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Preliminary communication

REACTIONS OF LITHIUM ALUMINUM HYDRIDE WITH NONCONJUGATED DIOLEFINS. SELECTIVE REDUCTIONS OF DIOLEFINS AND SELECTIVE PREPARATIONS OF HALOOLEFINS FROM DIOLEFINS

FUMIE SATO*, SHIGEMI SATO and MASAO SATO

Department of Chemical Engineering, Tokyo Institute of Technology, Meguro, Tokyo 152 (Japan)

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Summary

Titanium tetrachloride is a very effective catalyst for the addition of lithium aluminum hydride to olefins. This facile reaction provides a convenient laboratory method for the selective reduction of nonconjugated diolefins or for the selective preparation of haloolefins from diolefins.

Recently it was shown that zirconium tetrachloride catalyzes the addition of lithium aluminum hydride to olefinic double bonds to afford lithium tetraalkylaluminum compounds, and that the success of this addition reaction is dependent on the structure of the olefin. Thus mono-substituted terminal olefins, such as 1-hexene reacted much more rapidly than olefins of type $RR'C=CH_2$, such as 2-methyl-1-pentene. Unstrained internal olefins, such as *cis*- and *trans*-2-hexene and cyclohexene, were essentially unreactive [1]. These characteristics should permit the selective addition of lithium aluminum hydride to the last hindered C=C bond of polyolefins.

We have found that other transition metal halides also catalyze the $LiAlH_4$/olefin reaction. As shown in Table 1, in addition to $ZrCl_4$ [1], $TiCl_4$*, VCl_4, $(\eta^5\text{-}C_5H_5)_2TiCl_2$** and $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ are effective. Titanium tetrachloride is clearly the most effective catalyst.

To explore the possibility of selective lithium aluminum hydride addition to a particular double bond of a nonconjugated diolefin, we selected 4-vinyl-1-cyclohexene, 1,4-hexadiene and 2-methyl-1,5-hexadiene as representative substrates. In such an experiment, 300 mg (7.9 mmol) of $LiAlH_4$ was added to a mixture of

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*Reduction of alkynes and monosubstituted alkenes by using equimolar quantities of $LiAlH_4$ and $TiCl_4$ has been reported [2].

**$(\eta^5\text{-}C_5H_5)_2TiCl_2$ was reported recently to catalyze the addition of $LiAlH_4$ to 1-octene, using ethyl ether as solvent, to afford $LiAlH_3C_8H_{17}$ [3].

TABLE 1

HYDROLYSIS PRODUCTS AFTER REACTION OF $LiAlH_4$ WITH 1-HEXENE

Catalyst	Reaction condition[a]		Conversion[b] (%)	Product distribution	
	Time (h)	Temperature (°C)		n-Hexane	2-Hexene[c]
$ZrCl_4$	30	25	100	99	1
$TiCl_4$	0.5	25	100	99	1
VCl_4	20	25	46	61	39
$(\eta^5\text{-}C_5H_5)_2TiCl_2$	20	25	99	75	25
$(\eta^5\text{-}C_5H_5)_2ZrCl_2$	20	25	31	97	3

[a] 38 mmol of 1-hexene, 10.6 mmol of $LiAlH_4$ and 0.7 mmol of catalyst in THF. [b] Based on 1-hexene. [c] Isomerization product.

57 mg (0.3 mmol) of $TiCl_4$ and 3.0 g (28 mmol) of 4-vinyl-1-cyclohexene in 30 ml of tetrahydrofuran. The reaction mixture was kept under nitrogen for 12 hours at room temperature and then was hydrolyzed. Gas chromatographic analysis of the product indicated the formation of the 4-ethyl-1-cyclohexene* in 97% yield.

The reaction of $LiAlH_4$ with 1,4-hexadiene gave a 94% yield of 2-hexene, together with n-hexane (4%) and 1-hexene (1%). Similarly, 2-methyl-1,5-hexadiene was converted to a mixture of 2-methyl-1-hexene (90%), 2-methylhexane (7%) and 5-methyl-1-hexene (3%) by such a procedure.

