One-pot Synthesis of 5-Ethylidene-2-Norbornene from 1,3-Butadiene and Cyclopentadiene in the Presence of \( \text{Cp}_2\text{TiCl}_2\)-LiAlH\(_4\)

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One-pot synthesis of 5-ethylidene-2-norbornene (ENB), which is used as a third component of ethylene-propylene rubbers produced from 1,3-butadiene (BD) and cyclopentadiene (CP) in the presence of \( \text{Cp}_2\text{TiCl}_2\)-LiAlH\(_4\) was investigated. It was found that ENB could be produced in yields up to 35% by one-pot reaction from BD and CP under the influence of \( \text{Cp}_2\text{TiCl}_2\) (1/450 mole) and LiAlH\(_4\) (4/450 mole) to the starting dienes. Yields of 1 : 1 adducts other than ENB were almost similar to those of Diels-Alder reaction of BD with CP. 5-Vinyl-2-norbornene (VNB) was isomerized to ENB by \( \text{Cp}_2\text{TiCl}_2\)-LiAlH\(_4\) under similar reaction conditions. The rate of Cope rearrangement from VNB to \( \text{cis-3a,4,7,7a-tetrahydroindene (THI)} \) was slower than that of isomerization from VNB to ENB. From these results, it was found that VNB formed by the reaction of BD with CP was readily isomerized to ENB without rearranging to THI under the influence of \( \text{Cp}_2\text{TiCl}_2\)-LiAlH\(_4\).

1. Introduction

The Diels-Alder reaction of 1,3-butadiene (BD) and cyclopentadiene (CP) yields mainly co-adducts, 5-vinyl-2-norbornene (VNB) and \( \text{cis-3a,4,7,7a-tetrahydroindene (THI)} \) and homo-adducts, 4-vinyl-1-cyclohexene (VCH) and dicyclopentadiene (DCP), along with some 1 : 2 adducts.\(^1\)

 structural formula 1

5-Ethylidene-2-norbornene (ENB), which is used as a third component of ethylene-propylene rubbers, is now manufactured industrially by the isomerization of VNB obtained from the above reaction.\(^*\)

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 Many patents concerning the production of ENB, especially the isomerization of VNB to ENB, are presently available. Various catalytic systems have been used for isomerization of VNB to ENB. For instance, isomerization of VNB to ENB was usually catalyzed by some bases\(^2\),\(^3\) and organometallic catalysts consisting of Ti-species.\(^4\)-\(^9\) Recently, Osokyn\(^10\) has reported the isomerization of VNB to ENB catalyzed by \( \text{Fe (CO)}_5 \) and \( \text{Fe}_3\text{(CO)}_{12} \).

In a previous paper, we reported a direct synthesis of ENB from the Diels-Alder reaction of 1,2-butadiene and CP.\(^11\) The one-pot synthesis of ENB from BD and CP is very attractive, but it is not successful yet.

In this paper, we describe one-pot synthesis of ENB from BD and CP in the presence of \( \gamma^2\text{-C}_8\text{H}_6\) \( \text{TiCl}_2\)-LiAlH\(_4\).

2. Experimental

2.1 Materials

Unless otherwise noted the materials were ob-
tained from commercial suppliers and used without further purification except the solvents. CP was prepared by destructive distillation of commercially available endo-DCP. The solvents were purified by conventional methods.

\((\eta^5-C_5H_5)TiCl_2 \) \((Cp_2TiCl_2)\) was prepared following procedures found in the literature.\(^{12}\)

### 2.2 Reaction

All reactions were carried out in an autoclave under prescribed conditions. A typical reaction is as follows: a solution of \(Cp_2TiCl_2\) \((0.267\ \text{mmol}, \ 67\ \text{mg})\) and \(LiAlH_4\) \((1.64\ \text{mmol}, \ 41\ \text{mg})\) in benzene \((7\ \text{cm}^3)\) was placed in an autoclave to which BD \((80\ \text{mmol})\) and CP \((40\ \text{mmol})\) were added in an argon stream at \(-78^\circ\text{C}\). The mixture was allowed to react by stirring at \(180^\circ\text{C}\) for 3 hrs. After the solvent was evaporated the residue was distilled under reduced pressure to give 1:1 adducts.

