December, 1993] © *1993 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***66***, *3783—3789(1993)* 3783

Regioselective Hydroalumination of Allenes and Their Synthetic Application

Shigeru NAGAHARA,* Keiji MARUOKA,† and Hisashi YAMAMOTO†
Department of Industrial Chemistry, Suzuka College of Technology, Shiroko, Suzuka 510-02
† Department of Applied Chemistry, Nagoya University, Chikusa, Nagoya 464-01

(Received June 25, 1993)

The hydroalumination of a terminal allene, 1,2-nonadiene, with $LiAlH_4$ in THF using $[TiCl_2(Cp)_2]$, $TiCl_4$, $TiCl_3$, $ZrCl_4$, and $[ZrCl_2(Cp)_2]$ catalysts afforded a wide variety of deuterated species by quenching hydroalumination products with D_2O, while $PhB(OH)_2$-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 $PhB(OH)_2$-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 $PhB(OH)_2$ 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)

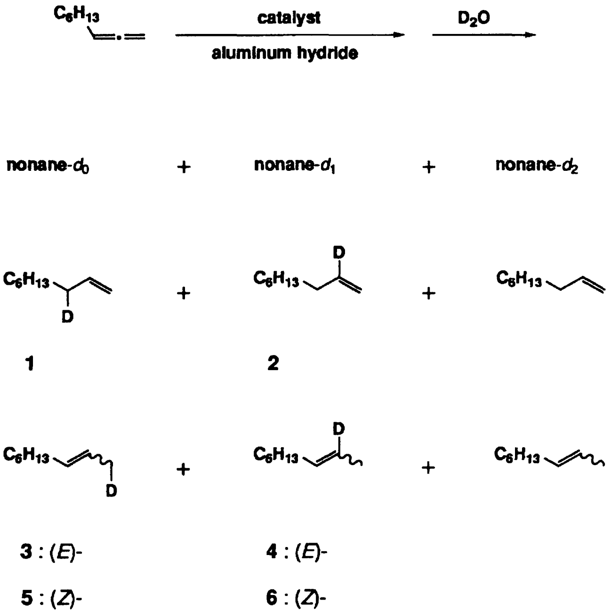
Results and Discussion

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 $[ZrCl_2(Cp)_2]$ 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 ($Li[AlH_3(C_5H_{11})]$), 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 $Li[AlH_3(C_5H_{11})]$, 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 $Li[AlH_3(C_5H_{11})]$ 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)]

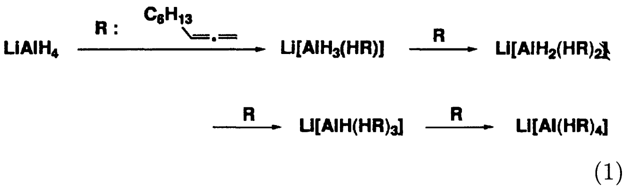
Entry	Catalyst	Conditions	Yield/%[b)]				Conv./%[b)]
			Nonane	1-Nonene	(*E*)-2-Nonene	(*Z*)-2-Nonene	
1	$[TiCl_2(Cp)_2]$	$LiAlH_4$	16 (5/12/83)[c)]	35 (62)[d)]	14 (58)[e)]	35 (29)[f)]	92
2		$AlHCl_2$[g)]	2	74 (60)	6	18	95
3	$TiCl_4$	$LiAlH_4$	23 (17/40/43)	48 (76)	15 (89)	14 (58)	88
4	$TiCl_3$	$LiAlH_4$	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		$Li[AlH_3(C_5H_{11})]$[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 $LiAlH_4$ (0.25 equiv), and was then quenched with D_2O 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 ^{13}C 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) $AlHCl_2$ (1.2 equiv, prepared from $LiAlH_4$ (0.3 equiv) and $AlCl_3$ (0.9 equiv)). h) At 30 °C for 1 h and was then refluxed for 24 h. i) $Li[AlH_3(C_5H_{11})]$ (0.33 equiv, prepared by $ZrCl_4$-catalyzed hydroalumination of 1-pentene with $LiAlH_4$ in THF at 30 °C for 24 h) at 30 °C for 1 h and was then refluxed for 24 h.



Scheme 1.

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 $[TiCl_2(Cp)_2]$-catalyzed hydroalumination (Entry 2).



