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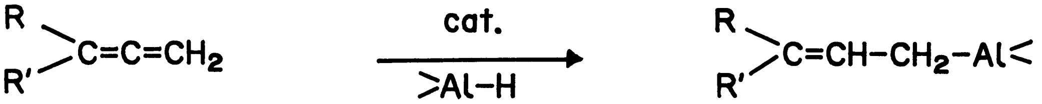
Organoborane-Catalyzed Hydroalumination of Terminal Allenes

Shigeru NAGAHARA,* Keiji MARUOKA,† Yoshiharu DOI,†† 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
†† Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
Midori, Yokohama 227

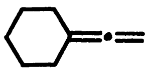
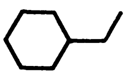
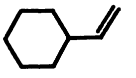
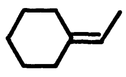
Organoborane-catalyzed hydroalumination of terminal allenes with dichloroaluminum hydride gives rise to the corresponding allylaluminum compounds under mild conditions with high regioselectivity.

Although hydroalumination of allenes is a reasonably convenient method for the generation of allylaluminum compounds, surprisingly few studies have been made on this subject.1) One recent study, however, includes the hydroalumination of allenes with DIBAH which gives excellent yields of allylaluminum compounds regioselectively, but this system is not satisfactory for subsequent functionalization due to its inertness towards carbonyl compounds.1a) In this context, we are interested in the development of the regioselective hydroalumination of terminal allenes with inorganic aluminum hydride-type reagents. Here we wish to report the realization of such a reaction under the influence of organoborane catalyst.



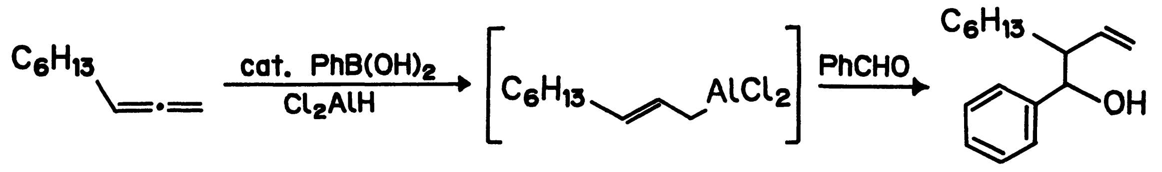
First, we examined various combinations of transition-metal catalysts with $LiAlH_4$ or Cl_2AlH in THF for effecting hydroalumination of 1,2-nonadiene2) as illustrated in Table 1 (entries 1-9).3,4) Unfortunately, all of the transition-metal catalysts provided a mixture of the corresponding alkane and alkenes under various reaction conditions. According to mass spectral analysis, the alkenes incorporated a high yield of deuterium(>90%) on hydrolysis with D_2O, but the nonane contained nonane-d_0, nonane-d_1 and nonane-d_2. In $ZrCl_4$ catalyst, the NMR spectrum showed a nearly quantitative yield of the deuterium incorporation at the allyl position of alkenes (>95%); in contrast, Cp_2ZrCl_2 and Ti-catalysts indicated 1:3—8:1 ratio of the allyl position of alkenes to vinyl position. A similar tendency of low product-selectivity was also observed in the transition-metal-catalyzed hydroalumination of conjugated dienes and alkynes.3,4g,4h)

Table 1. Catalytic Hydroalumination of Terminal Allenesa)

Entry	Catalyst	Conditionb)	Yield/%c)			Conv./%c)
1,2-nonadiene			nonane	1-nonene	2-nonene (E) / (Z)	
1	$ZrCl_4$	A	25	50 (>95)d)	15 (>95) / 10 (>95)	50
2		B	20	62 (>95)	10 (>95) / 8 (>95)	72
3		C	21	75 (>95)	1 / 3	90
4	Cp_2ZrCl_2	A	31	48	13 / 8	10
5		B	17	48 (59)	16 (82) / 19 (46)	61
6	Cp_2TiCl_2	A	16	35 (62)	14 (58) / 35 (29)	92
7		C	2	74 (60)	6 / 18	95
8	$TiCl_4$	A	23	48 (76)	15 (89) / 14 (58)	88
9	$TiCl_3$	A	20	52 (77)	12 (89) / 16 (51)	55
10	$PhB(OH)_2$	D	6	92 (>95)	2	75
						
11	$PhB(OH)_2$	E	6	93 (>95)	1	87

a) Reaction was quenched with D_2O at 0 ℃. b) Condition A: 2.5 mol% catalyst with $LiAlH_4$(1/4 equiv.) in THF at 30 ℃ for 24 h. B: 2.5 mol% catalyst with $LiAlH_4$(1/4 equiv.) in THF at 30 ℃ for 1 h and then refluxed for 24 h. C: 2.5 mol% catalyst with Cl_2AlH(1.2 equiv., prepared from $LiAlH_4$ and $AlCl_3$) in THF at 30 ℃ for 24 h. D: 5.0 mol% catalyst with Cl_2AlH(2 equiv.) in ether at room temperature for 4 h. E: 5.0 mol% catalyst with Cl_2AlH(2 equiv.) in ether at room temperature for 15 h. c) Determined by GLC based on an internal standard. d) Values in parentheses are relative ratio/% of allyl-deuterio-alkenes based on allyl- and vinyl-deuterated alkenes. Determined by ^{1}H and ^{13}C NMR (gated decoupling without NOE) spectra of isolated products.

