

HYDROBORATION OF ALKENES AND ALKYNES WITH SODIUM BOROHYDRIDE
CATALYZED BY TITANIUM COMPLEX

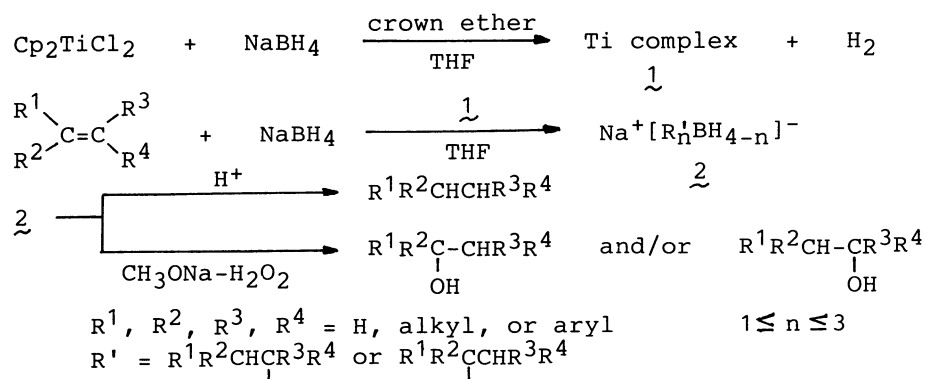
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The titanium complex prepared from Cp_2TiCl_2 and NaBH_4 in THF in the presence of crown ethers efficiently promotes the catalytic hydroboration of alkenes and alkynes with NaBH_4 to give sodium alkyl- and alkenyl-borohydrides which are converted into alcohols and alkenes, respectively.

Crown ethers have found wide application as catalysts in a variety of organic reactions.¹⁾ However, the utility of crown ethers in organotransition metal chemistry has little been explored. Previously, we have reported that the titanium complex generated by the reaction of Cp_2TiCl_2 with LiBH_4 catalytically promotes the hydroboration of alkenes with LiBH_4 in THF to give lithium alkylborohydrides.²⁾ However, under the same reaction conditions, NaBH_4 , which is less expensive but less soluble in THF than LiBH_4 , is not an efficient reagent for this reaction. We now report that when the reaction is carried out in the presence of a crown ether, the catalytic hydroboration of alkenes and alkynes occurs smoothly by using NaBH_4 . Alkylborohydrides thus produced are converted to alcohols on oxidation and alkenylborohydrides to alkenes on protonolysis. Thus, this work constitutes an example of the utility of crown ethers in transition metal catalyzed reactions.

A typical procedure of the hydroboration-oxidation reaction of alkenes is illustrated in the conversion of styrene to phenylethanol: A freshly recrystallized Cp_2TiCl_2 (0.51 mmol) was added to a mixture of NaBH_4 (2.65 mmol) and 18-crown-6 (0.49 mmol) in THF (10 ml) and the mixture was stirred for 1 h at 65 °C



Scheme 1.

under argon atmosphere. During this period, the color of the mixture changed from gray to violet with evolution of H_2 . Styrene (2,60 mmol) was added, and the mixture was stirred for 5 h at the same temperature. A 3 mol dm^{-3} methanolic CH_3ONa solution (3 ml), subsequently 30% aqueous H_2O_2 (5 ml) were added to the mixture. After being stirred for 0.5 h, the resulting mixture was extracted with diethyl ether. The extract was dried and concentrated. The GLC analysis of the residue using dodecane as an internal standard showed that the reaction mixture contains 1- and 2-phenylethanols (70%) in a 69:31 ratio along with a trace amount of unreacted styrene.

The efficiency of this reaction varied with metal cations in metal borohydrides and crown ethers employed. The results are given in Table 1. The combination of $NaBH_4$ and 18-crown-6³⁾ was found to be an efficient reagent system for the hydroboration in THF. The conversion of styrene to phenylethanols was conducted by using the reagent system consisting of various amounts of $NaBH_4$, 18-crown-6, and styrene. The results are given in Table 2. The hydroboration of styrene occurred catalytically with respect to titanium and 18-crown-6. The ratio of 1-phenylethanol/2-phenylethanol was almost independent of composition of the reagents in the reaction system and of the reaction time.

