The hydrogenation by the catalyst system based on the reaction of reducing agents with various salts of cobalt, nickel, and other metals has been reported. It has been reported that the titanium complex from Cp₂TiCl₂(Cp : η-cyclopentadienyl) and LiAlH₄ is the effective catalyst for the isomerization and the hydroalumination of alkenes. The similar hydroalumination and the hydromagnesiation in TiCl₄ or Cp₂TiCl₂ have also been reported. Recently, the hydroboration of alkenes with LiBH₄ or NaBH₄ in the presence of Cp₂TiCl₂ has been developed.

In this paper, we investigated the catalytic hydrogenation of alkenes by the complex prepared from Cp₂TiCl₂ and LiAlH₄ under atmospheric hydrogen pressure. The effect of substituents in the hydrogenation of p-substituted styrenes was described.

LiAlH₄(0.64mmol) and anhydrous diethyl ether (15ml) were placed in a 50ml flask under hydrogen atmosphere, and a freshly recrystallized Cp₂TiCl₂(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 H₂. 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 Cp₂TiCl₂ and an equimolar amount of LiAlH₄ in diethyl ether gives hydrogen in the accordance with the stoichiometric equation (1).

\[
\text{Cp}_2\text{TiCl}_2 + \text{LiAlH}_4 \rightarrow \text{Diethyl ether}
\]

\[
\text{Cp}_2\text{TiCl(AIH}_3)_2 + \text{LiCl} + 1/2\text{H}_2
\]

(1)

\[
\text{R=alkyl or aryl}
\]
\[
\text{R' = H, alkyl, or aryl}
\]

Recent publications on the application of titanium compounds in organic syntheses were reviewed with respect to the isomerization, and the hydromagnesiation of alkenes in the
Table 1. Catalytic hydrogenation of alkenes

<table>
<thead>
<tr>
<th>Alkene</th>
<th>Reaction time/h</th>
<th>Product</th>
<th>Yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6H5C=CH—CH3</td>
<td>0.5</td>
<td>C6H6</td>
<td>96</td>
</tr>
<tr>
<td>C6H5C=CH—CH2</td>
<td>1.5</td>
<td>C6H6</td>
<td>95</td>
</tr>
<tr>
<td>C6H5C—CH3</td>
<td>1.0</td>
<td>C6H5CH2CH3</td>
<td>98</td>
</tr>
</tbody>
</table>

* All the reactions were conducted at 25°C in diethyl ether by using the reagent system: alkene : LiAlH4 : Cp2TiCl2 = 20 : 1 : 1. Yields were determined by GLC and based on alkenes used. * 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-cyclohexene 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.

REFERENCES