkenes. A similar tendency of low regioselectivity was also observed in the Ti-catalyzed hydroalumination of conjugated dienes and terminal alkynes.^{2e,2i,2j,6)} In contrast, ZrCl_4 catalyst showed a nearly quantitative yield (>95%) of the deuterium incorporation at the allyl position of each alkene, resulting in a mixture of 1-nonene-3-*d* (**1**), (*E*)-2-nonene-1-*d* (**3**), and (*Z*)-2-nonene-1-*d* (**5**) (Entries 5 and 6) (Scheme 1). Accordingly, we studied some modifications of aluminum hydride using ZrCl_4 -catalyzed hydroalumination to circumvent the problems of low product-selectivity. Use of lithium trihydridopentylaluminate ($\text{Li}[\text{AlH}_3(\text{C}_5\text{H}_{11})]$), which was easily prepared in situ by ZrCl_4 -catalyzed hydroalumination of 1-pentene with LiAlH_4 , has efficiently controlled to give monohydroalumination products and/or to gain regioselectivity in the catalytic hydroalumination of isoprene and 1-alkynes.⁶⁾ The combination of ZrCl_4 catalyst with $\text{Li}[\text{AlH}_3(\text{C}_5\text{H}_{11})]$, however, had no effect on the product ratios in this allene hydroalumination (Entry 7). Hence we anticipated that the combination of ZrCl_4 catalyst with a certain aluminum monohydride might be suitable for effecting the selective hydroalumination if the low product-selectivity in hydroalumination with LiAlH_4 and $\text{Li}[\text{AlH}_3(\text{C}_5\text{H}_{11})]$ is attributable to the steric and electronic requirements of each successive addition step (Eq. 1). Among various aluminum monohydrides, a stronger Lewis acid AlHCl_2 , which can be readily prepared from LiAlH_4 and AlCl_3 , might be expected to be a powerful aluminum hydride agent. When the ZrCl_4 -catalyzed hydroalumination with AlHCl_2 (1.2 equiv) was carried out at 30 °C for 24 h, in fact, the yield of 1-nonene slightly increased (75%), as did the conversion

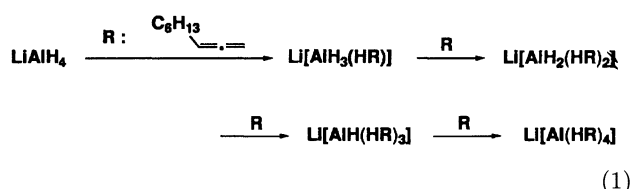
Table 1. Transition Metal-Catalyzed Hydroalumination of 1,2-Nonadiene^{a)}

Entry	Catalyst	Conditions	Yield/% ^{b)}				Conv./% ^{b)}
			Nonane	1-Nonene	(<i>E</i>)-2-Nonene	(<i>Z</i>)-2-Nonene	
1	[TiCl ₂ (Cp) ₂]	LiAlH ₄	16 (5/12/83) ^{c)}	35 (62) ^{d)}	14 (58) ^{e)}	35 (29) ^{f)}	92
2		AlHCl ₂ ^{g)}	2	74 (60)	6	18	95
3	TiCl ₄	LiAlH ₄	23 (17/40/43)	48 (76)	15 (89)	14 (58)	88
4	TiCl ₃	LiAlH ₄	20 (14/51/35)	52 (77)	12 (89)	16 (51)	55
5	ZrCl ₄	LiAlH ₄	25 (11/77/12)	50 (>95)	15 (>95)	10 (>95)	50
6		LiAlH ₄ , reflux ^{h)}	20	62 (>95)	10 (>95)	8 (>95)	72
7		Li[AlH ₃ (C ₅ H ₁₁)] ⁱ⁾	13	64 (>95)	10	13	51
8		AlHCl ₂ ^{g)}	21	75 (>95)	1	3	90
9	[ZrCl ₂ (Cp) ₂]	LiAlH ₄	31	48	13	8	10
10		LiAlH ₄ , reflux ^{h)}	17	48 (59)	16 (82)	19 (46)	61
11	VCl ₃	LiAlH ₄	28 (36/48/16)	39	11	22	16

a) Unless otherwise noted, reaction was carried out in THF at 30 °C for 24 h using transition metal catalysts (2.5 mol%) with LiAlH₄ (0.25 equiv), and was then quenched with D₂O at 0 °C. b) Determined by GLC analysis using the internal standard method. c) Values in parentheses are relative ratio/% of nonane-*d*₀, nonane-*d*₁, and nonane-*d*₂. Determined by mass spectral analysis. d) Relative ratio/% of allyl-deuterated isomer **1** based on **1** and **2**. Determined by ¹³C NMR (inverse gated decoupling) spectra of isolated products. e) Relative ratio/% of allyl-deuterated isomer **3** based on **3** and **4**. f) Relative ratio/% of allyl-deuterated isomer **5** based on **5** and **6**. g) AlHCl₂ (1.2 equiv, prepared from LiAlH₄ (0.3 equiv) and AlCl₃ (0.9 equiv)). h) At 30 °C for 1 h and was then refluxed for 24 h. i) Li[AlH₃(C₅H₁₁)] (0.33 equiv, prepared by ZrCl₄-catalyzed hydroalumination of 1-pentene with LiAlH₄ in THF at 30 °C for 24 h) at 30 °C for 1 h and was then refluxed for 24 h.