In another experiment, the reaction product of $LiAlH_4$ and 4-vinyl-1-cyclohexene was treated with *N*-chlorosuccinimide, *N*-bromosuccinimide or iodine to afford the respective 2-(4-cyclohexenyl)ethyl halides in excellent yield. Similarly, 6-bromo-2-hexene and 6-bromo-2-methyl-1-hexene were obtained in high yield

TABLE 2

HYDROLYSIS AND HALOGENOLYSIS REACTIONS OF DIOLEFINS

Diolefin	Hydrolysis or Halogenolysis	Product	Yield[a] (%)
4-Vinyl-1-cyclohexene	H_2O	4-Ethyl-1-cyclohexene	97
4-Vinyl-1-cyclohexene	*N*-Chlorosuccinimide	2-(4-Cyclohexenyl)ethyl chloride	76[b]
4-Vinyl-1-cyclohexene	*N*-Bromosuccinimide	2-(4-Cyclohexenyl)ethyl bromide	79[b]
4-Vinyl-1-cyclohexene	I_2	2-(4-Cyclohexenyl)ethyl iodide	63[b]
1,4-Hexadiene[c]	H_2O	2-Hexene	94
		n-Hexane	4
		1-Hexene	1
1,4-Hexadiene	*N*-Bromosuccinimide	6-Bromo-2-hexene	70[b]
2-Methyl-1,5-hexadiene	H_2O	2-Methyl-1-hexene	90
		2-Methylhexane	7
		5-Methyl-1-hexene	3
2-Methyl-1,5-hexadiene	*N*-Bromosuccinimide	6-Bromo-2-methyl-1-hexene	71[b]

[a] Yields were determined by GLC analysis and are based on the olefin. [b] No other mono-haloolefins were detected by GLC analysis. [c] *trans/cis* = 97/3.

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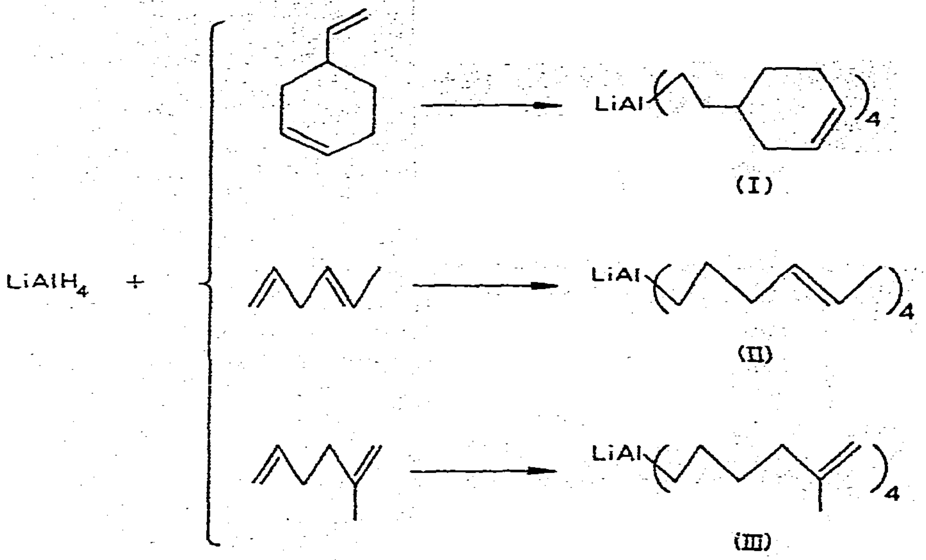
*This product and all halo-olefins obtained were identified by GLC and ^1H NMR.

from 1,4-hexadiene and 2-methyl-1,5-hexadiene, respectively. The results, summarized in Table 2, clearly demonstrate the selective addition of lithium aluminum hydride to the less hindered double bond of diolefins as shown in eq. 1.



(1)

Diethylaluminum hydride [4], disiamylborane [5] and $(\eta^5\text{-}C_5H_5)_2Zr(Cl)H$ [6] have been used as reagents for selective reduction of diolefins or for the selective preparation of haloolefins from diolefins. The $LiAlH_4/TiCl_4$ system is an attractive alternative to these reagents. Moreover, the latter system has some advantages over the other reagents: (1) $LiAlH_4$ and $TiCl_4$ are commercially available and inexpensive. (2) One mole of aluminum is effective in bringing 4 moles of the diolefin into reaction, so the yield of product per mole of aluminum is high. (3) As $LiAlH_4$ contains no other organic ligands, it is easy to isolate the products after work-up. This is not always the case with the organometallic hydrides mentioned above.

As we noted in the case of the $ZrCl_4$-catalyzed $LiAlH_4$—olefin reactions [1], the mechanisms of these reactions very likely involves intermidiate transition metal hydrides as the actual hydrometalation reagents.

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