(1)

We then studied the possibility of organoborane catalysts with aluminum hydride-type reagents in diethyl ether (Et_2O).[3)] First, $PhB(OH)_2$-catalyzed hydroalumination of 1,2-nonadiene was carried out with a slight excess of the stronger Lewis acidic monohydride, $AlHCl_2$ (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-nonenes in 55% conversion by protonolysis, as indicated in Table 2 (Entry 1). With 2 equivalents of $AlHCl_2$, 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, AlH_2Cl and AlH_3, 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 Et_3B-catalyzed hydroalumination with $AlHCl_2$ (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 D_2O was performed to determine the regioselectivity of $PhB(OH)_2$-catalyzed hydroalumination with $AlHCl_2$ (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_2Cl[d)], 4h				4
7		24 h				12
8		AlH_3[e)], 4 h				0
9		24 h				4
10	Et_3B	$AlHCl_2$[f)], 1h				g)

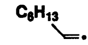
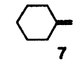
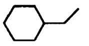
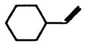
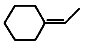
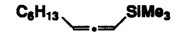
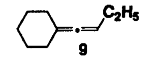
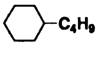
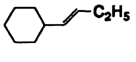
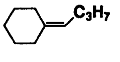
a) Unless otherwise noted, reaction was carried out in Et_2O at room temperature using 5 mol% organoborane catalysts, and was then quenched with a saturated solution of NH_4Cl at 0 °C. b) $AlHCl_2$ (1.2 equiv) was employed. c) $AlHCl_2$ (2 equiv). d) AlH_2Cl (2 equiv, prepared from $LiAlH_4$ (1 equiv) and $AlCl_3$ (1 equiv)). e) AlH_3 (2 equiv, prepared from $LiAlH_4$ (1.5 equiv) and $AlCl_3$ (0.5 equiv)). f) $AlHCl_2$ (1.2 equiv, prepared from DIBAH (1.2 equiv) and $AlCl_3$ (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 allenes, vinylidenecyclohexane (**7**) and 1-trimethylsilyl-1,2-nonadiene (**8**), were also successfully hydroaluminated using $PhB(OH)_2$ catalyst (5—20 mol%) with $AlHCl_2$, 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 $AlHCl_2$.[8)] The intermediary alkenylboranes, thus generated, undergo the transmetallation with $AlHCl_2$ 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 allenes, **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 transmetallation followed by deuterolysis (Scheme 2).

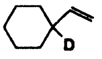
On the other hand, the trisubstituted allene **9** is more susceptible to central attack of the boron atom by the electronic and steric effects of pentamethylene and ethyl substituents on each terminal carbon of this allenyl system,[10)] thus this nature causing the nonregioselective hydroalumination due to the formation of a mixture of allyl- and vinylborane intermediates. In Et_3B-catalyzed hydroalumination of these allenes, 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 Et_2O 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	$PhB(OH)_2$, 4h	6	92(>95)[b]	2	75
 7					
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_3B, 0.5 h[d]	100			86
 8				$C_9H_{19}SiMe_3$	
5	$PhB(OH)_2$, 24 h		>99(>95)	<1[e]	37
6	$PhB(OH)_2$, 24 h[c]		>99(>95)	<1	53
7	Et_3B, 0.5 h[d]				f)
8	Et_3B, 4 h[g]		>99(>95)	<1	20
 9					
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_3B, 0.5 h[d]	100			91

a) Unless otherwise noted, reaction was carried out in Et_2O at room temperature using 5 mol% organoborane catalysts with $AlHCl_2$ (2 equiv), and was then quenched with D_2O 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) $AlHCl_2$ (1.2 equiv) in 1,2-dichloroethane. e) It was not detected by GLC analysis. f) Nonane was observed. g) $AlHCl_2$ (2 equiv) in Et_2O. h) Values in parenthesis are relative ratio/% of butylcyclohexane-d_0, butylcyclohexane-d_1, and butylcyclohexane-d_2.



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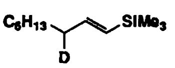

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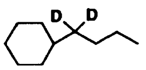

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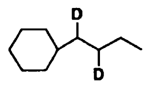
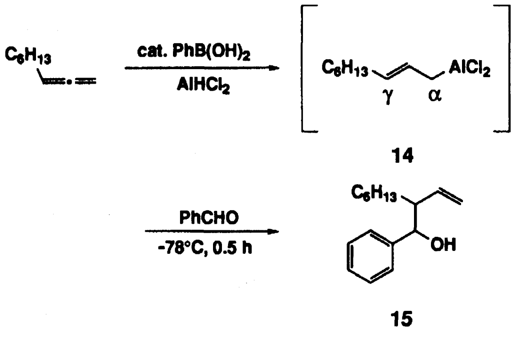


13

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 atom[14] (Scheme 3).



