

Ti-Catalyzed Selective Hydrogenation of Olefins

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The catalytic selective hydrogenation of olefins on homogeneous catalysts is one of the important methods in organic synthesis.¹ Among the catalysts reported, Ni-based catalysts such as P-2 nickel² and nickel complex reducing agent (NiCRA),³ and Pd-based catalysts such as Lindlar catalyst⁴ and Pd CRA⁵ show very good selectivity in the hydrogenation of olefins. Some other systems, such as NaBH₄-CoCl₂,⁶ FeCRA,⁷ LiH-VCl₃,⁸ LaNi₅H₆,⁹ and BER-Ni₂B¹⁰ have also been reported to be selective hydrogenation systems.

We have studied the hydrometalation and hydrogenation of unsaturated hydrocarbons using titanium complexes.¹¹⁻¹³ We report here a selective hydrogenation of olefins with the complex generated from bis(pentamethylcyclopentadienyl)-titanium dichloride [$\text{C}_5(\text{CH}_3)_5_2\text{TiCl}_2$] and lithium aluminum hydride (LiAlH₄).

Experimental Section

All glassware used was predried in an oven, assembled hot, and cooled with a stream of hydrogen. All reactions were carried out under hydrogen atmosphere. THF and diethyl ether were distilled from sodium benzophenone ketyl prior to use. All other solvents were distilled and stored over an appropriate drying agent. Titanium compounds and LiAlH₄ were purchased from Strem Co., and used without further purification. All olefins were purified before use.

¹H NMR spectra were recorded in CDCl₃ on Varian Gemini-200 (200 MHz) spectrometer with tetramethylsilane as an internal standard. IR spectra were measured in a KBr pellet with a Mattson Polaris FT-IR infrared spectrophotometer. GC analyses were carried out with a YongIn GC-600D gas chromatograph equipped with HP-5 capillary column.

Typical procedure for hydrogenation of olefins. The hydrogenation of myrcene is representative. $[\text{C}_5(\text{CH}_3)_5]_2\text{TiCl}_2$ (118.2 mg, 0.30 mmol) was added to a solution of LiAlH₄ (25.0 mg, 0.66 mmol) in THF (15 mL) under hydrogen atmosphere. The color of the solution was changed from gray to dark violet after stirring for 1 h, and myrcene (409 mg, 3.0 mmol) was introduced to the mixture over 5 min. The mixture was stirred at 0 °C for 1 h. Complete reaction was confirmed by GC, and the mixture was treated with a dilute hydrochloric acid (10 mL) and then extracted with diethyl ether. The organic layer was dried over sodium sulfate, and the solvent was evaporated under reduced pressure. The residue was chromatographed on alumina with pentane as the eluent, and pentane was evaporated to yield pure 2-ethyl-6-methyl-1,5-heptadiene (311 mg, 75%). ¹H NMR (CDCl₃): δ 5.12 (*t*, 1H, =CH=), 4.70 (*s*, 2H, =CH₂), 1.97-2.13 (*m*, 6H, -CH₂), 1.60 (*s*, 3H, -CH₃), 1.67 (*s*, 3H, -CH₃), 1.02 (*t*, 3H,

-CH₃). IR (cm⁻¹): 3082, 2967, 2928, 1645, 1451, 1376.

4-Ethyl-1-cyclohexene: ¹H NMR (CDCl₃): δ 5.64-5.65 (*s*, 2H, -CH=), 2.02 (*m*, 4H, CH₂-C=), 1.62-1.63 (*m*, 1H, -CH), 1.21-1.32 (*m*, 4H, -CH₂), 0.90 (*t*, 3H, -CH₃). IR (cm⁻¹): 2961, 2914, 1653, 1457, 1378, 724, 654.

Propyl phenyl ether: ¹H NMR (CDCl₃): δ 6.85-7.29 (*m*, 5H, aromatic), 3.87 (*t*, 2H, -CH₂), 1.72-1.83 (*m*, 2H, -CH₂), 1.01 (*t*, 3H, -CH₃). IR (cm⁻¹): 3065, 3038, 2965, 2877, 1599, 1496, 1392, 1248, 1077, 1048.