The isomerization of VNB to ENB was performed by allowing VNB \((10\ \text{mmol}, \ 1.2\ \text{g})\) to react with \(Cp_2TiCl_4\) \((0.067\ \text{mmol}, \ 17\ \text{mg})\) and \(LiAlH_4\) \((0.267\ \text{mmol}, \ 7\ \text{mg})\) in benzene \((2.5\ \text{cm}^3)\) under prescribed conditions. The Cope rearrangement of VNB to THI was carried out by heating VNB \((10\ \text{mmol}, \ 1.2\ \text{g})\) in benzene \((2.5\ \text{cm}^3)\) at \(180^\circ\text{C}\) for 1-5 hr.

Cycloaddition of 1,2-butadiene and CP was carried out by the same method used in a previous paper.\(^{11}\)

### 2.3 Analysis

The GLC analysis was carried out with a Yanagimoto G 1800 apparatus employing a thermal conductivity detector and a 3 mm \(\times\) 3 m stainless steel column packed with Apiezone Grease L 10% on Chromosorb W. The yields of products were estimated from the peak areas using the internal standard technique.

The \(^1\text{H}-\text{NMR}\) and \(^{13}\text{C}-\text{NMR}\) were recorded with a JEOL PMX-60 and a JNM-PS-100 FT-NMR spectrometer, respectively.

### 3. Results and Discussion

The Diels-Alder reaction of BD with CP produces 1 : 1 adducts (VNB, THI, VCH, DCP) and several kinds of 1 : 2 adducts.\(^{1,3}\) The optimum reaction conditions to obtain the 1 : 1 adducts have been established in our previous work\(^{13,14}\); thus, the reaction conditions employed in the present work have been referred to them of previous works.

Reactions of BD with CP in the presence of \(Cp_2TiCl_4-LiAlH_4\) were compared with those in the absence of a catalyst under varying reaction conditions. The results are summarized in Table 1.

It was found that the reaction of BD with CP under the influence of \(Cp_2TiCl_4-LiAlH_4\) gave ENB in relatively good yields, for instance, a yield of 35\% was obtained reacting them at \(180^\circ\text{C}\) for 3 hrs in benzene. The yield of ENB was slightly superior to that of VNB derived from uncatalyzed reaction of BD and CP, and the yields of 1:1 adducts other than ENB were similar to those of Diels–Alder reaction of BD with CP.

The influence of the ratio of catalyst on ENB yields is shown in Table 2.

The maximum yield of ENB attained was by using 1/450 equiv. of \(Cp_2TiCl_4\) and 4/450 equiv. of \(LiAlH_4\).

### Table 1 Yields of 1:1 Adducts in the Reaction of BD with CP in Presence or in Absence of \(Cp_2TiCl_4-LiAlH_4\)

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Yield (%)</th>
<th>ENB</th>
<th>VNB</th>
<th>THI</th>
<th>VCH(^{12})</th>
<th>DCP</th>
<th>others(^{12})</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>12.3(0)</td>
<td>1.4(18.6)</td>
<td>2.1(2.5)</td>
<td>5.5(5.7)</td>
<td>17.3(23.5)</td>
<td>6.2(0.6)</td>
<td></td>
</tr>
<tr>
<td>160</td>
<td>24.8(0)</td>
<td>5.1(28.8)</td>
<td>3.8(5.8)</td>
<td>13.5(13.2)</td>
<td>18.8(17.4)</td>
<td>9.7(0.8)</td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>34.8(0)</td>
<td>6.0(30.2)</td>
<td>9.3(12.6)</td>
<td>9.8(10.2)</td>
<td>5.3(6.6)</td>
<td>9.8(1.0)</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>19.3(0)</td>
<td>trace(17.9)</td>
<td>16.0(18.4)</td>
<td>9.2(8.3)</td>
<td>trace(1.6)</td>
<td>10.0(0.9)</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) BD \((80\ \text{mmol})\) and CP \((40\ \text{mmol})\) were allowed to react with \(Cp_2TiCl_4(1/450\ \text{equiv.})\) and \(LiAlH_4(4/450\ \text{equiv.})\) to the starting dienes (BD+CP) in benzene \((7\ \text{cm}^3)\) for 3 hrs.