14

15

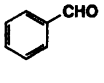
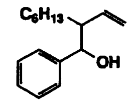
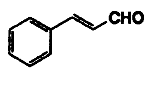
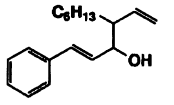
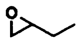
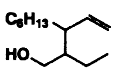
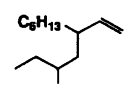
62% (2)

To apply this regioselective $PhB(OH)_2$-catalyzed hydroalumination of allenes 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 DIBAH, 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

16 **17**

Scheme 3.

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

Entry	Electrophile	Product	Yield/%$^{b)}$
1		 **15**	62$^{c)}$
2		 **18**	37$^{d)}$
3		 **19**  **20** **19** : **20**=60 : 40$^{f)}$	40$^{e)}$

a) Reaction was generally carried out at -78 °C for 0.5—1 h by adding an electrophile (2 equiv) to allylaluminum compound **14**, which was prepared in situ by PhB(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 ^{1}H NMR analysis. d) *Erythro*/*threo* ratio is 7 : 2 or 2 : 7 by ^{1}H NMR analysis. e) The reaction was conducted at -20 °C for 0.5 h. f) Determined by ^{1}H NMR analysis.

Lewis acidity.

In conclusion, the present method demonstrates a convenient and highly regioselective way to generate allylaluminum 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 ^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL FX-60Q and Varian Gemini-200 spectrometers, using tetramethylsilane (Me$_4$Si) 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$_2$O) 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] vinylidenecyclohexane (**7**),[16] and 1-butenylidenecyclohexane (**9**)[17] were available by the literature procedure. The allenes were identified by the following data.

1,2-Nonadiene: ^{1}H NMR (CDCl$_3$) δ=0.86 (3H, t, J=6.5 Hz, CH$_3$), 1.2—1.5 (8H, m, C$_4$H$_8$), 1.9—2.1 (2H, m, CH$_2$–C=), 4.62 (2H, dt, J=3.3 and 6.7 Hz, =CH$_2$), 5.07 (1H, tt, J=6.7 and 6.7 Hz, CH=); ^{13}C NMR (CDCl$_3$) δ=14.12, 22.79, 28.47, 28.96, 29.32, 31.88, 74.41, 90.09, 208.68 (=C=); IR (neat) 2965, 2934, 2864, 1959, 1468, 1380, 844 cm^{-1}.

Vinylidenecyclohexane (7): ^{1}H NMR (CDCl$_3$) δ= 1.4—1.7 (6H, m, C$_3$H$_6$), 2.0—2.2 (4H, m, (CH$_2$)$_2$–C=), 4.51 (2H, tt, J=2.4 and 2.4 Hz, =CH$_2$); ^{13}C NMR (CDCl$_3$) δ= 26.17, 27.21, 31.23, 72.36, 101.16, 203.49 (=C=); IR (neat) 2929, 2854, 1961, 1447, 1293, 842 cm^{-1}.

1-Butenylidenecyclohexane (9): ^{1}H NMR (CDCl$_3$) δ=0.98 (3H, t, J=7.3 Hz, CH$_3$), 1.3—2.1 (12H, m, C$_5$H$_{10}$ and =C–CH$_2$), 5.01 (1H, m, =CH); ^{13}C NMR (CDCl$_3$) δ= 13.51, 22.47, 26.36, 27.69, 32.01, 90.51, 103.07, 197.97 (=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 (30mL) was added a 1.4 M hexane solution (1 M=1 mol dm^{-3}) of *n*-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] ^{1}H NMR (CDCl$_3$) δ=0.09 (9H, s, Me$_3$Si), 0.89, (3H, t, J=7.0 Hz, CH$_3$), 1.26 (8H, m, C$_4$H$_8$), 1.9—2.0 (2H, m, CH$_2$–C=), 4.74 (1H, dt, J=6.8 and 7.0 Hz, CH=), 4.87 (1H, dt, J=3.5 and 7.0 Hz, =CH–Si); ^{13}C NMR (CDCl$_3$) δ=-0.88 (Me$_3$Si), 14.12, 22.73, 27.92, 28.96, 29.77, 31.82, 82.36, 83.44, 210.08 (=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 THF[19] (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$_2$O 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.[2j] 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 [TiCl$_2$(Cp)$_2$]-catalyzed hydroalumination (Table 1, Entry 1) showed that the signals of deuterated C$_3$–D and C$_2$–D carbons splited into triplet (J_{C_3-D}=19.1 Hz and J_{C_2-D}=23.1 Hz) and shifted upper field ($\Delta\delta_{C_3}$=0.39 ppm and $\Delta\delta_{C_2}$=0.34 ppm by comparison with the isotopic C$_3$–H and C$_2$–H carbon signals of 1-nonene-*d*$_0$), respectively. Additionally, due to the ^{13}C$_3$–C$_2$–D and ^{13}C$_2$–C$_3$–D spin–spin coupling the broad triplet signals were observed by overlapping to C_3–H and C_2–H carbon signals ($^2J_{C-D}$ could not be determined with certainty). By determining the integration ratio of C_3–D signal to $^{13}C_3$–C_2–D and C_3–H signals (56 : 44) and those of C_2–D to $^{13}C_2$–C_3–D and C_2–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 ^{13}C NMR data were observed ($\Delta\delta(\delta_{C-H}-\delta_{C-D})$ in ppm upper field from the corresponding isotopic C–H carbon signal).