We then studied the possibility of the organoborane catalyst, $PhB(OH)_2$, with aluminum hydride-type reagents in ether.[5] For example, $PhB(OH)_2$-catalyzed hydroalumination of 1,2-nonadiene with Cl_2AlH was found to be highly regioselective, giving >95% pure 3-deuterio-1-nonene (**1**) and a small amount of the nonane and 2-nonene in 75% yield on hydrolysis with D_2O (entry 10). In contrast, conversion of 1,2-nonadiene by hydroalumination with other aluminum hydrides after 4 h at room temperature was as follows: $PhB(OH)_2/ClAlH_2$, 4%; $PhB(OH)_2/AlH_3$, trace. Furthermore, the disubstituted allene, vinylidenecyclohexane,[6] was also successfully hydrometalated under similar conditions, producing >95% pure 1-deuterio-1-vinyl-cyclohexane (**2**) in excellent yields (entry 11). The positions of the C-D bonds in the resulting allyl-deuterio-1-alkenes, **1** and **2**, would reliably label the positions of the C-Al bonds in the hydroalumination products only if hydrolysis did not involve rearrangement. However, the formation of hindered allyl-alumino-1-alkenes is most unfavorable, and would require the addition of Al-H bond to internal C=C linkage of allenes. Accordingly, we carried out the regiochemical characterization of the substitution product by the reaction of organoborane-catalyzed hydroalumination product with benzaldehyde to account for the regiochemical structure of hydroalumination product.[7] As shown in Eq.1, the reaction of the resulting allylaluminum compound with benzaldehyde(2 equiv.) in Et_2O at -78 ℃ for 0.5 h gave rise to a homoallylic alcohol in 62% yield,[8] suggesting that the intermediary allylaluminum compound possesses C-Al bond at the least hindered terminal carbon.[1a)]



(1)

A typical experimental procedure follows(entry 11): To a solution of anhydrous $AlCl_3$(200 mg, 1.5 mmol) in ether(1 ml) was added $LiAlH_4$(19 mg, 0.5 mmol) at 0 ℃. After 15 min, catalytic $PhB(OH)_2$(6 mg, 0.05 mmol) followed by vinylidenecyclohexane(0.142 ml, 1 mmol) was added at 0 ℃. The resulting mixture was allowed to warm to room temperature where it was stirred for 15 h. The reaction was quenched with D_2O and the product ratios were determined by GLC. Each product was collected from a gas chromatograph and submitted for mass spectral analysis. The regioselectivity of reaction was monitored by ^1H and ^{13}C NMR spectroscopy. The following data were obtained for 1-deuterio-1-vinyl-cyclohexane: ^1H NMR ($CDCl_3$) δ 5.75 (1H, dd, J= 10.7 and 17.7 Hz, CH=), 4.92 (1H, dd, J= 1.8 and 17.7 Hz, $=CH_2$), 4.85 (1H, dd, J= 1.8 and 10.7 Hz, $=CH_2$), 0.8-2.1(10H, m, C_6H_{10}); ^{13}C NMR ($CDCl_3$) δ 144.72, 111.58, 41.19 (t, J_{C-D} = 19.0 Hz, -CD-), 32.69, 26.36, 26.13.

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8) ^{1}H NMR ($CDCl_3$) δ 7.2-7.3 and 7.30 (5H, m, erythro and threo C_6H_5), 5.48 and 5.64 (1H, ddd, J= 9.1, 10.4, and 17.0 Hz, erythro and threo CH=), 5.04 and 5.23 (1H, dd, J= 2.0 and 10.4 Hz, erythro and threo $=CH_2$), 4.98 and 5.17 (1H, dd, J= 2.0 and 17.0 Hz, erythro and threo $=CH_2$), 4.59 (1H, dd, J= 4.8 and 5.8 Hz, erythro or threo CH-O), 4.37 (1H, dd, J= 2.3 and 8.0 Hz, erythro or threo CH-O), 2.3-2.5 (1H, m, erythro or threo CH), 2.27 (1H, m, erythro or threo CH), 2.15 (1H, d, J= 2.3 Hz, erythro or threo OH), 1.99 (1H, d, J= 4.8 Hz, erythro or threo OH), 1.20 and 1.50 (10H, m, erythro and threo C_5H_{10}), 0.83 (3H, t, J=6.0 Hz, erythro and threo CH_3). The erythro/threo ratio of this alcohol is 3:2 or 2:3.

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