

단 신

**Cp₂TiCl₂를 촉매로 하는 LiAlH₄-CH₃OH에 의한
알킨의 수소화 알루미늄 첨가반응**

李炯秀* · 金一禎

효성여자대학교 화학교육과

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**Hydroalumination of Alkynes with LiAlH₄-CH₃OH
Catalyzed by Cp₂TiCl₂**

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Transition metal complexes have been widely used in recent years as reagents or catalysts for organic synthesis^{1,2}. The chemistry of titanium compounds among transition metals has been concerned about function of low valent titanium complexes and their derivatives have been reported as the useful reagents for organic synthesis^{3,4}.

Recently, it has been shown that titanium complexes are the effective catalysts for isomerization and hydroalumination of alkenes and alkynes^{5,6}. The hydroboration of alkenes with NaBH₄ catalyzed by Cp₂TiCl₂ and TiCl₃ has been developed⁷. The alkoxy derivatives of the alkali metal aluminohydrides have been widely used as mild and selective reducing agents in reduction of carbonyl compounds and in the synthesis of optically active compounds^{8,9}. But little works have been reported on the hydroalumination of unsaturated hydrocarbons with LiAlH₄-CH₃OH by using the titanium complexes.

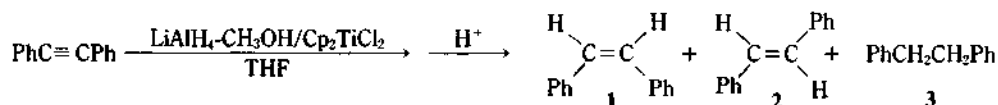
The object of this work has been placed on the catalytic behavior of the titanium complex in the hydroalumination of alkynes with LiAlH₄-CH₃OH reagent system. Also the attention has been focused on the utility of LiAlH₄ derivatives as mild and selective reducing agents in unsaturated hydrocarbons and the new application of the above

hydroalumination in organic synthesis.

The hydroalumination of alkynes was carried out by a similar manner as described previously⁶. LiAlH₄ (10 mmol) and THF (30 ml) were placed a 50 ml flask under argon atmosphere, and methanol (10 mmol) was slowly added at room temperature, hydrogen was evolved. After stirring for 1 h, Cp₂TiCl₂ (1.0 mmol) was introduced to the above solution, the color of the solution was changed from gray to violet. After stirring for 1 h, alkyne (10 mmol) was added to the solution over 5 min. The reaction mixture was further stirred for 3 h at 30°C, treated with dil-HCl (or D₂O) at 0°C and extracted with n-pentane. The organic layer was dried over Na₂SO₄. The products were obtained by distillation or evaporation. The yield was determined by GC. The products were identified by means of NMR, IR, and mass spectra by comparing with those of authentic samples.

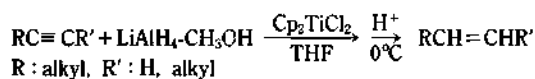
To examine the effect of the reagent system, the hydroalumination of diphenylethyne was carried out in THF by the variety of reagent systems consisting of LiAlH₄, CH₃OH, and Cp₂TiCl₂. The results are given in Table 1.

The reaction of diphenylethyne with LiAlH₄ hardly occurred at 30°C. When the reaction was refluxed at 65°C for 28 h, *cis*- and *trans*-diphenyle-

Table 1. Effects of reagent system in hydroalumination of diphenylethyne^a

| PhC≡CPh (mmol) | LiAlH ₄ (mmol) | CH ₃ OH (mmol) | Cp ₂ TiCl ₂ (mmol) | Time (h) | Ratio of Products ^b | | |
|-------------------|------------------------------|------------------------------|---|-------------|--------------------------------|----|----|
| | | | | | 1 | 2 | 3 |
| 10 ^c | 10 | 0 | 0 | 28 | 27 | 72 | 1 |
| 10 | 10 | 0 | 1 | 5 | 56 | 35 | 9 |
| 10 | 10 | 0 | 1 | 24 | 30 | 24 | 46 |
| 10 | 10 | 10 | 0 | 10 | 0 | 0 | 0 |
| 10 | 10 | 10 | 1 | 5 | 56 | 44 | 0 |

^aAll the reactions were conducted at 30°C. ^bThe yields were determined by GC and based on diphenylethyne used. ^cThe mixture was refluxed at 65°C.

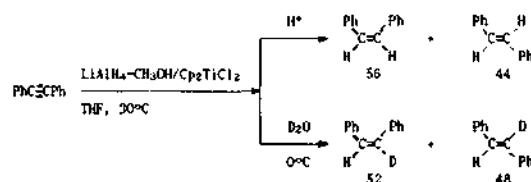
Table 2. Hydroalumination of alkynes^a

| Alkyne | Product | Yield (%) ^b |
|--|--|------------------------|
| CH ₃ (CH ₂) ₃ C≡CH | CH ₃ (CH ₂) ₃ C=CH ₂ | 76 |
| CH ₃ (CH ₂) ₂ C≡CCH ₃ | CH ₃ (CH ₂) ₂ C=CH-CH ₃ | 70 |
| CH ₃ (CH ₂) ₅ C≡CH | CH ₃ (CH ₂) ₅ CH=CH ₂ | 72 |
| CH ₂ (CH ₂) ₂ ≡ | CH ₃ (CH ₂) ₂ CH= | 65 |
| C(CH ₂) ₂ CH ₃ | CH(CH ₂) ₂ CH ₃ | |
| PhC≡CH | PhCH=CH ₂ | 68 |
| PhCH ₂ C≡CH | PhCH ₂ CH=CH ₂ | 62 |

^aCp₂TiCl₂: LiAlH₄: CH₃OH: Alkyne = 1: 10: 10: 10; All the reactions were performed at 30°C for 5 h. ^bThe yield was determined by GC.

thenes were obtained in the ratio of 27:72^{6,10}. By the use of catalytic amounts of Cp₂TiCl₂, the reaction was smoothly proceeded with formation of alkane. The reaction was investigated with LiAlH₄-CH₃OH as more mild reducing agent than LiAlH₄. The hydroalumination of alkynes using LiAlH₄-CH₃OH reagent system catalyzed by Cp₂TiCl₂ shows applicability in conversion of alkyne to alkenes without formation of alkane. This reagent system was also successfully applied to the hydroalumination of some aliphatic and aromatic alkynes. The results were listed in Table 2.

The hydroalumination of aliphatic and aromatic alkynes gave the corresponding alkenes as the major products in good yield. It has been shown



Scheme 1.

that the formation of dihydroaluminated products precedes in the hydroalumination of alkynes with LiAlH₄ in the presence of Cp₂TiCl₂^{5,6}. In contrast to this, the hydroalumination of alkynes with LiAlH₄-CH₃OH catalyzed by Cp₂TiCl₂ affords preferentially monohydroaluminated products. The results suggest that LiAlH₄-CH₃OH reagent system is more mild and selective reducing reagent than LiAlH₄ itself, and no dihydroalumination of alkynes may be occurred during the reaction. In the hydroalumination of diphenylethyne as internal alkyne, the formation of *cis*-1,2-diphenylethene predominated in the initial stage (Scheme 1). In the hydroalumination of internal alkenes, the *cis*-isomer is major product in preference to the *trans*-isomer. The reaction takes preferentially place in *cis* addition rather *trans* addition¹¹, but the selectivity for *cis*- and *trans*-alkenes is not good. A possible pathways of the reaction is not clear in this study.

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