1-Nonene-3-*d* (1): C_3–D (δ=33.67, t, J_{C-D}=19.1 Hz, $\Delta\delta(\delta_{C-H}-\delta_{C-D})$=0.39).

1-Nonene-2-*d* (2): C_2–D (δ=138.64, t, J_{C-D}=23.1 Hz, $\Delta\delta(\delta_{C-H}-\delta_{C-D})$=0.34).

(*E*)-2-Nonene-1-*d* (3): C_1–D (δ=17.64, t, J_{C-D}=19.4 Hz, $\Delta\delta(\delta_{C-H}-\delta_{C-D})$=0.24).

(*E*)-2-Nonene-2-*d* (4): C_2–D (δ=124.17, t, J_{C-D}=22.7 Hz, $\Delta\delta(\delta_{C-H}-\delta_{C-D})$=0.29).

(*Z*)-2-Nonene-1-*d* (5): C_1–D (δ=12.47, t, J_{C-D}=19.1 Hz, $\Delta\delta(\delta_{C-H}-\delta_{C-D})$=0.15).

(*Z*)-2-Nonene-2-*d* (6): C_2–D (δ=123.24, t, J_{C-D}=23.8 Hz, $\Delta\delta(\delta_{C-H}-\delta_{C-D})$=0.29).

$ZrCl_4$-Catalyzed Hydroalumination of 1,2-Nonadiene with $Li[AlH_3(C_5H_{11})]$. To a clear filtered solution of $LiAlH_4$ in THF (3.3 mmol in 25 mL of THF) was added 1-pentene (3.3 mmol) followed by a solution of $ZrCl_4$ in THF (0.25 mmol) at 30 °C. The reaction mixture was stirred at 30 °C for 24 h to prepare $Li[AlH_3(C_5H_{11})]$ (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.

$ZrCl_4$-Catalyzed Hydroalumination of 1,2-Nonadiene with $AlHCl_2$. To a solution of anhydrous $AlCl_3$ (9 mmol) in THF (25 mL) was added $LiAlH_4$ (3 mmol) at 0 °C. After 15 min, the resulting solution of $AlHCl_2$ (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 $ZrCl_4$ (0.25 mmol) and was then stirred for 24 h.

$PhB(OH)_2$-Catalyzed Hydroalumination of Allenes.[3] To a solution of anhydrous $AlCl_3$ (1.5 mmol) in Et_2O (1 mL) was added $LiAlH_4$ (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 D_2O or a saturated solution of NH_4Cl. 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-nonene was prepared by the reduction of 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 ^{1}H NMR and/or ^{13}C NMR data were observed ($\Delta\delta(\delta_{C-H}-\delta_{C-D})$ in ppm upper field from the corresponding isotopic C–H carbon signal).

1-Vinylcyclohexane-1-*d* (10): (Chart 1) ^{1}H NMR ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) C–D (δ=41.19, t, J_{C-D}=19.0 Hz, $\Delta\delta(\delta_{C-H}-\delta_{C-D})$=0.46).

(*E*)-1-Trimethylsilyl-1-nonene-3-*d* (11): (Chart 2) ^{1}H NMR ($CDCl_3$) Me_3Si (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-d_2-cyclohexane (12): (Chart 3) ^{13}C NMR ($CDCl_3$) C–D_2 (δ=36.60, quintet, J_{C-D_2}=19.0 Hz, $\Delta\delta(\delta_{C-H}-\delta_{C-D})$=0.90).

