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HYDROMETALATION AND ISOMERIZATION OF OLEFINS BY THE TITANIUM COMPLEX

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The reagent system generated from Cp_2TiCl_2(Cp=cyclopentadienyl) and $LiAlH_4$ promoted the catalytic hydrometalation and isomerization of olefins, the catalytic ability of the reagent system for both reactions strongly depending on the composition of two reagents in the reagent system. The hydrometalation occurred in the anti-Markownikoff fashion. By these two catalytic reactions, 1-octene was effectively converted to 1-bromooctane and 2,3-dibromooctane.

Low valent titanium compounds have been shown to be useful reagents for organic syntheses.1) 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. The different complexes thus prepared exhibited their inherent and unique reducing abilities, and were utilized for the reduction of unsaturated compounds2) and halogenated compounds,3) the reductive coupling of carbonyl compounds,1),4) and also for the reductive elimination of halohydrins,5) epoxides,6) allyl ethers,7) and hydroxy thioethers.8)

We report here that the reagent system generated from Cp_2TiCl_2 (Cp = cyclopentadienyl) and $LiAlH_4$ promotes the catalytic hydrometalation and isomerization of olefins, and these two catalytic reactions can be discriminated from one another by the composition of two reagents in the reagent system.

A typical procedure of the catalytic hydrometalation is shown in the example of the conversion of 1-octene to 1-bromooctane: A freshly prepared $Cp_2TiCl_2$9) (319 mg, 1.28 mmol) was added to a stirred suspension of $LiAlH_4$ (973 mg, 25.6 mmol) in 30 ml of ether at room temperature under argon atmosphere, and the mixture was stirred for 1 h. Immediately after the addition of Cp_2TiCl_2, a dark gray solution was obtained,

$$\begin{tikzcd}
RCH_2CH{=}CH_2 \arrow[r, "Cp_2TiCl_2 + m\ MH"] \arrow[dr, "Cp_2TiCl_2 + n\ MH"'] & RCH{=}CHCH_3 \arrow[r, "Br_2"] & RCHBrCHBrCH_3 \\
 & RCH_2CH_2CH_2M \arrow[r, "Br_2"] & RCH_2CH_2CH_2Br
\end{tikzcd}$$

$$RCH{=}CHCH_3 \xrightarrow{Cp_2TiCl_2 + n\ MH} RCH_2CHMCH_3 + RCH_2CH_2CH_2M \xrightarrow{Br_2}$$

$$RCH_2CHBrCH_3 + RCH_2CH_2CH_2Br$$

$$(m < 3, \quad n \geq 3, \quad M = LiAlH_3)$$

accompaning hydrogen evolution. 1-Octene (2.87 g, 25.6 mmol) was introduced to the mixture over a period of 10 min. The resulting mixture was further stirred at 35°C for 5 h (during this period the solution became dark red), treated with an excess of Br_2 at -5 - 0°C, and then filtered. The filtrate was washed with an aqueous $NaHSO_3$ solution and evaporated. Distillation of the residue gave 1-bromooctane as a main product. The GLC analysis of the reaction mixture revealed that the mixture contained 1-bromooctane (22.2 mmol) and octane (2.75 mmol) along with trace amounts of 2-bromo-, 1,2-dibromo-, and 2,3-dibromooctanes.

The catalytic isomerization was performed by use of smaller quantities of $LiAlH_4$. The conversion of 1-octene to 2,3-dibromooctane is shown as a typical example of this reaction: 1-Octene (25.6 mmol) was allowed to react with the reagent system generated from 1.28 mmol of Cp_2TiCl_2 and 2.56 mmol of $LiAlH_4$ in a

Table 1 Hydrometalation and Isomerization of 1-Octene[a)]

Run	Cp_2TiCl_2 mmol	$LiAlH_4$ mmol	1-Octene mmol	Yield of products (mmol)[b),c)] Octane	1-Bromo-octane	1,2-Dibromo-octane	2,3-Dibromo-octane
1	1.28	2.56	1.28	0.27	0.45	trace	0.56
2	1.28	2.56	25.60	2.79	2.21	trace	20.59
3	1.28	3.84	1.28	0.29	0.96	0	trace
4	1.28	3.84	25.60	3.53	3.09	trace	19.06
5	1.28	25.60	25.60	2.75	22.16	trace	trace

a) At 35°C for 5 h.

b) The yield was determined by GLC analysis using n-dodecane as a standard.

c) In all experiments, trace amounts of 2-bromooctane were obtained.

Table 2 Hydrometalation and Isomerization of 2-Octene[a)]

Run	Cp_2TiCl_2 mmol	$LiAlH_4$ mmol	2-Octene mmol	Yield of products (mmol)[b),c)]			
				Octane	1-Bromo-octane	2-Bromo-octane	2,3-Dibromo-octane
6	1.28	3.84	1.28	0.24	0.86	0.20	trace
7	1.28	3.84	3.84	0.54	1.09	0.41	1.82
8	1.28	25.60	25.60	2.64	trace	3.80	19.00

a) At 35°C for 5 h.

b) The yield was determined by GLC analysis using n-dodecane as a standard.

c) In all experiments, trace amounts of 1,2-dibromooctane were obtained.

similar manner as above. Treatment with an excess of Br_2 and then work-up of the resulting reaction mixture gave a mixture of 2,3-dibromooctane (20.6 mmol), octane (2.79 mmol), 1-bromooctane (2.21 mmol), and trace amounts of 2-bromo- and 1,2-dibromooctanes.

These reactions are illustrated in the Scheme, and the related experimental results are summarized in Tables 1 and 2. These results indicate that the reactions presented here have the following characteristics.

(1) The hydrometalation of 1-octene is preferentially promoted by use of the reagent system generated from more than three molar quantities of $LiAlH_4$ and one molar quantity of Cp_2TiCl_2 (run 5). On the other hand, the use of the reagent system generated from less than three molar quantities of $LiAlH_4$ and one molar quantity of Cp_2TiCl_2 preferentially promotes the isomerization of 1-octene to 2-octene (run 2). These two reactions are all catalytic in nature with regard to the titanium complexes. One molar quantity of $LiAlH_4$ is consumed for the hydrometalation of one molar quantity of olefins.

(2) The catalytic hydrometalation takes places in the anti-Markownikoff fashion; namely, 1-octene is metalated at the 1-position so that upon quenching the reaction mixture with Br_2, 1-bromooctane is produced.

(3) In the case of 2-octene, the isomerization is scarcely observed. Moreover, the rate of the catalytic hydrometalation of 2-octene is much slower than that of 1-octene (runs 5 and 8).

(4) Formation of the hydrogenated product, octane, is always observed, although its yield is relatively low.

It is natural to suppose that the above catalytic reactions proceed through a low valent titanium complex coordinated with olefin. The scope and detailed mechanism of these catalytic reactions will be reported in subsequent papers.10)

References and Notes

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10) Treatment of the reaction mixture, which had been obtained by the reaction of 1-octene with Cp_2TiCl_2-$LiAlH_4$ under the conditions similar to those employed for run 3, with 6N HCl afforded octane in a quantitative yield. This result strongly supports that an essential intermediate for the catalytic hydrometalation is $C_8H_{17}M$ ($M = LiAlH_3$).

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