of the hydroalumination (90%), although a significant proportion of nonane (21%) was produced (Entry 8). It should be noted that a similar result was also observed in the [TiCl₂(Cp)₂]-catalyzed hydroalumination (Entry 2).



We then studied the possibility of organoborane cat-

alysts with aluminum hydride-type reagents in diethyl ether (Et₂O).³⁾ First, PhB(OH)₂-catalyzed hydroalumination of 1,2-nonadiene was carried out with a slight excess of the stronger Lewis acidic monohydride, AlHCl₂ (1.2 equiv) at room temperature for 4 h, giving 1-nonene (91%) as a major product and a small amount of the nonane and 2-nonenenes in 55% conversion by protonolysis, as indicated in Table 2 (Entry 1). With 2 equivalents of AlHCl₂, the conversion yield increased with the longer reaction time without affecting the product selectivity (Entries 2–4). When the reaction was allowed to continue for 7 h, however, the yield of nonane increased by compensation of the yield of 1-nonene (Entry 5). Therefore, it seems reasonable that the nonane produced in this reaction was a result of dihydroalumination of alkenylaluminum intermediates. In contrast, the use of other aluminum hydrides, AlH₂Cl and AlH₃, lowered the conversion of hydroalumination of 1,2-nonadiene even with a two-fold quantity of hydride and after a prolonged reaction time (24 h) (Entries 6–9). Attempted Et₃B-catalyzed hydroalumination with AlHCl₂ (1.2 equiv) in 1,2-dichloroethane, which has been an effective system for the hydroalumination of internal alkenes,³⁾ resulted in unidentified side products with complete consumption of the starting 1,2-nonadiene (Entry 10). A separate study quenching with D₂O was performed to determine the regioselectivity of PhB(OH)₂-catalyzed hydroalumination with AlHCl₂ (2 equiv), and indicated that 89% of the isolated 1-nonene contained deuterium and this deuterated 1-nonene was >95% pure 1-nonene-3-*d* (**1**) without contamination of any deuterated isomers.

Other selected examples of the allene hydroalumination were studied under similar conditions and

Table 2. Organoborane-Catalyzed Hydroalumination of 1,2-Nonadiene^{a)}

Entry	Catalyst	Conditions	Yield/%			Conv./%
			Nonane	1-Nonene	2-Nonene	
1	PhB(OH) ₂	AlHCl ₂ ^{b)} , 4h	7	91	2	55
2		AlHCl ₂ ^{c)} , 2h	7	90	3	75
3		3h	8	90	2	88
4		4h	9	89	2	95
5		7h	14	81	5	100
6		AlH ₂ Cl ^{d)} , 4h				4
7		24 h				12
8		AlH ₃ ^{e)} , 4 h				0
9		24 h				4
10	Et ₃ B	AlHCl ₂ ^{f)} , 1h				g)

a) Unless otherwise noted, reaction was carried out in Et₂O at room temperature using 5 mol% organoborane catalysts, and was then quenched with a saturated solution of NH₄Cl at 0 °C. b) AlHCl₂ (1.2 equiv) was employed. c) AlHCl₂ (2 equiv). d) AlH₂Cl (2 equiv, prepared from LiAlH₄ (1 equiv) and AlCl₃ (1 equiv)). e) AlH₃ (2 equiv, prepared from LiAlH₄ (1.5 equiv) and AlCl₃ (0.5 equiv)). f) AlHCl₂ (1.2 equiv, prepared from DIBAH (1.2 equiv) and AlCl₃ (2.4 equiv)) in 1,2-dichloroethane. g) Nonane, nonenes, and 1,2-nonadiene were not detected by GLC analysis. See also text.