In a similar manner, various alkenes were converted to the corresponding alcohols. The results are listed in Table 3.

Striking features of this hydroboration-oxidation reaction may be summarized as follows: (1) The crown ether, 18-crown-6, mediates the formation of a reactive titanium complex from Cp_2TiCl_2 and $NaBH_4$ and also the subsequent catalytic hydroboration of alkenes with $NaBH_4$; in the absence of 18-crown-6, both the complex formation and the catalytic hydroboration hardly occur. (2) Initial products of the reaction are not alkylboranes but sodium alkylborohydrides.²⁾ (3) The hydroboration takes place preferentially in an anti-Markownikoff fashion.

Possible pathways of the catalytic reaction are outlined in Scheme 2. The titanium complex 1 is formed by the reaction of the Na-crown complex 3 with Cp_2TiCl_2 ,

Table 1. Effects of Metal Borohydrides and Crown Ethers on the Hydroboration-Oxidation Reaction of Styrene^{a)}

Borohydride	Crown ether	Reaction time / h	Color	Yield of Phenyl-ethanols / % ^{b)}
$LiBH_4$	None	5	Violet	70
$LiBH_4$	12-crown-4	5	Violet	77
$NaBH_4$	None	24	Red	trace
$NaBH_4$	12-crown-4	24	Brown	<1
$NaBH_4$	15-crown-5	24	Violet	59
$NaBH_4$	18-crown-6	5	Violet	70
KBH_4	12-crown-4	24	Brown	<1
KBH_4	15-crown-5	24	Violet	20
KBH_4	18-crown-6	5	Violet	20

a) All the reactions were conducted at 65 °C in THF by using the reagent system; styrene : MBH_4 : Cp_2TiCl_2 : crown ether = 5 : 5 : 1 : 1.

b) Yields were determined by GLC and based on styrene used.

Table 2. Effects of Reagent System and Reaction Conditions on the Hydroboration-Oxidation Reaction of Styrene^{a)}

Cp ₂ TiCl ₂ :NaBH ₄ :18-crown-6:styrene	Molar ratio			Reaction time / h	Total yield / % ^{b)}	Ratio of	
	5	1	5			2-ol / 1-ol	1-ol
0	5	1	5	5	0	—	—
1	5	0	5	5	0	—	—
1	3	1	3	3	77 (237)	26	74
1	3	3	3	3	77 (231)	31	69
1	5	1	5	5	70 (359)	31	69
1	10	1	10	24	42 (429)	30	70
1	20	1	20	24	38 (798)	26	74
1	20	1	20	48	49(1030)	26	74

a) All the reactions were conducted at 65 °C in THF. b) GLC yields based on styrene used. Figures in parentheses indicate the yields based on Cp₂TiCl₂ used.

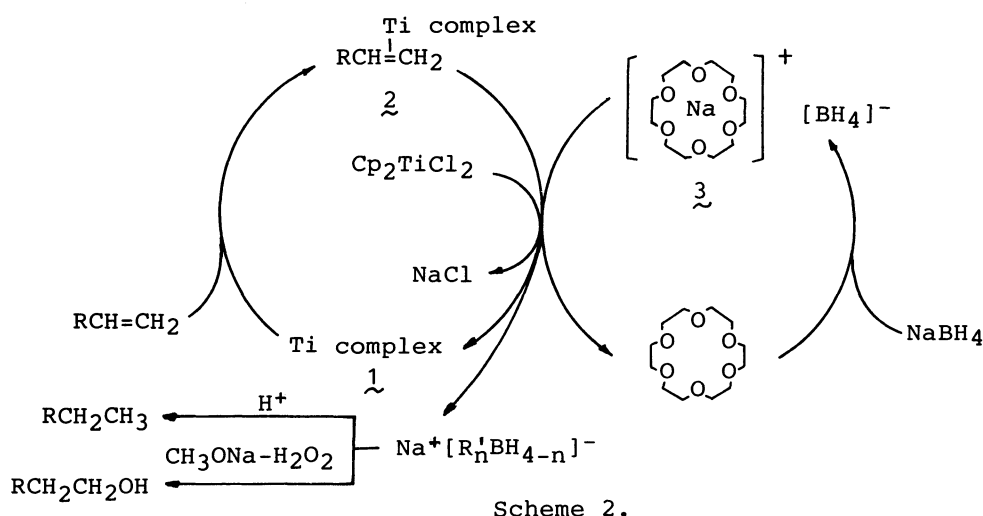
Table 3. Hydroboration-Oxidation Reaction of Alkenes^{a)}

