

단 신

$[C_5(CH_3)_5]_2TiCl_2$ 를 촉매로 한 $LiAlH_4$ 에 의한 Alkene 및 Alkyne의 수소화 알루미늄 첨가반응

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Hydroalumination of Alkenes and Alkynes with $LiAlH_4$ Catalyzed by $[C_5(CH_3)_5]_2TiCl_2$

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INTRODUCTION

The titanium compounds have been widely used as reagents or catalysts for organic synthesis.^{1,2} A variety of Ti(III) and Ti(IV) compounds were reduced by various kinds of reducing agents to produce the complexes containing titanium in lower oxidation states.^{3,4} The hydroalumination of olefins catalyzed by titanium or zirconium compounds has been developed as a convenient route to a variety of alkylaluminum compounds, however most of these reactions require long reaction time or elevated temperature.^{4,5} In particular, $TiCl_4$, $ZrCl_4$, and UCl_4 are effective catalysts for the addition of lithium aluminum hydride or alane to olefinic double bonds to afford the corresponding organoaluminate or organoalane, respectively. These reactions are not only restricted to terminal olefins, but internal olefins react with $LiAlH_4$.⁶ It was recently reported that $ZrCl_4$ -catalyzed hydrostannation of alkynes with Bu_3SnH enables to produce the *trans* hydrostannation product with high regio- and stereoselectivities,⁷ and that the allylstannation of alkynes proceeds in the presence of catalytic amounts of $ZrCl_4$ or

$EtAlCl_2$ in the *trans* addition manner.⁸ We have directed our attention to the selective reactions of unsaturated hydrocarbons by using titanium and zirconium compounds.⁹⁻¹¹ In this paper, we describe a rapid and convenient procedure for the regioselective hydroalumination of alkenes with $LiAlH_4$ in the presence of $[C_5(CH_3)_5]_2TiCl_2$, and an efficiency of the reaction was evaluated by converting the alkenes to the alkylaluminates under mild conditions. The catalytic hydroalumination of terminal alkynes to alkenes is also described together with reaction of the internal alkynes.

EXPERIMENTAL SECTION

All glassware used was predried in an oven, assembled hot and cooled with a stream of argon in glove box. All reactions were carried out under argon atmosphere. All solvents were distilled and stored over an appropriate drying agent. $[C_5(CH_3)_5]_2TiCl_2$, and $LiAlH_4$ purchased from Strem Co. were used without further purification. All alkenes and alkynes were purified before use. 1H NMR spectra were recorded in $CDCl_3$ on Varian Gemini-200 spec-

trometer with tetramethylsilane as an internal standard. Infrared spectra were measured in a KBr pellet by a Matterson Genesis II FT-IR spectrophotometer. GC analyses were carried out by a Younglin GC-600D gas chromatograph equipped with HP-5 (Hewlett Packard, 0.32 mm, 30 m) or BP-5 (SGE, 0.32 mm, 60 m) capillary columns. Mass spectra were obtained by using a Shimadzu GC/MS QP-5000.

Typical procedure for hydroalumination. The mixture of $[C_5(CH_3)_2]_2TiCl_2$ (0.098 g, 0.25 mmol), $LiAlH_4$ (0.201 g, 5.30 mmol), and THF (15 mL) was placed in a vessel under argon. After stirring for 1 h, and allylbenzene (1.205 g, 10.2 mmol) was slowly introduced to the mixture at 0 °C. The complete reaction was confirmed by GC, and the mixture was treated with dilute hydrochloric acid (10 mL) and extracted with *n*-pentane. The organic layer was dried over sodium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on alumina with *n*-pentane as an eluent, and *n*-pentane was removed to yield the propylbenzene (0.930 g, 76%). 1H NMR ($CDCl_3$): δ 7.12~7.27 (m, 5H, C_6H_5), 2.55 (t, 2H, CH_2), 1.65 (m, 2H, CH_2), 0.92 (t, 3H, CH_3). IR (cm^{-1}): 3026, 2870, 1608, 1475, 1375, 753, 697.

