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HYDROALUMINATION OF ALLYL ALCOHOLS AND ETHERS BY LITHIUM ALUMINUM HYDRIDE IN THE PRESENCE OF ZIRCONIUM CATALYST

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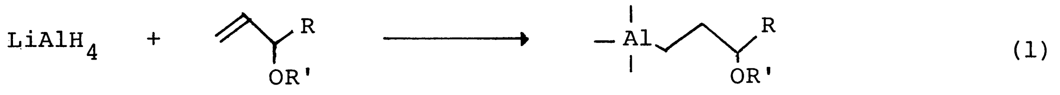
Allyl alcohols and ethers were readily hydroaluminated by $LiAlH_4$ in the presence of zirconium compounds to give organoaluminum compounds in which the aluminum atom is placed at the terminal position of the substrate. $ZrCl_4$ was the most effective catalyst for hydroalumination of allyl alcohols, whilst Cp_2ZrCl_2 was more effective than $ZrCl_4$ for allyl ethers.

The hydroalumination reaction of olefins catalyzed by titanium or zirconium compounds has opened up a new and convenient route to a variety of alkylaluminum compounds.[1] Owing to the ability of organoaluminum compounds to undergo numerous chemical transformations, this new hydroalumination process promises to become a useful methodology for organic synthesis starting from olefins.[2] Application of the hydroalumination reaction to various olefin derivatives would not only provide access to new types of organoaluminum compounds, but would also significantly extend the synthetic usefulness of hydroalumination.

Though reactions of $i\text{-}Bu_2AlH$ with allyl alcohols or ethers have been known to proceed at elevated temperatures (100-120°C) to give hydroaluminated products and/or hydrogenolysis products depending on the substrates,[3] it appears to be difficult to hydroaluminate these substances with $LiAlH_4$ which has the tendency to hydrogenate allyl alcohols and ethers.[4] We wish to report here that allyl alcohols or ethers can be hydroaluminated regioselectively with $LiAlH_4$ in the presence of a catalytic amount of zirconium compounds under mild conditions.



(1)

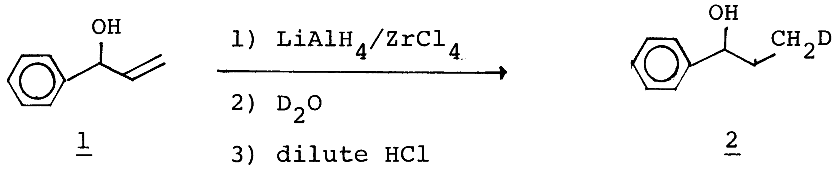
[R = alkyl or phenyl, R' = Al, alkyl or phenyl]

Titanium compounds, especially $TiCl_4$ or Cp_2TiCl_2, are most effective as the catalysts for hydroalumination of ordinary olefins. Thus, in preliminary studies, the reaction of allyl alcohols with $LiAlH_4$ was undertaken in the presence of $TiCl_4$ or Cp_2TiCl_2. However, deoxygenation occurred considerably. This finding is not entirely unprecedented, because low-valent titanium compounds have been shown to be effective deoxygenating reagents.[5,6,7,8]

In the hope that zirconium compounds such as $ZrCl_4$ or Cp_2ZrCl_2 would prevent this side reaction, allyl alcohols were treated with $LiAlH_4$ in the presence of such zirconium compounds, and it was found that the regioselective hydroalumination proceeded readily with minimal deoxygenation of the alcohols. Both $ZrCl_4$ and Cp_2ZrCl_2 are effective as the catalysts, but the former was found to be superior. Similarly, allyl ethers were hydroaluminated with $LiAlH_4$ in the presence of zirconium compounds, though, in this case, Cp_2ZrCl_2 was more effective than $ZrCl_4$.

Table 1 shows the results of hydrolysis or halogenolysis of hydroaluminated products of allyl alcohols and ethers.

The halogenolysis results demonstrate that the reaction proceeds specifically to place the aluminum at the terminal carbon atom as shown in eq 1. This finding was also supported by isolation of deuterated product 2 after addition of D_2O following hydroalumination of 1-phenyl-2-propen-1-ol (1).[9]



(2)

This regiospecificity is noteworthy, because it is known that in the hydroboration of allyl alcohols or ethers with BH_3, the directive influence of the electronegative substituents places as much as 20% of the boron to the 2-position of the substrates, and it is necessary to use disiamylborane to minimize the formation of organoboranes in which the boron atoms combine with secondary carbons.[10]

TABLE 1

REACTION PRODUCTS OF HYDROALUMINATION OF ALLYL ALCOHOLS AND ETHERS

Substrate R in $RCH(OH)CH{=}CH_2$	Catalyst	Hydrolysis or Halogenolysis	Product (yield, %)[a] X in $RCH(OH)CH_2CH_2X$
H	$ZrCl_4$	H_2O	H (76)
		Br_2	Br (50)[b]
CH_3	$ZrCl_4$	H_2O	H (75)
	Cp_2ZrCl_2	H_2O	H (64)
C_3H_7	$ZrCl_4$	H_2O	H (82)
		Br_2	Br (65)[b]
C_6H_5	$ZrCl_4$	H_2O	H (72)[b]
R in $R\text{-}O\text{-}CH_2CH{=}CH_2$			X in $R\text{-}O\text{-}CH_2CH_2CH_2X$
C_6H_{13}	$ZrCl_4$	H_2O	H (45)
	Cp_2ZrCl_2	H_2O	H (70)
		Br_2	Br (52)[b]
$CH(CH_3)CH_2CH_3$	Cp_2ZrCl_2	H_2O	H (70)
$C(CH_3)_2CH_2CH_3$	Cp_2ZrCl_2	H_2O	H (75)
$CH_2C_6H_5$	Cp_2ZrCl_2	H_2O	H (77)
C_6H_5	Cp_2ZrCl_2	H_2O	H (70)

[a] GLC yield. [b] Isolated yield.

In a typical procedure, 1-hexen-3-ol (12.5 g, 0.125 mol) was added dropwise at 0°C to a stirred solution of $LiAlH_4$ (2.7 g, 0.07 mol) in 50 ml of THF. The reaction mixture was warmed up to around 30°C and then $ZrCl_4$ (0.8 g, 3.4 mmol) was added to the mixture. After stirring for 3 h, in one experiment, the reaction mixture was quenched with 1N HCl and the products were analyzed by GLC to give 3-hexanol in 82% yield together with hexane (7%) and 2-hexene (11%). In another experiment, a benzene solution of bromine (0.28 mol) was added dropwise at 0°C after the hydroalumination reaction, and the reaction mixture was stirred for 1 h at room temperature and then treated with 1N HCl. The organic layer was washed with saturated $Na_2S_2O_3$ and brine, and the solvent was evaporated. Distillation of the residue under reduced pressure gave 1-bromo-3-hexanol (14.7 g, 65% yield), b.p. 75°C/3 Torr.

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References and Notes

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9) Compound 2 was isolated in 68% yield and its structure was determined by ^1H NMR.

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