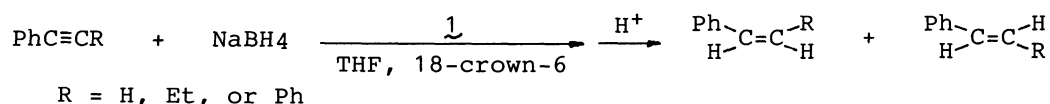
Alkene	Reaction time / h	Product(s)	Yield / % ^{b)}	Ratio of 1-ol/2-ol
1-Octene	24	1-Octanol	72	94
		2-Octanol	5	6
2-Octene	24	1-Octanol	5	10
		2-Octanol	45	90
Styrene	5	2-Phenyl-ethanol	48	69
		1-Phenyl-ethanol	22	31
α-Methylstyrene	5	2-Phenyl-1-propanol	71	—

a) All the reactions were conducted at 65 °C by the reagent system; alkene : NaBH₄ : Cp₂TiCl₂ : 18-crown-6 = 5 : 5 : 1 : 1.

b) GLC yields based on alkenes used.

and **3** promotes the catalytic hydroboration of alkenes to give sodium alkylborohydrides, presumably via the alkene coordinated Ti complex **2**.





The hydroboration of alkynes with NaBH₄ in THF was also catalyzed by the complex **1**. Initial products of this reaction were sodium alkenylborohydrides which upon protonolysis gave the corresponding alkenes. The results are shown in Table 4.

It has been shown that in the hydroboration of terminal alkynes with diborane, the formation of dihydroborated products usually predominates.^{4,5)} In contrast to this, the titanium complex catalyzed hydroboration with NaBH₄ affords preferentially monohydroborated products even in the presence of excess NaBH₄. In the hydroboration of internal alkynes, the formation of *cis*-alkenes predominates in the initial stage. However, the detailed studies strongly suggested that in the presence of excess NaBH₄, the isomerization of the *cis*-isomers to the *trans*-isomers occurs during the reaction.⁶⁾

Table 4. Hydroboration of Alkynes with NaBH₄ in the Presence of Titanium Complex in THF^{a)}

Alkyne	Reaction time / h	Product(s)	Yield(s) of product(s) / % ^{b)}	Recovered alkyne / %
C ₆ H ₁₁ C≡CH	8	C ₆ H ₁₁ CH=CH ₂	74	5 ^{c)}
PhC≡CH	3	PhCH=CH ₂	70	20 ^{d)}
PhC≡CEt	14	<i>cis</i> -PhCH=CH ₂	41	trace
		<i>trans</i> -PhCH=CH ₂	51	
PhC≡CPh	23	<i>cis</i> -PhCH=CHPh	68	trace
		<i>trans</i> -PhCH=CHPh	26	

a) All the reactions were conducted at 65 °C by using the reagent system; alkyne : NaBH₄ : Cp₂TiCl₂ : 18-crown-6 = 5 : 5 : 1 : 1. b) Yields based on alkynes used. c) Octane was obtained as a by-product in a 9% yield. d) Ethylbenzene was obtained as a by-product in a 3% yield.

References

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- 2) K. Isagawa, H. Sano, M. Hattori, and Y. Otsuji, Chem. Lett., 1979, 1069, and references cited therein.
- 3) It has been well established that Na⁺ ion is strongly captured by 18-crown-6 in THF: K. H. Wong, G. Konizer, and J. Smid, J. Am. Chem. Soc., 92, 666 (1970).
- 4) H. C. Brown and G. Zweifel, J. Am. Chem. Soc., 83, 3834 (1961).
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- 6) In the case of 1-phenyl-1-butyne, the reaction mixture obtained by the hydroboration was quenched by CH₃COOH at appropriate intervals. The product analyses showed that the mixture contains the *cis*- and *trans*-isomers in a 83:17 ratio after 6 h, in a 45:55 ratio after 14 h and in a 30:70 ratio after 20 h.

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