Butyl-1,2-d_2-cyclohexane (13): (Chart 4) ^{13}C NMR ($CDCl_3$) C_1–D (δ=36.91, t, J_{C-D}=19.0 Hz, $\Delta\delta(\delta_{C-H}-\delta_{C-D})$=0.59), C_2–D (δ=28.85, t, J_{C-D}=19.0 Hz, $\Delta\delta(\delta_{C-H}-\delta_{C-D})$=0.61).

Et_3B-Catalyzed Hydroalumination of Allenes.[3] To a vigorously stirred suspension of anhydrous $AlCl_3$ (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 Et_3B 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 NH_4Cl.

General Method for Reaction of Allylaluminum Compound 14 with Electrophiles. The hydroalumination product **14**, which was prepared in situ by $PhB(OH)_2$-catalyzed hydroalumination of 1,2-nonadiene (1 mmol) in Et_2O (1 mL) at room temperature for 4 h, was diluted with more Et_2O (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 NH_4Cl at 0 °C, and extracted with Et_2O. The combined extracts were dried, concentrated, and purified by column chromatography on silica gel (Et_2O/hexane as eluant) to give a mixture of isomeric alcohols as listed in Table 4. The isomeric ratio was determined by ^{1}H NMR analysis.

Homoallylic Alcohol 15: ^{1}H NMR ($CDCl_3$) δ=0.83 (3H, t, J=6.0 Hz, *erythro* and *threo* CH_3), 1.20 and 1.50 (10H, m, *erythro* and *threo* C_5H_{10}), 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,

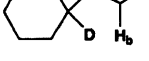


Chart 1.

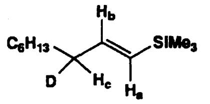


Chart 2.

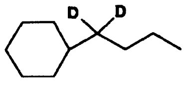


Chart 3.

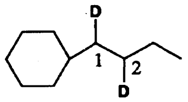


Chart 4.

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* $=\mathrm{CH_2}$), 5.04 and 5.23 (1H, dd, $J=$ 2.0 and 10.4 Hz, *erythro* and *threo* $=\mathrm{CH_2}$), 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* $\mathrm{C_6H_5}$). Found: C, 82.69; H, 10.52%. Calcd for $\mathrm{C_{16}H_{24}O}$: C, 82.70; H, 10.41%. The *erythro*/*threo* ratio of **15** is 3 : 2 or 2 : 3.

Homoallylic Alcohol 18: ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta=$ 0.8—0.9 (3H, m, *erythro* and *threo* $\mathrm{CH_3}$), 1.2—1.5 (10H, m, *erythro* and *threo* $\mathrm{C_5H_{10}}$), 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* $=\mathrm{CH_2}$), 5.16 and 5.21 (1H, dd, $J=2.3$ and 10.4 Hz, *erythro* and *threo* $=\mathrm{CH_2}$), 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 $\mathrm{C_{18}H_{26}O}$: C, 83.66; H, 10.14%. The *erythro*/*threo* ratio of **18** is 7 : 2 or 2 : 7.

***Primary δ,ε*-Unsaturated Alcohol 19:** ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta=0.8$—1.0 (6H, m, $\mathrm{CH_3}$), 1.2—1.5 (14H, m, CH, $\mathrm{CH_2}$, OH and $\mathrm{C_5H_{10}}$), 2.0—2.2 (1H, m, CH–C=), 3.5—3.6 (2H, m, $\mathrm{CH_2}$–O), 4.9—5.1 (2H, m, $=\mathrm{CH_2}$), 5.5—5.7 (1H, m, CH=). Found: C, 78.86; H, 13.16%. Calcd for $\mathrm{C_{13}H_{26}O}$: C, 78.72; H, 13.21%.

***Secondary δ,ε*-Unsaturated Alcohol 20:** ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta=0.8$—0.9 (6H, m, $\mathrm{CH_3}$), 1.2—1.6 (15H, m, $\mathrm{CH_2}$, OH and $\mathrm{C_5H_{10}}$), 1.9—2.0 (1H, m, CH–C=), 3.44 (1H, m, CH–O), 5.0—5.2 (2H, m, $=\mathrm{CH_2}$), 5.5—5.7 (1H, m, CH=). Found: C, 78.71; H, 13.20%. Calcd for $\mathrm{C_{13}H_{26}O}$: C, 78.72; H, 13.21%.

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