\(^{b}\) Based on CP used.

\(^{c}\) Unidentified 1 : 1 adducts.

\(^{d}\) Parentheses show the yields without catalyst.

### Table 2 Influence of Catalyst Ratio\(^{a}\)

<table>
<thead>
<tr>
<th>Molar Ratio(^{b})</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Cp_2TiCl_4)</td>
<td>(LiAlH_4)</td>
</tr>
<tr>
<td>1/600</td>
<td>1/600</td>
</tr>
<tr>
<td>1/600</td>
<td>2/600</td>
</tr>
<tr>
<td>1/600</td>
<td>4/600</td>
</tr>
<tr>
<td>1/450</td>
<td>4/450</td>
</tr>
<tr>
<td>1/450</td>
<td>6/450</td>
</tr>
<tr>
<td>1/300</td>
<td>4/300</td>
</tr>
</tbody>
</table>

\(^{a}\) CP \((40\ \text{mmol})\) and BD \((80\ \text{mmol})\) were allowed to react at \(180^\circ\text{C}\) for 3 hrs in benzene.

\(^{b}\) The ratio to starting dienes.
LiAlH₄ to the starting dienes (CP + BD). The most favorable amount of LiAlH₄ to use was 4 times that of Cp₂TiCl₂; and the use of an amount more than 4 times slight decreased the yield of ENB (Table 2). The same reaction in the presence of 1/300 equiv. of Cp₂TiCl₂ to the dienes resulted in considerable amounts of polymers whose structures were not identified because of the complexity of their NMR spectra.

The isomerization of vinyl group to ethylidene group is effected by various catalytic systems. Unfortunately, most catalysts are found to be ineffective for the one-pot synthesis of ENB from BD and CP, because the catalysts decompose at the temperatures employed in the Diels-Alder reaction of BD with CP. Moreover, these catalysts react preferentially with the starting dienes rather than with VNB. For example, in the reaction of BD with CP under the influence of Fe(CO)₅ or Fe₃(CO)₁₂ in which isomerization of VNB to ENB readily takes place under the same conditions of Diels-Alder reaction of BD with CP, these catalysts did not bring about the desired ENB probably because of degradation of the iron species.

The reaction path to ENB from BD and CP catalysed by Cp₂TiCl₂-LiAlH₄ was considered as follows. As can be seen from Table 1, yields of 1:1 adducts other than ENB in the reaction of BD and CP are similar to each other whether the reaction occurs in the presence or in the absence of Cp₂TiCl₂-LiAlH₄. In addition, the available patents show that some Ti-system catalysts have been found to be effective for the isomerization of VNB to ENB. From these facts, the ENB seems to be formed by the subsequent isomerization of VNB derived from the Diels-Alder reaction of BD with CP. In order to confirm these points, VNB was allowed to react in the presence of Cp₂TiCl₂-LiAlH₄ under varied conditions. Isomerization of VNB occurred smoothly at lower temperatures than those of the Diels-Alder reaction of BD with CP to form ENB in almost quantitative yield (Table 3). Thus, it was found that VNB was first formed by the Diels-Alder reaction of BD with CP followed by isomerization to ENB by Cp₂TiCl₂-LiAlH₄.

The ¹³C-NMR spectrum of the resulting ENB indicated that it consisted of an isomeric mixture of E- and Z-ENB. The Diels-Alder reaction of BD with CP gave a stereoisomeric mixture of endo- and exo-VNB whose ratio was dependent on reaction conditions, e.g., the reaction at 180°C gave an isomeric mixture of approximately endo/exo=6/4. The isomerization of VNB (endo/exo=6/4) catalyzed by Cp₂TiCl₂-LiAlH₄ at 160°C for 1 hr in benzene gave an isomeric mixture of E- and Z-ENB (6:4). Although, it is uncertain whether this E/Z ratio of ENB came from the isomeric ratio of the starting VNB or it reflected the thermodynamic equilibrium of 1 and 2 (Scheme 1), the VNB may be isomerized.
via the formation of \(\pi\)-allyl complex such as 1 and 2 arising from the oxidative addition of the vinyl group to a low valent titanium generated by Cp\(_2\)TiCl\(_2\) and LiAlH\(_4\) followed by reductive elimination to form E- and Z-ENB.