All hydrogenated products are known and were characterized by comparison with authentic samples using GC or other spectral data.

Results and Discussion

We have studied the hydrogenation of various representative olefins, using catalytic amounts of $[\text{C}_5(\text{CH}_3)_5]_2\text{TiCl}_2\text{-LiAlH}_4$ reagent system in THF. The results are summarized in Table 1. As shown there, the hydrogenation of 1-octene, styrene, and 3-phenyl-1-propene occurs at 0 °C in an excellent yield. Monosubstituted olefins have been hydrogenated quantitatively without affecting aliphatic and aromatic functionalities. We examined hydrogenation of 1,1-disubstituted and 1,2-disubstituted olefins, such as 2-octene, 2-phenyl-2-propene, 1-phenyl-1-propene, and *trans* stilbene, but these substrates were not hydrogenated at 0 °C even after 3 hours. The hydrogenation of 4-vinyl-1-cyclohexene and myrcene was carried out at 0 °C to examine the selectivity of this system. As shown in Table 1, 4-ethyl-1-cyclohexene and 2-ethyl-6-methyl-1,5-heptadiene were obtained quantitatively (entry 9, 12). We found that the monosubstituted double bonds were selectively hydrogenated, leaving 1,1-disubstituted, 1,2-disubstituted, and trisubstituted double bonds intact.

In several cases, the selectivity of this reagent was compared with that of Cp₂TiCl₂-LiAlH₄ reagent.¹³ In the hydrogenation of 1-octene and 3-phenyl-1-propene in the presence of Cp₂TiCl₂-LiAlH₄, products obtained by isomerization, such as 2-octene and 1-phenyl-1-propene, were observed in 8% and 7% yield, respectively. The system competitively promotes the catalytic hydrogenation¹³ and isomerization¹⁴ of olefins, and the products isomerized were rarely hydrogenated under hydrogen atmosphere at room temperature. However, these substrates were cleanly hydrogenated without isomerization in the presence of $[\text{C}_5(\text{CH}_3)_5]_2\text{TiCl}_2\text{-LiAlH}_4$ (entry 1, 5). Cp₂TiCl₂-LiAlH₄ reagent was found to be an excellent catalyst for the hydrogenation of 1,1-disubstituted and 1,2-disubstituted olefins. However, $[\text{C}_5(\text{CH}_3)_5]_2\text{TiCl}_2\text{-LiAlH}_4$ reagent shows very good selectivity toward the monosubstituted olefins. The hydrogenation of *n*-butyl allyl ether and phenyl allyl

Table 1. Selective hydrogenation of olefins^a

Entry	Substrate	Time (h)	Product	Yield (%) ^b
1 ^c		1		98
2 ^d		3		trace
3		1		99
4		1		99
5 ^e		1		99
6		3		No reaction
7		3		No reaction
8		3		No reaction
9		1		99(80)
10 ^f		3		trace
11		3		No reaction
12		1		97(75)
13		1		99
14		1		99(70)

^a[C₅(CH₃)₅]₂TiCl₂ : LiAlH₄ : Substrate=1 : 2 : 10; 0 °C. ^bGC yields, isolated yields in parenthesis. ^cIsomerized products were obtained with Cp₂TiCl₂-LiAlH₄. ^{d,f}A mixture of *cis* and *trans* isomers was used.

ether were smoothly hydrogenated without a reductive C-O bond cleavage with this reagent (entry 13, 14), but the cleavage reaction occurred with Cp₂TiCl₂-LiAlH₄,^{12,15} and hydrogenation was not carried out.

In conclusion, the titanium complex prepared from [C₅-(CH₃)₅]₂TiCl₂ and LiAlH₄ in THF is an excellent catalyst for the selective hydrogenation of monosubstituted olefins under

hydrogen atmosphere. Another advantage of this reagent is that no degradative C-O bond cleavage was observed during the hydrogenation of oxygen-containing unsaturated compounds.

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