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CATALYTIC HYDROBORATION OF OLEFINS BY USE OF TITANIUM COMPLEX AS CATALYST

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The reagent system generated from Cp_2TiCl_2 and $LiBH_4$ promotes the catalytic hydroboration of olefins with $LiBH_4$ to give lithium alkylborohydrides which can be converted into alcohols by treating with sodium methoxide and H_2O_2.

Previously, we have shown that a titanium-aluminium complex generated from Cp_2TiCl_2 and $LiAlH_4$ in a 1:2 molar ratio promotes the catalytic hydroalumination of olefins with $LiAlH_4$ to give lithium alkylhydroaluminates.$^{1)}$ Similar hydroalumination is also effected by the use of $TiCl_4$-$LiAlH_4$ reagent system.$^{2)}$ The alkylaluminates thus produced can be utilized as an intermediate in a wide variety of synthetic organic reactions.$^{3,4)}$

We now wish to report that a titanium-boron complex generated from Cp_2TiCl_2 and $LiBH_4$ induces the catalytic hydroboration of olefins with $LiBH_4$ to give lithium alkylborohydrides (lithium alkylhydroborates).$^{5)}$

A freshly recrystallized Cp_2TiCl_2 (0.565 mmol) was added to a solution of $LiBH_4$ (11.2 mmol) in THF (15 ml), and the mixture was stirred at room temperature under argon for 1 h. During this period, a violet solution was obtained with evolution of H_2. 1-Octene (11.3 mmol) was then added over 5 min, and the reaction mixture was stirred at 45°C for 21 h. A 3 M methanolic sodium methoxide (5.5 ml) and then 30% aqueous H_2O_2 (12 ml) was added at 30°C to the mixture. The resulting mixture was stirred for 1 h and extracted with ether. The ethereal extract was washed with water, dried ($MgSO_4$), and evaporated. Distillation of the residue gave 1-octanol as a major product. The GLC analysis showed that the reaction mixture contained 1-octanol (79%), 2-octanol (4%), and octane (5%) along with unreacted 1-octene (12%).

Table 1. Formation of Octanols via Hydroboration of 1-Octene[a]

Run	Molar ratio Cp_2TiCl_2:$LiBH_4$:1-Octene	Reaction time (h)	Total yield of alcohols[b] (%)	Molar ratio of alcohols produced 1-ol	: 2-ol	Theoretical maximum yield of alcohols based on 1-octene[c] (%)
1	1 : 1 : 4	93	trace	--	--	0
2	1 : 2 : 4	97	15	93	7	0
3	1 : 3 : 4	50	66	94	6	75
4	1 : 4 : 4	74	100	95	5	100
5	1 : 4 : 10	48	59	95	5	60
6	1 : 4 : 16	96	38	95	5	38
7	1 : 20 : 20	21	83	95	5	100

a. All the reactions (the hydroboration step) were run at 45°C. b. The yields were determined by GLC and based on 1-octene used. c. The theoretical yields were calculated on the assumptions that (1) the catalyst is formed by the reaction of one molar quantity of Cp_2TiCl_2 with two molar quantities of $LiBH_4$, and (2) three molar quantities of 1-octene react with one molar quantity of $LiBH_4$ to form lithium trioctylborohydrides.

The above transformation of 1-octene to alcohols was conducted under similar conditions by using reagent systems consisting of various amounts of Cp_2TiCl_2, $LiBH_4$, and 1-octene. The results of Table 1 indicate that the reaction is catalytic in nature with respect to titanium complex (see also Table 2). The variation of yields of products with change in the composition of reagents can be explained in terms of the pathways represented in Scheme 1.

$$Cp_2TiCl_2 + LiBH_4 \longrightarrow \underset{[1]}{\text{titanium-boron complex}} \qquad (1)$$

$$n\ C_6H_{13}CH{=}CH_2 + LiBH_4 \xrightarrow{[1]} \underset{[2]}{LiR_nBH_{4-n}} \qquad (2)$$

$$[2] \xrightarrow{CH_3ONa\text{-}H_2O_2} \underset{[3]}{C_6H_{13}CH_2CH_2OH} + \underset{[4]}{C_6H_{13}CH(OH)CH_3} \qquad (3)$$

$$R{=}C_6H_{13}CH_2CH_2\text{-} \text{ or } C_6H_{13}\overset{|}{C}HCH_3, \quad 1 \leq n \leq 3$$

Scheme 1.