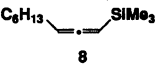
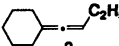
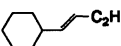
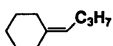
the results are depicted in Table 3. The disubstituted allenenes, vinylidenecyclohexane (**7**) and 1-trimethylsilyl-1,2-nonadiene (**8**), were also successfully hydroaluminated using PhB(OH)₂ catalyst (5–20 mol%) with AlHCl₂, producing >95% pure 1-vinylcyclohexane-1-*d* (**10**) (88–93%) and >95% pure (*E*)-1-trimethylsilyl-1-nonene-3-*d* (**11**) (>99%), respectively (Entries 2, 3, 5, and 6).⁷⁾ However, trisubstituted allene, 1-butenylidenecyclohexane (**9**), afforded an approximately 50/50 mixture of corresponding alkane/alkenes (Entries 9 and 10). The resulting saturated product, butylcyclohexane, was a mixture of monodeuteriobutylcyclohexane (butylcyclohexane-*d*₁) and dideuteriobutylcyclohexane (butylcyclohexane-*d*₂) in 18/82 proportions (Entry 10). Interestingly, this butylcyclohexane-*d*₂ was a 3:1 mixture of the butyl-1,1-*d*₂ compound **12** and butyl-1,2-*d*₂ compound **13** which would have arisen from the dihydroalumination involving di- or monoaddition of aluminum atom on the central allene carbon followed by deuterolysis. These results can be interpreted as follows. According to the mechanism proposed for the transition metal-catalyzed hydroalumination,²⁾ an allene adds to B–H bond in a catalytic boron hydride species formed by the reaction of PhB(OH)₂ with AlHCl₂.⁸⁾ The intermediary alkenylboranes, thus generated, undergo the transmetalation with AlHCl₂ to yield the corresponding alkenylaluminum compounds with regeneration of the active boron hydride.⁹⁾ Therefore, the regiochemistry of reaction may be determined by the formation of the alkenylborane intermediates. Hydroalumination of 1,2-nonadiene and the disubstituted allenenes, **7** and **8**, is considered as resulting in allylborane intermediates, which are observed from terminal attack of the boron atom at the more favored of the two sites of the allenic linkage; hence these exclusively and respectively gave the allyl-deuterated alkenes

(deuterated on α-allylic position), **1**, **10**, and **11**, via the transmetalation followed by deuterolysis (Scheme 2).

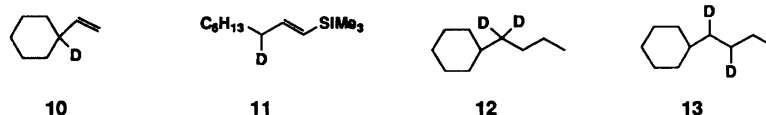
On the other hand, the trisubstituted allene **9** is more susceptible to central attack of the boron atom by the electronic and steric effects of pentamethylene and ethyl substituents on each terminal carbon of this allenyl system,¹⁰⁾ thus this nature causing the nonregioselective hydroalumination due to the formation of a mixture of allyl- and vinylborane intermediates. In Et₃B-catalyzed hydroalumination of these allenenes, unfavorable results were observed, that is, only the corresponding saturated products were provided as hydrolysis products (Entries 4, 7, and 11).¹¹⁾

That the allyl-deuterated alkenes, **1**, **10**, and **11**, are derived from the deuterolysis of the corresponding, more hindered allylaluminum intermediates as hydroalumination products appears extremely doubtful. The reaction of allylic organometallics with electrophiles such as aldehydes and ketones is generally known to proceed through the S_E'-type substitution with a concomitant allylic rearrangement.¹²⁾ Accordingly, we carried out the reaction of PhB(OH)₂-catalyzed hydroalumination product with benzaldehyde to account for the regiochemical feature of hydroalumination products. As shown in Eq. 2, the allylation of benzaldehyde (2 equiv) using the hydroalumination product of 1,2-nonadiene in Et₂O at –78 °C for 0.5 h gave rise to the homoallylic alcohol **15** in 62% yield, suggesting that the intermediary allylaluminum compound **14** actually possesses C–Al bond at less hindered terminal carbon. Consequently, the deuterolysis of allylaluminum intermediates, **14** and **16**, led to the allyl-deuterated alkenes, **1** and **10**, respectively, with high γ-selectivity via the allylic rearrangement. Similarly, hydroalumination product of 1-trimethylsilyl-1,2-nonadiene (**8**) may be (1-trimethylsilyl-2-nonenyl)aluminum dichloride (**17**). In

Table 3. Organoborane-Catalyzed Hydroalumination of Allenes^{a)}

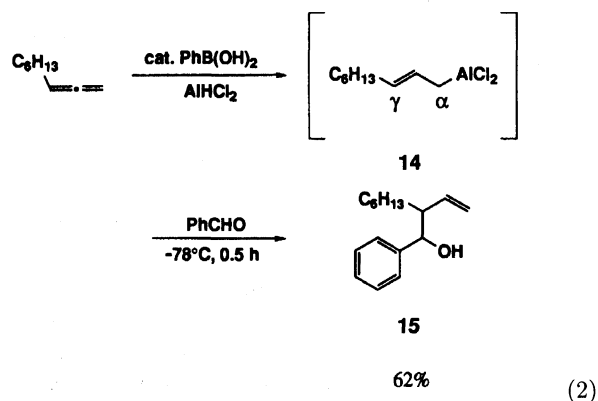
Entry	Conditions	Yield/%			Conv./%
		nonane	1-nonene	2-nonenes	
1	PhB(OH) ₂ , 4 h	6	92(>95) ^{b)}	2	75
					
