CHEMISTRY LETTERS, pp. 1117-1120, 1977. Published by the Chemical Society of Japan

PREPARATION OF ALCOHOLS VIA HYDROALUMINATION OF OLEFINS BY USE OF THE Cp_2TiCl_2-$LiAlH_4$ REAGENT SYSTEM[1)]

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The oxidation of lithium alkylhydroaluminates, which are produced by the catalytic hydroalumination of 1-olefins with the Cp_2TiCl_2-$LiAlH_4$ reagent system, gives the corresponding 1-alcohols. By a similar method, dienes having a double bond at the terminal position can be converted selectively to the corresponding alken-1-ols, in which the internal double bond remains intact. The yields of alcohols depend on the oxidizing agents used.

Recently, we have shown that the titanium complex $Cp_2Ti(AlH_3)_2$ is produced by the reaction of one molar quantity of Cp_2TiCl_2 with two molar quantities of $LiAlH_4$.[2)] This complex efficiently promotes the catalytic hydroalumination or the catalytic isomerization of olefins, depending on the composition of reagents present in the reaction system.[2,3)] Use of a large excess of $LiAlH_4$ and olefins preferentially promotes the catalytic hydroalumination to give lithium alkyl-1-trihydroaluminates, if both the reagents are present in a 1:1 molar ratio. In this communication, we report a new convenient method for the preparation of alcohols via the catalytic hydroalumination of olefins.[4,5)]

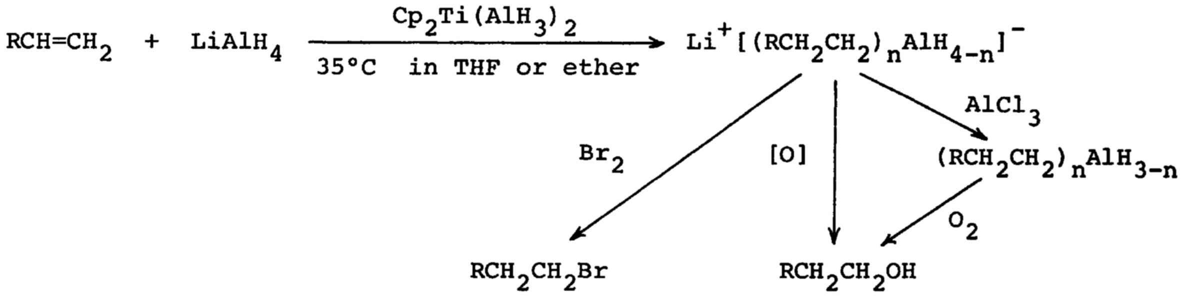
The catalytic hydroalumination of various olefins was carried out by a method similar to that described previously.[3)] The efficiency of the reaction was evaluated by converting the resulting alkylaluminates to the corresponding bromides (Table 1).

Table 1. Preparation of Bromoalkanes via Hydroalumination of Olefins

Run	Olefin	Product(s)[a)]	Yield(s),(%)[b)]
1	$C_4H_9CH{=}CH_2$	n-$C_6H_{13}Br$	79
2	$C_6H_{13}CH{=}CH_2$	n-$C_8H_{17}Br$	87
3	$C_8H_{17}CH{=}CH_2$	n-$C_{10}H_{21}Br$	85
4	$PhCH{=}CH_2$	$PhCH_2CH_2Br$	50
		$PhCHBrCH_3$	trace
5	$C_5H_{11}CH{=}CHCH_3$	$C_6H_{13}CH_2CH_2Br$	trace
		$C_6H_{13}CHBrCH_3$	15

a) Bromoalkanes were identified by their IR, NMR, and Mass spectral data.
b) The yields based on olefins used.

Then, transformation of alkylaluminates to the corresponding alcohols was performed by the following three methods: 1) oxidation of an alkylaluminate with O_2 and H_2O_2, followed by the hydrolysis of the resulting mixture with an aqueous NaOH solution (Method A),$^{6)}$ 2) oxidation of an alkylaluminate with m-chloroperbenzoic acid, followed by the hydrolysis of the resulting mixture with an aqueous NaOH solution (Method B), and 3) oxidation of an alkylaluminium with O_2, followed by the hydrolysis of the resulting mixture with an aqueous HCl solution (Method C). In the last case, alkylaluminiums can readily be obtained by treating alkylaluminates with $AlCl_3$.



Scheme 1.

