

티탄착물을 촉매로하는 알켄류의 수소화 반응

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Hydrogenation of Alkenes Catalyzed by the Titanium Complex

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The hydrogenation by the catalyst system based on the reaction of reducing agents with various salts of cobalt,¹ nickel,² and other metals³ has been reported. It has been reported that the titanium complex from Cp_2TiCl_2 (Cp: η -cyclopentadienyl) and LiAlH_4 is the effective catalyst for the isomerization⁴ and the hydroalumination⁵ of alkenes. The similar hydroalumination⁶ and the hydromagnezation⁷ in TiCl_4 or Cp_2TiCl_2 have also been reported. Recently, the hydroboration of alkenes with LiBH_4 or NaBH_4 in the presence of Cp_2TiCl_2 has been developed.⁸

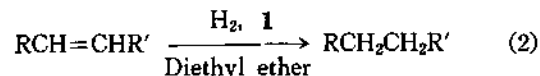
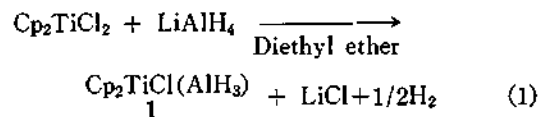
In this paper, we investigated the catalytic hydrogenation of alkenes by the complex prepared from Cp_2TiCl_2 and LiAlH_4 under atmospheric hydrogen pressure. The effect of substituents in the hydrogenation of *p*-substituted styrenes was described.

LiAlH_4 (0.64mmol) and anhydrous diethyl ether (15ml) were placed in a 50ml of flask under hydrogen atmosphere, and a freshly recrystallized Cp_2TiCl_2 (0.6mmol) was added at 25°C. The color of the solution was changed from gray to dark brown after stirring for 1h with evolution of H_2 . Alkene (12.0mmol) was

introduced to the mixture solution over 5 min.

The mixture was further stirred for appropriate time at 25°C, treated with a dilute hydrochloric acid (10ml) and then extracted with diethyl ether. The organic layer was dried over sodium sulfate. The products were obtained by distillation or recrystallization. The products were characterized by their ^1H NMR, IR, and mass spectral data and identified by comparing with those of authentic samples.

The reaction of Cp_2TiCl_2 and an equimolar amount of LiAlH_4 in diethyl ether gives hydrogen in the accordance with the stoichiometric equation (1).⁹













R=alkyl or aryl

R'=H, alkyl, or aryl

Recent publications on the application of titanium compounds in organic syntheses were reviewed with respect to the isomerization,⁴ and the hydromagnezation⁷ of alkenes in the

Table 1. Catalytic hydrogenation of alkenes^a

Alkene	Reaction time/h	Product	Yield/% ^b
C ₆ H ₁₃ CH=CH ₂	0.5	C ₈ H ₁₈	95
C ₅ H ₁₁ CH=CHCH ₃	1.5	C ₈ H ₁₈	85
C ₆ H ₅ C=CH ₂	1.0	C ₆ H ₅ CHCH ₃	98
	1.0		98
	2.0		6 ^c
	1.5		95
	2.0	PhCH ₂ CH ₂ Ph	98
	1.5	PhCH ₂ CH ₂ Ph	98
	1.5	PhCH ₂ CH ₂ CH ₃	98
	1.0	PhCH ₂ CH ₂ CH ₃	98

^a All the reactions were conducted at 25°C in diethyl ether by using the reagent system; alkene : LiAlH₄ : Cp₂TiCl₂ = 20 : 1 : 1. ^b Yields were determined by GLC and based on alkenes used. ^c The starting alkene was recovered.

presence of catalytic amounts of Cp₂TiCl₂. In this study, the complex 1 showed a powerful catalytic function for the hydrogenation of 1-octene to octane under atmospheric hydrogen pressure, while Cp₂Ti(AlH₃)₂ showed catalytic activities for the isomerization⁴ of 1-octene to 2-octene under argon. In a similar manner, various alkenes were converted to the corresponding alkanes (2). The results are summarized in Table 1.

The hydrogenation of 1-methyl-1-cyclohexene to methylcyclohexane hardly occurred, also, the reaction of 4-isopropenyl-1-methyl-1-cyclohex-

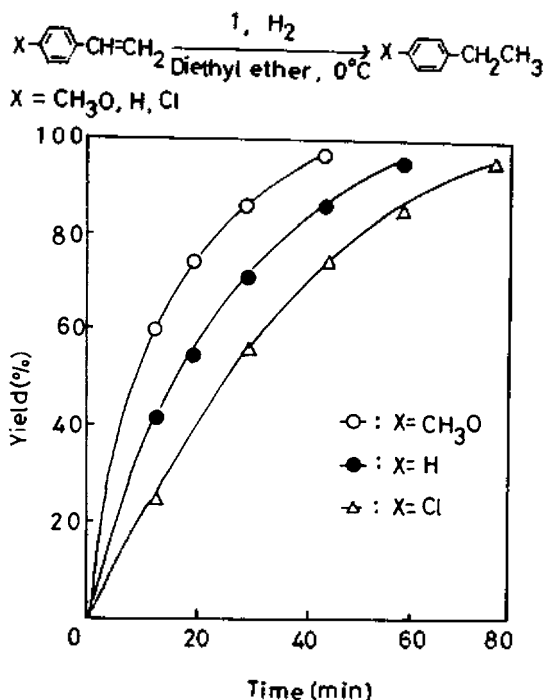


Fig. 1. Catalytic hydrogenation of *p*-substituted styrenes. All reactions were carried out at 0°C by using Cp₂TiCl₂ : 0.6mmol, LiAlH₄ : 0.64mmol, alkene : 20mmol. Yields were determined by GLC.

ene occurred to give 4-isopropyl-1-methyl-1-cyclohexene exclusively. By the results, mono- and disubstituted alkenes are smoothly hydrogenated, but the reactions of trisubstituted alkenes hardly occur under the same conditions.

The hydrogenation of styrene, *p*-chlorostyrene, and *p*-methoxystyrene was performed in the presence of the complex 1 at 0°C in diethyl ether under hydrogen atmosphere. The yields of products were plotted as the function of the reaction time (Fig. 1).

In the hydrogenation of *p*-substituted styrenes, the reactivity seemed to be decreased in the order of CH₃O > H > Cl. We would say that the electron releasing group accelerates the hydrogenation, whereas the electron withdrawing group suppressing the reaction.

However, the detailed mechanism of this

catalytic hydrogenation of alkenes will be discussed in a full paper.

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