Preparation of (2-bromoethyl)benzene. To a solution of $LiAlH_4$ (0.417 g, 11.0 mmol) and $[C_5(CH_3)_2]_2TiCl_2$ (0.197 g, 0.51 mmol) in THF (20 mL) was added styrene (2.093 g, 20.1 mmol). The reaction mixture was stirred at 0 °C for 3 h. Bromine (7.724 g, 48.3 mmol) in diethyl ether (40 mL) was added dropwise at 0 °C. After completion of bromine addition, the reaction mixture was allowed to remain 0.5 h at room temperature. Then the mixture was washed with 10% sodium thiosulfate solution, and saturated sodium chloride solution. The organic layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane). The product was obtained (3.20 g, 86%). 1H NMR: δ 7.17~7.31 (m, 5H C_6H_5), 3.54 (t, 2H, CH_2), 3.14 (t, 2H, CH_2). IR (cm^{-1}): 3062, 3028, 2964, 1602, 1453, 1262, 749, 698. Mass m/e 184

(M^+), 186 ($M^+ + 2$).

Hydroalumination of diphenylethyne. The mixture of $[C_5(CH_3)_2]_2TiCl_2$ (0.104 g, 0.27 mmol), $LiAlH_4$ (0.201 g, 5.30 mmol), and THF (10 mL) was stirred for 1 h. Diphenylethyne (1.853 g, 10.4 mmol) in diethyl ether (10 mL) was added dropwise at 0 °C to the mixture, and stirred at 0 °C for 5 h. The reaction mixture was treated with dilute hydrochloric acid (10 mL), and extracted with *n*-pentane. The organic layer was dried over sodium sulfate and filtered through a short alumina column (*n*-pentane) to eliminate inorganic salts. Removal of the solvents left a residue of oil and solid phase (1.80 g). GC analysis of the above residue indicated that the mixture contained *cis*-1,2-diphenylethene (62%), diphenylethyne (38%), and *trans*-1,2-diphenylethene (trace). *cis*-1,2-Diphenylethene (oil): 1H NMR ($CDCl_3$): δ 7.11~7.26 (m, 10H, C_6H_5), 6.59 (s, 2H, =CH-Ph). IR (cm^{-1}): 3057, 1600, 1493, 1447, 992, 908.

The products are known and were characterized by comparison with authentic samples using GC and spectral data.

RESULTS AND DISCUSSION

The hydroalumination was examined with reagent systems consisting of various amounts of $LiAlH_4$, 1-octene, and $[C_5(CH_3)_2]_2TiCl_2$ in THF.¹¹ In the same method, the reaction of 1-hexene with $LiAlH_4$ in the presence of catalytic amounts of $[C_5(CH_3)_2]_2TiCl_2$ in THF proceeded in an excellent yield under the reaction conditions outlined in Table 1. The reactivity of Cp_2TiCl_2 and $[C_5(CH_3)_2]TiCl_3$ was compared with that of $[C_5(CH_3)_2]_2TiCl_2$ in the hydroalumination of 1-octene and styrene with $LiAlH_4$, respectively. When using Cp_2TiCl_2 and $[C_5(CH_3)_2]TiCl_3$ as the catalyst, the reactions proceeded in lower yields and a lower regioselectivity under the same conditions, and require long time (up to 24 h) or elevated temperature (65 °C). The hydroalumination of the representative alkenes with $LiAlH_4$ was carried out in the presence of catalytic amounts of $[C_5(CH_3)_2]_2TiCl_2$ in THF at 0 °C. Table 1 shows the results of bromination (entries 1~5) and hydrolysis

Table 1. The hydroalumination of alkenes^a

Entry	Alkene	Time (h)	Product	Yield (%) ^b
1	CH ₃ (CH ₂) ₅ CH=CH ₂	3	CH ₃ (CH ₂) ₅ CH ₂ Br	98
2	CH ₃ (CH ₂) ₇ CH=CH ₂	3	CH ₃ (CH ₂) ₇ CH ₂ Br	99(87)
3	CH ₃ (CH ₂) ₄ CH=CHCH ₃	5	CH ₃ (CH ₂) ₄ CH(Br)CH ₃	trace
4	CH ₃ (CH ₂) ₂ C(CH ₃)=CH ₂	5	CH ₃ (CH ₂) ₂ CH(CH ₃)CH ₂ Br	trace
5	PhCH=CH ₂	3	PhCH ₂ CH ₂ Br	99(86)
6	<i>trans</i> -PhCH=CHPh	5	PhCH ₂ CH ₂ Ph	trace
7	PhCH ₂ CH=CH ₂	5	PhCH ₂ CH ₂ CH ₃	93(76)
8	PhC(CH ₃)=CH ₂	5	PhCH(CH ₃) ₂	3

^a[C₃(CH₃)₃]₂TiCl₂ : LiAlH₄ : alkene = 1:10:20, 0 °C.