2	PhB(OH) ₂ , 15 h	6	93(>95)	1	87
3	PhB(OH) ₂ , 2 h ^{c)}	10	88(>95)	2	84
4	Et ₃ B, 0.5 h ^{d)}	100			86
					
5	PhB(OH) ₂ , 24 h	>99(>95)		<1 ^{e)}	37
6	PhB(OH) ₂ , 24 h ^{c)}	>99(>95)		<1	53
7	Et ₃ B, 0.5 h ^{d)}				f)
8	Et ₃ B, 4 h ^{g)}	>99(>95)		<1	20
					
9	PhB(OH) ₂ , 6 h	48	32	20	19
10	PhB(OH) ₂ , 6 h ^{c)}	45 (0/18/82) ^{h)}	38	17	71
11	Et ₃ B, 0.5 h ^{d)}	100			91

a) Unless otherwise noted, reaction was carried out in Et₂O at room temperature using 5 mol% organoborane catalysts with AlHCl₂ (2 equiv), and was then quenched with D₂O at 0 °C. b) Values in parentheses are purity/% of allyl-deuterated isomer **1**, **10**, or **11**, respectively. c) 20 mol% PhB(OH)₂ catalyst was employed. d) AlHCl₂ (1.2 equiv) in 1,2-dichloroethane. e) It was not detected by GLC analysis. f) Nonane was observed. g) AlHCl₂ (2 equiv) in Et₂O. h) Values in parenthesis are relative ratio/% of butylcyclohexane-*d*₀, butylcyclohexane-*d*₁, and butylcyclohexane-*d*₂.



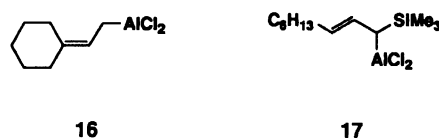
Scheme 2.

this case, our assumption is based on the trimethylsilyl group principally exerting the electronic effect, rather than the steric effect, which is the electron-donating ability comparable to vinylsilane compounds,¹³⁾ the aluminum being located in the terminal carbon adjacent to the silicon atom¹⁴⁾ (Scheme 3).



To apply this regioselective PhB(OH)₂-catalyzed hydroalumination of allenenes in organic synthesis, we

carried out the C–C bond formation of the hydroalumination product **14** with various electrophiles. Selected examples are summarized in Table 4. The reaction of *trans*-cinnamaldehyde (2 equiv) with **14** at –78 °C for 1 h furnished only the corresponding 1,2-adducted homoallylic alcohol **18** with high γ -selectivity in 37% yield based on the starting 1,2-nonadiene (Entry 2). The intermediate **14** also reacted with 1,2-epoxybutane in both of the two types of ring-opening reaction to produce an almost 1 : 1 mixture of *primary* and *secondary* δ,ϵ -unsaturated alcohols, **19** and **20**, in 40% yield (Entry 3). It is noteworthy that this hydroalumination product **14** exhibited a high chemoselectivity, leaving the ketone functionality intact. For example, the reaction of **14** with acetone and acetophenone gave no addition products even at ambient temperature. In noncatalytic allene hydroalumination using DIBALH, however, the resulting allyldiisobutylaluminum intermediates are reported to be inert towards aldehydes and acid chlorides.^{1a)} The high reactivity of allyldichloroaluminum intermediate **14** observed herein might be attributable to its lower steric bulkiness and stronger



Scheme 3.

Table 4. Reaction of Allyl aluminum Compound **14** with Various Electrophiles^{a)}

Entry	Electrophile	Product	Yield/% ^{b)}
1			62 ^{c)}
2			37 ^{d)}
3			40 ^{e)} 19 : 20 = 60 : 40 ^{f)}

a) Reaction was generally carried out at -78°C for 0.5–1 h by adding an electrophile (2 equiv) to allyl aluminum compound **14**, which was prepared in situ by $\text{PhB}(\text{OH})_2$ -catalyzed hydroalumination (Entry 1 in Table 3). For experimental details, see text. b) Isolated yield based on the starting 1,2-nonadiene. c) *Erythro/threo* ratio is 3 : 2 or 2 : 3 by ^1H NMR analysis. d) *Erythro/threo* ratio is 7 : 2 or 2 : 7 by ^1H NMR analysis. e) The reaction was conducted at -20°C for 0.5 h. f) Determined by ^1H NMR analysis.

Lewis acidity.

