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DEALUMINOXYLATION OF ALUMINUM ALLYL OR BENZYL ALKOXIDES AND DEOXYGENATION OF ALLYL ETHERS BY LITHIUM ALUMINUM HYDRIDE IN THE PRESENCE OF TITANIUM CATALYST

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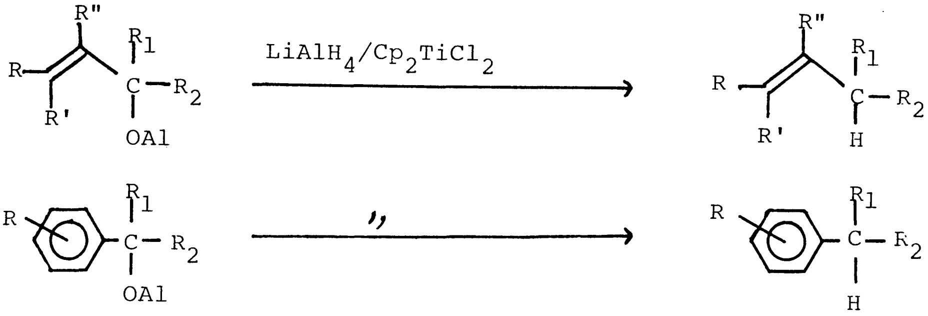
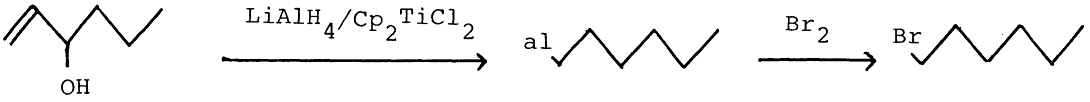
Various aluminum allyl and benzyl alkoxides and allyl ethers undergo hydrogenolysis by $LiAlH_4$ in the presence of a catalytic amount of $TiCl_4$ or Cp_2TiCl_2. Thus, the present reaction provides a convenient method for replacing oxygen-containing functional groups at the allylic or benzylic position by hydrogen.

In the course of our studies on the titanium compound-catalyzed hydroalumination reactions of olefins,[1] it was found that allyl alcohol reacted with $LiAlH_4$ in the presence of titanium compounds to afford a considerable amount of deoxygenated products.[2] A study to clarify the generality of this reaction revealed that various allyl and benzyl alkoxides undergo the hydrogenolysis reaction readily, leading to the corresponding deoxygenated products.



Addition of a catalytic amount of Cp_2TiCl_2 to a reaction mixture of a substrate and excess $LiAlH_4$ in THF and stirring of the mixture at the designated temperature followed by hydrolysis gave the hydrogenolysis products as shown in Table 1. It is apparent that the present reaction is a new type of dealuminoxylation reaction of aluminum allyl or benzyl alkoxides.[3] Thus, compounds which have oxygen-containing groups at the allylic or benzylic position afford the corresponding deoxygenated products. $TiCl_4$ also shows catalytic activity, but its activity and selectivity were far lower.

Several of the examples which illustrate the applications of these reactions in organic synthesis are worthy of special comment. In the case of substrates with terminal double bonds, reduction of the terminal bond took place simultaneously (entrys 1,4, and 10). These results indicate that hydroalumination of the terminal double bond also occurred, and thus, deoxygenation and introduction of new functional groups to these substrates in a one-pot process was found possible. In a typical sequence, 1-bromohexane was obtained in 62% yield from 1-hexen-3-ol by treatment with bromine after deoxygenation.



Although in the case of sterically hindered allyl alcohols such as geraniol or nerol neither reduction of the double bond nor allylic double bond migration took place, a significant amount of the double bond migration product was detected for 1-hexen-3-ol. Similarly, the production of hexane from 2-hexen-1-ol should be due to initial formation of 1-hexene via allylic migration and hydroalumination of the terminal double bond.

Titanium compounds have also been found to be effective catalysts for hydrogenolysis of allyl ethers by $LiAlH_4$. Although some transition metal compounds such as $NiCl_2$, $CoCl_2$ and CuCl were reported to be efficient catalysts for hydrogenolysis of allyl aryl ethers by $LiAlH_4$,[10] titanium compounds also catalyzed the hydrogenolysis reaction of alkyl allyl ethers as shown in Table 2. In this case $TiCl_4$ shows almost equal catalytic activity to Cp_2TiCl_2.