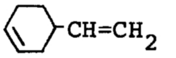
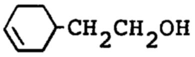
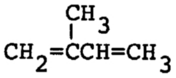
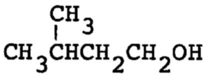
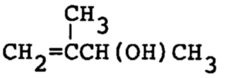
Typical experimental procedures are illustrated by taking the conversion of 1-octene to 1-octanol as an example. (Method A) A mixture of Cp_2TiCl_2 (1.28 mmol), $LiAlH_4$ (25.6 mmol), and 1-octene (25.6 mmol) in ether (30 ml) was stirred for 5 h at 35°C as described previously.$^{3)}$ Dry oxygen was then introduced into the black reaction mixture at room temperature until a dark yellow mixture appeared. A mixture of 30% H_2O_2 (4 ml) and 3M NaOH solution (3 ml) was added to the above reaction mixture at 35°C, and then the resulting mixture was filtered and extracted with ether. The ethereal extract was washed with a 10% $NaHSO_3$ solution, dried (Na_2SO_4), and evaporated. Distillation of the residue gave octane and 1-octanol as main products: the GLC analysis revealed that the reaction mixture contained 1-octanol (7.4 mmol) and octane (14.8 mmol) along with a trace amount of 2-octanol.

(Method B) A mixture of Cp_2TiCl_2 (0.64 mmol), $LiAlH_4$ (12.81 mmol), and 1-octene (25.83 mmol) in THF (15 ml) was stirred similarly for 5 h at 35°C. The resulting mixture was added to a solution of m-chloroperbenzoic acid (MCPBA) (25.6 mmol) in ether (10 ml) at 0°C. The mixture was stirred at 30°C for 10 min, and then treated with 3M NaOH solution (5 ml). Work-up of the reaction mixture gave 1-octanol as a major product.

(Method C) A mixture of Cp_2TiCl_2 (0.63 mmol), $LiAlH_4$ (13.00 mmol), and 1-octene (13.17 mmol) in THF (15 ml) was stirred for 5 h at 35°C, and the resulting mixture was refluxed with anhydrous $AlCl_3$ (4.61 mmol) for 2 h. Oxygen was passed into the reaction mixture, and then the resulting mixture was hydrolyzed with 6M HCl solution. Work-up of the reaction mixture gave 1-octanol as a major product.

The other olefins were reacted similarly. The results are given in Table 2. Striking features of the reactions presented above could be summarized as follows: (1) The hydroalumination of olefins occurs in the anti-Markownikoff fashion. (2) The reactivity of olefins in the hydroalumination strongly depends on the structure of olefins employed. Straight-chain 1-olefins react smoothly. Internal olefins

Table 2. Preparation of Alcohols via Hydroalumination of Olefins

Run	Olefin	Product(s)[a)]	Yield(s),(%)[b)]		
			Method A	Method B	Method C
6	$C_4H_9CH{=}CH_2$	$n\text{-}C_6H_{13}OH$	29	64	68
7	$C_6H_{13}CH{=}CH_2$	$n\text{-}C_8H_{17}OH$	38	56	70
8	$PhCH{=}CH_2$	$PhCH_2CH_2OH$	24	34	17
		$PhCH(OH)CH_3$	14	9	32
9			54	69	86
10	 $CH_2{=}\overset{CH_3}{C}CH{=}CH_3$	 $CH_3\overset{CH_3}{C}HCH_2CH_2OH$	15	23	10
		 $CH_2{=}\overset{CH_3}{C}CH(OH)CH_3$	7	1	19

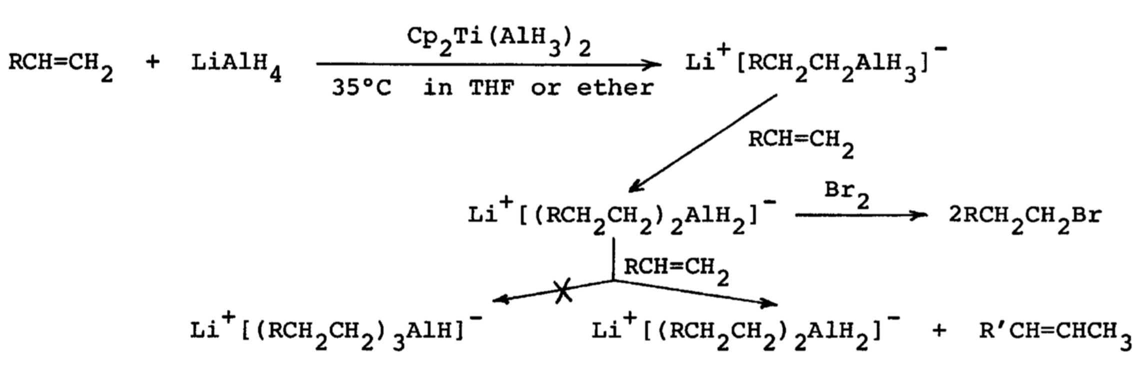
a) Alcohols were identified by their IR, NMR, and Mass spectral data.