A separate experiment showed that one molar quantity of Cp_2TiCl_2 reacts with two molar quantities of $LiBH_4$ to form a titanium-boron complex with evolution of one molar quantity of H_2.[6)] Unfortunately, the structure of this complex remaines

Table 2. Preparation of Alcohols via Hydroboration of Olefins by Cp_2TiCl_2-$LiBH_4$ System[a]

Run	Olefin	Reaction conditions Solvent	Temp(°C)	Time(h)	Product(s)	Yield(s),%[b]
8	1-Octene	THF	45	21	1-Octanol	79 (1580)
					2-Octanol	4 (75)
9	2-Octene	Diglyme	45	46	1-Octanol	3 (48)
					2-Octanol	17 (274)
10	2-Octene	Diglyme	150	1[c]	1-Octanol	8 (128)
					2-Octanol	52 (835)
11	2-Phenylpropene	THF	45	26	2-Phenyl-1-propanol	19 (361)
12	Cyclohexene	THF	45	22	Cyclohexanol	81 (1897)
13	1-Methylcyclopentene	THF	65	38	*trans*-2-Methylcyclopentanol[d]	65 (1254)

a. All the reactions (the hydroboration step) were conducted by using the reagent system: Cp_2TiCl_2:$LiBH_4$:Olefin = 1:20:20. b. Yields were determined by GLC and based on olefins used. Numbers in parentheses indicate the yields based on Cp_2TiCl_2 used. c. The reaction mixture which was produced from Cp_2TiCl_2, $LiBH_4$, and olefin was further heated at 150°C for 1 h, after stirring at 45°C for 46 h. d. The physical properties of this compound, n_D^{20} and melting point of p-nitrobenzoate, were identical with those reported in the literature.[7)]

unestablished at present. However, the results of Table 1 suggest that the complex thus produced acts as a catalyst for the hydroboration of 1-octene with $LiBH_4$ to produce a mixture of lithium octylborohydrides [2]. These pathways are similar to those of the titanium complex-catalyzed hydroalumination of olefins, in that $Cp_2Ti(AlH_3)_2$ acts as a catalyst.[1)] Finally, the oxidation of [2] with CH_3ONa-H_2O_2 gives alcohols [3] and [4].

The above catalytic hydroboration could be applied to other olefins. The results are given in Table 2. The striking characteristics of this reaction may be summarized as follows:

(1) In the catalytic hydroboration of olefins, the reaction smoothly takes place when the reagent system, $LiBH_4/Cp_2TiCl_2 > 2$, is employed, and a titanium-boron complex generated from Cp_2TiCl_2 and $LiBH_4$ acts as catalyst.

(2) The reaction occurs predominantly in the anti-Markownikoff fashion.

(3) Products produced by the catalytic reaction are lithium alkylborohydrides.[8,9)]

(4) The relative reactivity of olefins decreases in the order: 1-octene (terminal olefin) > cyclohexene (cyclic olefin) > 2-octene (internal olefin).

(5) The cis-addition predominates in the addition of $LiBH_4$ to carbon-carbon double bonds (Table 2, run 13).

References and Notes

1) K. Isagawa, K. Tatsumi, and Y. Otsuji, Chem. Lett., 1976, 1145; K. Isagawa, K. Tatsumi, H. Kosugi, and Y. Otsuji, Chem. Lett., 1977, 1017.

2) F. Sato, T. Oikawa, and M. Sato, Chem. Lett., 1979, 167, and references cited therein.

3) K. Isagawa, K. Tatsumi, and Y. Otsuji, Chem. Lett., 1977, 1117.

4) K. Isagawa, M. Ohige, K. Tatsumi, and Y. Otsuji, Chem. Lett., 1978, 1155.

5) A part of this work has been presented at the 37th CSJ Annual Meeting, Yokohama, April 1978, Abstr. No. 2L17.

6) The reaction of Cp_2TiCl_2 with $LiBH_4$ in THF proceeded smoothly at room temperature with evolution of H_2. Hydrogen gas evolved was collected in a sealed vessel and measured by the method reported previously.$^{1)}$

7) J. B. Umland and M. I. Jefaim, J. Am. Chem. Soc., 78, 2788 (1956).

8) There exists the other possibility that alkylboranes are produced as primary products of the catalytic reaction. However, this possibility was ruled out by the observation that the catalytic reaction of 2-octene gave the same products having similar distribution at 45°C and 150°C (runs 9 and 10 of Table 2). It is known that 2-octylborane readily isomerize to 1-octylborane at 150°C (H. C. Brown and G. Zweifel, J. Am. Chem. Soc., 88, 1433 (1966)). Therefor, if 2-octylborane is produced as a primary product in the reaction of 2-octene at 150°C, then 1-octanol should be obtained as a major product of this reaction. However, this is not the case.

9) The results of Table 1 suggest that if olefin is present in excess, lithium trialkylborohydride of the type $Li[R_3BH]$ is obtained as a major product (runs 5 and 6, and also see the footnote c of Table 1).

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