^bGC yields, isolated yields in parenthesis.

(entries 6-8) of alkylhydroaluminated products of alkenes. As shown there, the reaction of terminal monosubstituted alkenes such as 1-hexene, 1-octene, styrene, and 3-phenyl-1-propene occurred at 0 °C in excellent yields (entries 1, 2, 5, and 7). Terminal monosubstituted alkenes have been hydroaluminated quantitatively without affecting aliphatic and aromatic functionalities. 1-Bromohexane, 1-bromooctane, and (2-bromoethyl)benzene obtained by bromination of alkylhydroaluminated products of alkenes showed a selectivity in excellent yields (entries 1, 2, and 5). The bromination results indicate that the reaction proceeds specifically to place the aluminum at the terminal carbon atom. This reagent system was also applied to the reaction of disubstituted alkenes, such as 2-octene, 2-methyl-1-propene, *trans*-1,2-diphenylethene, and 2-phenyl-2-propene, but reactions of these alkenes were hardly occurred at 0 °C even after 5 h (entries 3, 4, 6, and 8). The reac-

tion permits the regioselective addition of LiAlH₄ to the terminal monosubstituted double bond of alkenes.

The hydroalumination of 1-octyne was carried out at 0 °C, treatment of the reaction mixture with hydrochloric acid gave 1-octene (87%) and *n*-octane (12%). Similarly, several other alkynes were converted to the corresponding alkenes, the results are shown in Table 2. The primary products of these reactions are lithium alkenylhydroaluminates which upon protonolysis afford the corresponding alkenes. In the reaction of terminal alkynes, the formation of alkanes such as ethylbenzene and *n*-octane was also observed, the result suggests that small amounts of dialuminates may be produced during the reaction (entries 1 and 3).¹⁰ Moreover, in the reaction of diphenylethyne, the formation of *cis*-diphenylethene predominated in the initial stage, but the *trans*-diphenylethene was gradually increased

Table 2. The hydroalumination of alkynes^a

Entry	Alkyne	Time(h)	Products	Yield(%) ^b	Ratio of <i>cis/trans</i>
1	PhC ≡ CII	5	PhCH=CH ₂ PhCH ₂ CH ₃	78 <5	
2	CH ₃ (CH ₂) ₇ C ≡ CII	2	CH ₃ (CH ₂) ₇ CH=CH ₂ CH ₃ (CH ₂) ₈ CH ₃	87 12	
3 ^c	PhC ≡ CCH ₃	3	PhCH=CHCH ₃ PhCH ₂ CH ₂ CH ₃	50 5	98/2
4 ^d	PhC ≡ CPh	5	PhCH=HCPh	62	99/1
5	CH ₃ (CH ₂) ₇ C ≡ CCH ₃	5	CH ₃ (CH ₂) ₇ CH=CHCH ₃	60	

^a[C₃(CH₃)₃]₂TiCl₂ : LiAlH₄ : alkyne = 1:10:20, 0 °C.

^bGC yields. ^{c,d}After isolation, a ratio of *cis/trans* was determined by GC.

during the reaction at 65 °C for 5 h (*trans/cis*=18/82). The selectivity in the above hydroalumination of alkynes is higher than that in the reaction catalyzed by Cp₂TiCl₂.¹⁰

In summary, the above results indicate that terminal monosubstituted alkenes can be hydroaluminated with LiAlH₄ in the presence of catalytic amounts of the [C₂(CH₃)₂]₂TiCl₂ under mild conditions. This reaction is rapid, and gives higher regioselectivity in excellent yields, and involves anti-Markovnikov addition. The reaction of alkynes affords preferentially monoaluminated products. In the case of internal alkynes, the formation of *cis*-alkenes predominates in the initial stage.

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