b) The yields based on olefins used.

such as 2-octene and cyclohexenes, and 2-alkyl-substituted 1-olefins such as α-methylstyrene, d-limonene, and β-pinene are highly unreactive, and they are in fact recovered unchanged in almost quantitative yield, although a hindered bicyclic olefin such as 2,5-norbornadiene is hydroaluminated with a low efficiency.

The hydroalumination of dienes is highly regioselective as examplified by the formation of 2-(3-cyclohexenyl)ethanol from 4-vinylcyclohexene: i.e., in this reaction, the internal double bond in the cyclohexene ring remains intact. (3) The oxidation of alkylaluminates with O_2 and H_2O_2 gives the corresponding alcohols in relatively low yields, and an improvement of the yields is attained by the use of MCPBA as an oxidizing agent. The oxidation of alkylaluminiums (Method C) is more effective for the preparation of alcohols. (4) The oxidation of alkylaluminates and alkylaluminiums with oxygen may involve alkyl radicals as an intermediate. In support of this view, the oxidation of aluminates from styrene and isoprene gives 1-phenylethanol and 3-methyl-3-buten-2-ol, respectively.[7)]

Another striking feature is that when 1-olefins and $LiAlH_4$ are used in the molar ratio of 2:1, lithium dialkyl-1-dihydroaluminates are obtained. However, an



Scheme 2.

additional use of 1-olefins produces no trialkyl-1-hydroaluminates, and instead the isomerization of 1-olefins to internal olefins occurs after the formation of dialkyl-1-dihydroaluminates. This conclusion was deduced from the fact that the reaction of 1-octene (77.3 mmol) with $LiAlH_4$ (25.6 mmol) in ether (30 ml) in the presence of Cp_2TiCl_2 (1.28 mmol) at 35°C for 5 h, followed by bromination of the reaction mixture with Br_2, gave a mixture of 1-bromooctane (44.2 mmol), 2,3-dibromooctane (22.9 mmol), and octane (10.0 mmol). The oxidation by Method B was indeed conducted on the basis of this observation: in Method B, 1-olefins and $LiAlH_4$ were used in the molar ratio of 2:1, and the olefins were converted to the corresponding 1-alcohols in moderately good yields via dialkyl-1-dihydroaluminates.

In conclusion, the present reaction provides a convenient, selective method for the preparation of alcohols from olefins.

References and Notes

1) A part of this work was presented at the 36th Spring Annual Meeting of the Chemical Society of Japan, Osaka, April, 1977; Abstr. No. 4E08.
2) K. Isagawa, K. Tatsumi, H. Kosugi, and Y. Otsuji, Chem. Lett., 1977, 1017.
3) K. Isagawa, K. Tatsumi, and Y. Otsuji, Chem. Lett., 1976, 1145.
4) The preparation of alcohols by the oxidation of lithium alkylhydroaluminates was carried out by the modification of the method reported by Ziegler et al.; K. Ziegler, F. Krupp, and K. Zosel, Ann. Chem., 629, 241 (1960).
5) Recently, Sato and his collaborators have independently reported the preparation of alcohols through the hydroalumination of olefins by use of the $TiCl_4$-$LiAlH_4$ reagent system. With this reagent system, lithium tetraalkylaluminates are preferentially obtained by the hydroalumination of olefins; F. Sato, H. Kodama, and M. Sato, Abstr. No. 1E15, the 36th Spring Annual Meeting of the Chemical Society of Japan, Osaka, April, 1977.
6) The oxidation of alkylaluminates with either O_2 or H_2O_2 alone gave the corresponding alcohols in very low yields. The use of both O_2 and H_2O_2 improved the yield of alcohols.
7) The oxidation of boranes with O_2 involves alkyl radicals as an intermediate; H. C. Brown, M. M. Midland, and G. W. Kobalka, J. Am. Chem. Soc., 93, 1024 (1971).

(Received July 23, 1977)