In conclusion, the present method demonstrates a convenient and highly regioselective way to generate allyl aluminum compounds, which can then be satisfactorily utilized for regioselective allylation of aldehydes.

Experimental

General. The GLC analyses were performed with a Shimadzu 7A gas chromatograph equipped with Silicone DC-710 (6 m) and VZ-7 (6 m) columns (N_2 as carrier gas). The ^1H NMR and ^{13}C NMR spectra were recorded on JEOL FX-60Q and Varian Gemini-200 spectrometers, using tetramethylsilane (Me_4Si) as an internal standard. Splitting patterns are indicated as s, singlet; t, triplet; q, quartet; m, multiplet. The mass spectra were recorded with a Shimadzu GCMS-7000 mass spectrometer. The IR spectra were measured on a Perkin-Elmer 1600 Series FT IR spectrometer.

Diethyl ether (Et_2O) was freshly distilled from sodium metal using diphenylketyl as indicator. Tetrahydrofuran (THF) was freshly distilled from LiAlH_4 . 1,2-Dichloroethane was freshly distilled before use. All experiments were carried out under an atmosphere of dry argon. Other simple, inorganic and organic chemicals were purchased and used as such, unless otherwise noted.

Preparation of Allenes. 1,2-Nonadiene,¹⁵⁾ vinylidene-cyclohexane (**7**),¹⁶⁾ and 1-butenyldienecyclohexane (**9**)¹⁷⁾ were available by the literature procedure. The allenes were identified by the following data.

1,2-Nonadiene: ^1H NMR (CDCl_3) δ = 0.86 (3H, t, J = 6.5 Hz, CH_3), 1.2–1.5 (8H, m, C_4H_8), 1.9–2.1 (2H, m, $\text{CH}_2\text{-C}=\text{C}$), 4.62 (2H, dt, J = 3.3 and 6.7 Hz, $=\text{CH}_2$), 5.07 (1H, tt, J = 6.7 and 6.7 Hz, $\text{CH}=\text{C}$); ^{13}C NMR (CDCl_3) δ = 14.12, 22.79, 28.47, 28.96, 29.32, 31.88, 74.41, 90.09, 208.68 ($=\text{C}=\text{C}$); IR (neat) 2965, 2934, 2864, 1959, 1468, 1380, 844 cm^{-1} .

Vinylidene-cyclohexane (7): ^1H NMR (CDCl_3) δ = 1.4–1.7 (6H, m, C_3H_6), 2.0–2.2 (4H, m, $(\text{CH}_2)_2\text{-C}=\text{C}$), 4.51 (2H, tt, J = 2.4 and 2.4 Hz, $=\text{CH}_2$); ^{13}C NMR (CDCl_3) δ = 26.17, 27.21, 31.23, 72.36, 101.16, 203.49 ($=\text{C}=\text{C}$); IR (neat) 2929, 2854, 1961, 1447, 1293, 842 cm^{-1} .

1-Butenyldienecyclohexane (9): ^1H NMR (CDCl_3) δ = 0.98 (3H, t, J = 7.3 Hz, CH_3), 1.3–2.1 (12H, m, C_5H_{10} and $=\text{C-CH}_2$), 5.01 (1H, m, $=\text{CH}$); ^{13}C NMR (CDCl_3) δ = 13.51, 22.47, 26.36, 27.69, 32.01, 90.51, 103.07, 197.97 ($=\text{C}=\text{C}$); IR (neat) 2963, 2928, 2853, 2359, 1965, 1447, 1316, 1265, 1238 cm^{-1} .

1-Trimethylsilyl-1,2-nonadiene (8). To a solution of 1,2-nonadiene (40 mmol) in THF (30 mL) was added a 1.4 M hexane solution (1 M = 1 mol dm^{-3}) of $n\text{-BuLi}$ (28.6 mL, 40 mmol) at -20°C . After 0.5 h, chlorotrimethylsilane (40 mmol) was added at this temperature. The resulting mixture was stirred at -20°C for 0.5 h and poured into sat. NaHCO_3 . Extraction with hexane followed by separation by column chromatography on silica gel (hexane as eluant) gave the title allene (20.6 mmol, 51.5%). The ^{13}C NMR spectrum agreed with that reported in the literature:¹⁸⁾ ^1H NMR (CDCl_3) δ = 0.09 (9H, s, Me_3Si), 0.89, (3H, t, J = 7.0 Hz, CH_3), 1.26 (8H, m, C_4H_8), 1.9–2.0 (2H, m, $\text{CH}_2\text{-C}=\text{C}$), 4.74 (1H, dt, J = 6.8 and 7.0 Hz, $\text{CH}=\text{C}$), 4.87 (1H, dt, J = 3.5 and 7.0 Hz, $=\text{CH-Si}$); ^{13}C NMR (CDCl_3) δ = -0.88 (Me_3Si), 14.12, 22.73, 27.92, 28.96, 29.77, 31.82, 82.36, 83.44, 210.08 ($=\text{C}=\text{C}$); IR (neat) 2957, 2927, 2856, 1938, 1466, 1379, 1248, 855, 841, 760, 699 cm^{-1} .