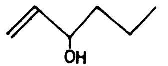
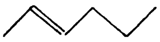
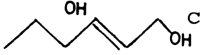
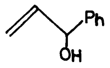
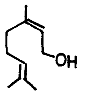
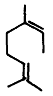
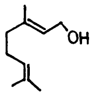
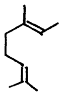
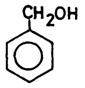
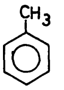
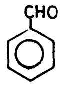
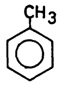
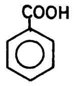
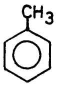
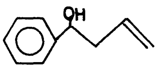
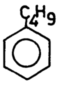
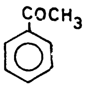
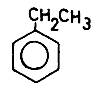
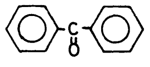
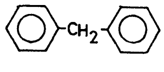
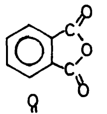
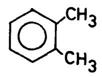
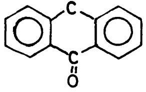
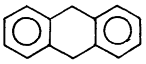
Although detailed understanding of the reaction mechanism must await further study, low valent titanium compounds may play an important role in these reactions, as it has been shown that low valent titanium compounds are the effective deoxygenating reagents.[6,11]

TABLE 2

Entry	Substrate R in $R-O-CH_2CH=CH_2$	Reaction conditions[a] Molar ratio Substrate/$LiAlH_4$	Reaction conditions[a] Catalyst	Yield of product, ROH[b] %
1	C_6H_5	3.6	Cp_2TiCl_2	50
2		1.0	Cp_2TiCl_2	92
3		1.0	$TiCl_4$	86
4	C_6H_{13}	1.0	Cp_2TiCl_2	84
5	$CH(CH_3)CH_2CH_3$	1.0	Cp_2TiCl_2	63
6		1.0	$TiCl_4$	71
7	$C(CH_3)_2CH_2CH_3$	1.0	$TiCl_4$	49

[a] 10.5 mmol of the substrate and 0.5 mmol of the catalyst in 40 ml of THF. Temp; room temp. Time; 8 h. [b] GLC analysis.

TABLE 1

Entry	Substrate	Reaction conditions[a]	Product (yield, %)[b]	
1		A	 (71)	 (15)
2	 [c]	A	 (15)	 (57)[d]
3	 [c]	A	 (13)	 (57)[d]
4		A	 (79)	
5		A	 (85)[e]	
6		A	 (78)[e]	
7		B	 (81)	
8		B	 (78)	
9		C	 (61)	
10		C	 (61)	
11		B	 (58)	
12		B C		(26) (49)
13		C	 (59)	
14		C	 (74)[f]	

[a] A: 13 mmol of the substrate, 26 mmol of $LiAlH_4$, and 0.6 mmol of Cp_2TiCl_2 in 40 ml of THF, at -20°C for 3 h followed then at room temperature overnight. B: 7 mmol of the substrate, 21 mmol of $LiAlH_4$, and 0.6 mmol of Cp_2TiCl_2 in 40 ml of THF, at boiling point of THF for 6 h. C: 7 mmol of the substrate, 42 mmol of $LiAlH_4$, and 0.6 mmol of Cp_2TiCl_2 in 40 ml of THF, at boiling point of THF for 6 h. [b] GLC analysis. [c] trans/cis = 95/5. [d] trans/cis = 90/10. [e] Identified by comparison of GLC and ^1H NMR with the authentic samples prepared by Corey's method[4]; no trans-cis isomerization was observed. [f] Isolated yield.

References and Notes

1. F. Sato, "Fundamental Reserch in Homogeneous Catalysis," vol. 2, Y. Ishii and M. Tsutsui (Eds.), Plenum, New York, 1978, p 81.
2. Allyl alcohols and ethers were hydroaluminated by $LiAlH_4$ in the presence of zirconium catalyst, see our preceding paper.
3. Deoxygenation of allyl and benzyl alcohols with $LiAlH_4$ is usually carried out by converting the hydroxy function into a suitable leaving group such as sulfate monoester.[4] Direct deoxygenation of allyl alcohols using mixed hydride reagents such as $LiAlH_4$-$AlCl_3$,[5] or $LiAlH_4$-$TiCl_4$,[6] has been reported. Hydrogenolysis of benzyl alkoxides having an electron donating group directly attached to the nucleus by $LiAlH_4$,[7] $LiAlH_4$-$AlCl_3$,[8] or $NaAlH_2(OC_2H_4OCH_3)_2$[9] has been reported. However, benzyl alkoxide itself was not reduced to toluene by these reagents.
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11. Low-valent titanium compounds prepared by reduction of Cp_2TiCl_2,[12] $TiCl_4$[6, 13] or $TiCl_3$[14] with proper reducing agents have been known to be effective for deoxygenation of oxygen-containing substances.
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