A similar mechanism for the isomerization of terminal olefines into internal olefines catalyzed by "Cp\(_2\)Ti" or "C\(_5\)Me\(_5\)Ti" generated from Cp\(_2\)TiCl\(_2\) or (C\(_5\)Me\(_5\))\(_2\)TiCl\(_2\) and several reducing agents has been presented.\(^{18}\) Mach\(^{19,20}\) has also reported a double bond shift catalyzed by \(\mu\)-(\(\gamma\)-\(\gamma\)-fulvalene)-di-\(\mu\)-hydride-bis(\(\gamma\)-cyclopentadienyltitanium), Fu\(_2\)-Cp\(_2\)Ti\(_2\)H\(_2\), which was prepared from Cp\(_2\)TiCl\(_2\) reacting with 4 equiv. of LiAlH\(_4\). The Al : Ti ratio = 4 appears to be optimum for the production of Fu\(_2\)Cp\(_2\)Ti\(_2\)H\(_2\), although the Al : Ti ratio = 2 is sufficient for its production.\(^{20}\)

In our experiments, the fact that no ENB was formed in a reaction employing 2 equiv. or less of LiAlH\(_4\) to Cp\(_2\)TiCl\(_2\) (Table 2) may be correlated to insufficient formation of the above Ti species.

It is interesting to compare the E/Z ratio of ENB formed by the Cp\(_2\)TiCl\(_2\)-LiAlH\(_4\)-catalyzed reaction with that of ENB formed by the reaction of 1,2-butadiene with CP.\(^{11}\) The latter reaction gave ENB almost exclusively of E-configuration. Therefore, the E/Z ratio of ENB due to the isomerization of VNB may reflect the endo/exo ratio of the starting VNB.

Previously, we have reported that VNB is converted to THI by the Cope rearrangement.\(^{21}\) It is probable, therefore, that the VNB formed by the Diels-Alder reaction of BD with CP competes for rearrangement to THI or for isomerization to ENB. Figure 1 shows a comparison between the rate of isomerization to ENB and the rate of rearrangement to THI at 180°C. The isomerization to ENB produced almost completely after 10 minutes, but the rearrangement to THI proceeded more slowly.

Consequently, in the reaction of BD with CP under the influence of Cp\(_2\)TiCl\(_2\)-LiAlH\(_4\), the resulting VNB seems to be isomerized immediately to ENB, while in the reaction without a catalyst the VNB rearranged slightly to THI. These reactions are outlined as Scheme 2.

4. Conclusion

It was established that ENB which is used as a third component of ethylene-propylene rubbers can be prepared by one-pot reaction from BD and CP by addition of Cp\(_2\)TiCl\(_2\) and LiAlH\(_4\) as catalysts. The maximum yield of ENB (35%) was attained when Cp\(_2\)TiCl\(_2\) (1/450 equiv.) and LiAlH\(_4\) (4/430 equiv.) to the starting dienes were made to react at 180°C for 3 hrs (Table 2). This yield is slightly superior to that of VNB by the Diels-Alder reaction of BD with CP in the absence of a catalyst. Furthermore, yields of 1 : 1 adducts other than VNB were similar to those of Diels-Alder reaction of BD with CP. The VNB was isomerized to ENB almost quantitatively by Cp\(_2\)TiCl\(_2\)-LiAlH\(_4\) under reaction conditions similar to above.

The rate of Cope rearrangement of VNB to THI

\[ \text{Scheme 2} \]
is slower than that of isomerization of VNB to ENB. Therefore, in the reaction of BD and CP under the influence of Cp₂TiCl₂-LiAlH₄, it was found that the VNB derived from the Diels-Alder reaction of BD with CP was immediately isomerized to ENB without rearranging to THI. It seems that the ratio of E/Z of the resulting ENB depends on the configuration of the starting VNB.

References