Transition Metal-Catalyzed Hydroalumination of 1,2-Nonadiene with LiAlH_4 .

To a clear filtered solution of LiAlH_4 in THF¹⁹⁾ (2.5 mmol in 25 mL of THF) was added 1,2-nonadiene (10 mmol) followed by a solution of transition metal halides in THF (0.25 mmol) at 30°C . The reaction mixture was stirred at 30°C for 24 h or 30°C for 1 h followed by reflux for 24 h, and was then quenched with D_2O to produce the deuterated species. The amount of recovered 1,2-nonadiene and products was determined by GLC analysis. Each product was collected from a gas chromatograph and submitted for mass spectral analysis.²¹⁾ The regioselectivity of reaction was monitored by ^{13}C NMR spectroscopy applied *inverse gated decoupling*⁵⁾ for resulting deuterated products. This technique allows the quantitative evaluation of proton-decoupled ^{13}C NMR spectra. For example, this ^{13}C NMR measurement of deuterated 1-nonene (a mixture of **1** and **2**) obtained by $[\text{TiCl}_2(\text{Cp})_2]$ -catalyzed hydroalumination (Table 1, Entry 1) showed that the signals of deuterated $\text{C}_3\text{-D}$ and $\text{C}_2\text{-D}$ carbons split into triplet ($J_{\text{C}_3\text{-D}} = 19.1$ Hz and $J_{\text{C}_2\text{-D}} = 23.1$ Hz) and shifted upper field ($\Delta\delta_{\text{C}_3} = 0.39$ ppm and $\Delta\delta_{\text{C}_2} = 0.34$ ppm by comparison with the isotopic $\text{C}_3\text{-H}$ and $\text{C}_2\text{-H}$ carbon signals of 1-nonene- d_0), respectively. Additionally, due to the $^{13}\text{C}_3\text{-C}_2\text{-D}$ and $^{13}\text{C}_2\text{-C}_3\text{-D}$ spin-spin coupling the broad triplet signals were

observed by overlapping to C₃-H and C₂-H carbon signals (²J_{C-D} could not be determined with certainty). By determining the integration ratio of C₃-D signal to ¹³C₃-C₂-D and C₃-H signals (56:44) and those of C₂-D to ¹³C₂-C₃-D and C₂-H (34:66), relative ratio of **1** based on **1** and **2** was established to be 62 %, as tabulated in Table 1. The deuterated products were identified by spectral comparison with authentic non-deuterated samples obtained commercially. The following characteristic ¹³C NMR data were observed (Δδ(δ_{C-H}-δ_{C-D}) in ppm upper field from the corresponding isotopic C-H carbon signal).

1-Nonene-3-d (1): C₃-D (δ=33.67, t, J_{C-D}=19.1 Hz, Δδ(δ_{C-H}-δ_{C-D})=0.39).

1-Nonene-2-d (2): C₂-D (δ=138.64, t, J_{C-D}=23.1 Hz, Δδ(δ_{C-H}-δ_{C-D})=0.34).

(E)-2-Nonene-1-d (3): C₁-D (δ=17.64, t, J_{C-D}=19.4 Hz, Δδ(δ_{C-H}-δ_{C-D})=0.24).

(E)-2-Nonene-2-d (4): C₂-D (δ=124.17, t, J_{C-D}=22.7 Hz, Δδ(δ_{C-H}-δ_{C-D})=0.29).

(Z)-2-Nonene-1-d (5): C₁-D (δ=12.47, t, J_{C-D}=19.1 Hz, Δδ(δ_{C-H}-δ_{C-D})=0.15).

(Z)-2-Nonene-2-d (6): C₂-D (δ=123.24, t, J_{C-D}=23.8 Hz, Δδ(δ_{C-H}-δ_{C-D})=0.29).

ZrCl₄-Catalyzed Hydroalumination of 1,2-Nonadiene with Li[AlH₃(C₅H₁₁)]. To a clear filtered solution of LiAlH₄ in THF (3.3 mmol in 25 mL of THF) was added 1-pentene (3.3 mmol) followed by a solution of ZrCl₄ in THF (0.25 mmol) at 30 °C. The reaction mixture was stirred at 30 °C for 24 h to prepare Li[AlH₃(C₅H₁₁)] (0.33 equiv, 3.3 mmol) where it was added 1,2-nonadiene (10 mmol). The mixture was stirred at 30 °C for 1 h and then refluxed for 24 h.

ZrCl₄-Catalyzed Hydroalumination of 1,2-Nonadiene with AlHCl₂. To a solution of anhydrous AlCl₃ (9 mmol) in THF (25 mL) was added LiAlH₄ (3 mmol) at 0 °C. After 15 min, the resulting solution of AlHCl₂ (1.2 equiv, 12 mmol) was allowed to warm to 30 °C where it was successively added 1,2-nonadiene (10 mmol) and a THF solution of ZrCl₄ (0.25 mmol) and was then stirred for 24 h.

PhB(OH)₂-Catalyzed Hydroalumination of Allenes.³⁾ To a solution of anhydrous AlCl₃ (1.5 mmol) in Et₂O (1 mL) was added LiAlH₄ (0.5 mmol) at 0 °C. After 15 min, PhB(OH)₂ (0.05 mmol) followed by an allene (1 mmol) was added at 0 °C. The resulting mixture was allowed to warm to room temperature where it was stirred for 4–24 h. The reaction was then quenched with D₂O or a saturated solution of NH₄Cl. Analysis of all products arising from the quenching of reactions was performed by the methods described above. The deuterated products were identified by spectral comparison with non-deuterated authentic samples obtained commercially. Authentic (*E*)-1-trimethylsilyl-1,2-nonadiene (**8**) with DIBAH (5 equiv) in hexane at 60 °C for 15 h (73 % yield; vinylsilane/alkylsilane=75:25).^{1a)} The following characteristic ¹H NMR and/or ¹³C NMR data were observed (Δδ(δ_{C-H}-δ_{C-D}) in ppm upper field from the corresponding isotopic C-H carbon signal).

1-Vinylcyclohexane-1-d (10): (Chart 1) ¹H NMR (CDCl₃) H_a (δ=4.92, 1H, dd, J_{ab}=1.8 and J_{ac}=17.7 Hz), H_b (δ=4.85, 1H, dd, J_{ab}=1.8 and J_{bc}=10.7 Hz), H_c (δ=5.75, 1H, dd, J_{ac}=10.7 and J_{bc}=17.7 Hz); ¹³C NMR (CDCl₃) C-D (δ=41.19, t, J_{C-D}=19.0 Hz, Δδ(δ_{C-H}-δ_{C-D})=0.46).

(E)-1-Trimethylsilyl-1-nonene-3-d (11): (Chart 2) ¹H NMR (CDCl₃) Me₃Si (δ=0.04, 9H), H_a (δ=5.62, 1H, dd, J_{ab}=18.6 and J_{ac}=1.4 Hz), H_b (δ=6.04, 1H, dd, J_{ab}=18.6 and J_{bc}=6.2 Hz), H_c (δ=2.0–2.2, 1H, m).

Butyl-1,1-d₂-cyclohexane (12): (Chart 3) ¹³C NMR (CDCl₃) C-D₂ (δ=36.60, quintet, J_{C-D₂}=19.0 Hz, Δδ(δ_{C-H}-δ_{C-D})=0.90).

Butyl-1,2-d₂-cyclohexane (13): (Chart 4) ¹³C NMR (CDCl₃) C₁-D (δ=36.91, t, J_{C-D}=19.0 Hz, Δδ(δ_{C-H}-δ_{C-D})=0.59), C₂-D (δ=28.85, t, J_{C-D}=19.0 Hz, Δδ(δ_{C-H}-δ_{C-D})=0.61).

Et₃B-Catalyzed Hydroalumination of Allenes.³⁾ To a vigorously stirred suspension of anhydrous AlCl₃ (2.4 mmol) in 1,2-dichloroethane (10 mL) was added a solution of DIBAH in hexane (1.2 mmol) at room temperature. After 30 min, a solution of Et₃B in hexane (0.05 mmol) and an allene (1 mmol) was successively added at 0 °C. The resulting mixture was allowed to warm to room temperature where it was stirred for 0.5 h. The reaction was then quenched with a saturated solution of NH₄Cl.

General Method for Reaction of Allylaluminum Compound 14 with Electrophiles. The hydro-

alumination product **14**, which was prepared in situ by PhB(OH)₂-catalyzed hydroalumination of 1,2-nonadiene (1 mmol) in Et₂O (1 mL) at room temperature for 4 h, was diluted with more Et₂O (5 mL) and cooled to -78 °C. To the resulting suspension was added an electrophile (carbonyl compounds or epoxides) (2 mmol) at -78 °C. The mixture was stirred for 0.5–1 h, poured into a saturated solution of NH₄Cl at 0 °C, and extracted with Et₂O. The combined extracts were dried, concentrated, and purified by column chromatography on silica gel (Et₂O/hexane as eluant) to give a mixture of isomeric alcohols as listed in Table 4. The isomeric ratio was determined by ¹H NMR analysis.

Homoallylic Alcohol 15: ¹H NMR (CDCl₃) δ=0.83 (3H, t, J=6.0 Hz, *erythro* and *threo* CH₃), 1.20 and 1.50 (10H, m, *erythro* and *threo* C₅H₁₀), 1.99 (1H, d, J=4.8 Hz, *erythro* or *threo* OH), 2.15 (1H, d, J=2.3 Hz, *erythro* or *threo* OH), 2.27 (1H, m, *erythro* or *threo* CH), 2.3–2.5 (1H, m, *erythro* or *threo* CH), 4.37 (1H, dd, J=2.3 and 8.0 Hz,

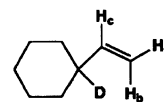


Chart 1.

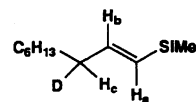


Chart 2.

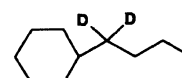


Chart 3.

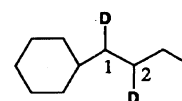


Chart 4.

erythro or *threo* CH-O), 4.59 (1H, dd, $J=4.8$ and 5.8 Hz, *erythro* or *threo* CH-O), 4.98 and 5.17 (1H, dd, $J=2.0$ and 17.0 Hz, *erythro* and *threo* =CH₂), 5.04 and 5.23 (1H, dd, $J=2.0$ and 10.4 Hz, *erythro* and *threo* =CH₂), 5.48 and 5.64 (1H, ddd, $J=9.1$, 10.4 , and 17.0 Hz, *erythro* and *threo* CH=), 7.2–7.3 and 7.30 (5H, m, *erythro* and *threo* C₆H₅). Found: C, 82.69; H, 10.52%. Calcd for C₁₆H₂₄O: C, 82.70; H, 10.41%. The *erythro*/*threo* ratio of **15** is 3:2 or 2:3.

Homoallylic Alcohol 18: ¹H NMR (CDCl₃) $\delta=0.8$ – 0.9 (3H, m, *erythro* and *threo* CH₃), 1.2–1.5 (10H, m, *erythro* and *threo* C₅H₁₀), 1.87 and 1.95 (1H, broad, *erythro* or *threo* OH), 2.1–2.2 (1H, m, *erythro* or *threo* CH), 2.2–2.4 (1H, m, *erythro* or *threo* CH), 3.92 (1H, dd, $J=2.4$ and 6.4 Hz, *erythro* or *threo* CH-O), 4.05 (1H, dd, $J=7.0$ and 7.2 Hz, *erythro* or *threo* CH-O), 5.12 and 5.15 (1H, dd, $J=2.3$ and 16.2 Hz, *erythro* and *threo* =CH₂), 5.16 and 5.21 (1H, dd, $J=2.3$ and 10.4 Hz, *erythro* and *threo* =CH₂), 5.5–5.8 (1H, m, *erythro* and *threo* CH=), 6.18 (1H, dd, $J=7.2$ and 16.0 Hz, *erythro* or *threo* Ph-C=CH), 6.20 (1H, dd, $J=6.4$ and 16.0 Hz, *erythro* or *threo* Ph-C=CH), 6.57 (1H, d, $J=16.0$ Hz, *erythro* or *threo* Ph-CH=), 6.58 (1H, d, $J=16.0$ Hz, *erythro* or *threo* Ph-CH=), 7.2–7.4 (5H, m, *erythro* and *threo* Ph). Found: C, 83.48; H, 10.42%. Calcd for C₁₈H₂₆O: C, 83.66; H, 10.14%. The *erythro*/*threo* ratio of **18** is 7:2 or 2:7.

Primary δ,ϵ -Unsaturated Alcohol 19: ¹H NMR (CDCl₃) $\delta=0.8$ – 1.0 (6H, m, CH₃), 1.2–1.5 (14H, m, CH, CH₂, OH and C₅H₁₀), 2.0–2.2 (1H, m, CH-C=), 3.5–3.6 (2H, m, CH₂-O), 4.9–5.1 (2H, m, =CH₂), 5.5–5.7 (1H, m, CH=). Found: C, 78.86; H, 13.16%. Calcd for C₁₃H₂₆O: C, 78.72; H, 13.21%.

Secondary δ,ϵ -Unsaturated Alcohol 20: ¹H NMR (CDCl₃) $\delta=0.8$ – 0.9 (6H, m, CH₃), 1.2–1.6 (15H, m, CH₂, OH and C₅H₁₀), 1.9–2.0 (1H, m, CH-C=), 3.44 (1H, m, CH-O), 5.0–5.2 (2H, m, =CH₂), 5.5–5.7 (1H, m, CH=). Found: C, 78.71; H, 13.20%. Calcd for C₁₃H₂₆O: C, 78.72; H, 13.21%.

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