Tetrahedron Letters, Vol. 34, No. 1, pp. 171-174, 1993
Printed in Great Britain

0040-4039/93 $5.00 + .00
Pergamon Press Ltd

An Unusual Anti-Markovnikov Hydration of Alkenes with Titanium(III) Tetrahydroborates

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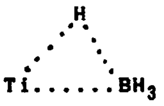
Abstract: Titanium(III) tetrahydroborate formed by the reaction of titanium tetrachloride and benzyltriethylammonium borohydride (1:4) reacts with alkenes in dichloromethane (-20°C) very readily to yield directly the corresponding alcohols in excellent yields after a simple aqueous work up.

The interaction of titanium tetrachloride with excess lithium borohydride has long been known to yield the unstable titanium(III) tetrahydroborate complex, $Ti(BH_4)_3$[1,2] and this species has been reported in the patent literature to be an active polymerization catalyst or a catalyst precursor.[3] Recently, Girolami[4,5] prepared several tertiary phosphine adducts of $Ti(BH_4)_3$ and then characterized by X-ray crystallography noting the presence of a highly unusual tetrahydroborate bonding mode in which two of the three borohydride ligands are bonded in a 'side on'fashion to the titanium center.

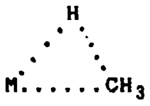
In the course of studying the reactivity of $Ti(BH_4)_3$ species towards organic substrates, we prepared this tetrahydroborate complex by the reaction of $TiCl_4$ with excess benzyltriethylammonium borohydride(1:4)[6]. A solution of this complex in dichloromethane (-20°C) reacts readily with alkenes to produce the corresponding alcohols directly in excellent yields (anti-Markovnikov addition). The results of this unusual reaction are summarized in Table. In all the reactions the alcohols are the only products that could be isolated after a simple aqueous work-up. In the reaction of 1-methylcyclohexene (entry 5), 1-phenylcyclohexene (entry 6) and (±)α-pinene (entry 7) the corresponding alcohols are formed as a mixture of cis and trans isomers. Thus, in contrast to normal hydroboration, the reaction of alkenes with $Ti(BH_4)_3$ is not stereoselective. A similar type of observation on the conversion of alkenes to alcohols using sodium borohydride under more vigorous conditions has also been reported.[7] When the reaction of $Ti(BH_4)_3$ with alkenes was performed in the presence of 2,6-ditertiarybutyl-p-cresol or ethylmercaptan, a complex material resulted[8] and the formation of the corresponding alcohol was almost negligible. Similarly, if the reaction of an alkene is carried out with the tetrahydroborate complex obtained by reacting $1:1/TiCl_4:BH_4^-$, the yield of the corresponding alcohol is very low (≈10%) indicating that $Ti(BH_4)_3$ is the important species needed for the reaction and not the intermediate mixture of chloroborohydrides. Interestingly, when an alkene was reacted with $Ti(BH_4)_3$ in THF[9], the corresponding alcohol was not formed whereas a complex material was isolated.[8] The reactions were also carried out in the presence of air and with anhydrous oxygen-free solvent and there was no dramatic change in the yield of the alcohols.

The mechanism of this reaction is not clear but a normal hydroboration-oxidation can be excluded as the reactivity of this reagent system is considerably different. The product alcohols may have been formed by air oxidation and/or hydrolysis of organotitanium intermediates via a radical mechanism.

It is possible that the novel reactivity of $Ti(BH_4)_3$ is partly because of the unusual 'side on' bonding mode A of the BH_4 ligands which has been compared with the one possible transition state B for the activation of methane by transition metals.[4,9]



A

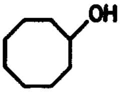
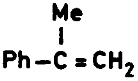
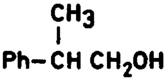
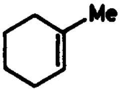
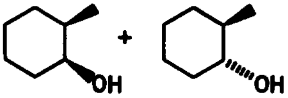
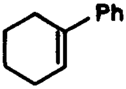
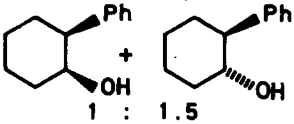
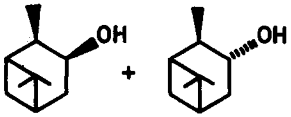
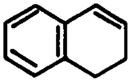
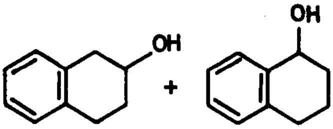
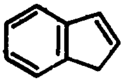
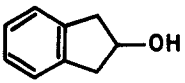
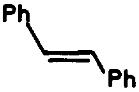
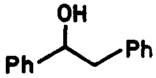


B

Further work is in progress to understand the mechanism of this reaction and its implications in organic synthesis.

Typical experimental procedure for the reaction of Titanium(III)tetrahydroborate with alkenes : To a solution of benzyltriethylammonium borohydride (4 mmol) in dry CH_2Cl_2 (4 ml), $TiCl_4$ (1 mmol) was slowly added under N_2 at -20°C and the reaction mixture was stirred for 0.5 h and the gaseous byproducts were removed under a positive pressure of dry N_2. Alkene(1 mmol) in dry CH_2Cl_2 (2 ml)was added into the reaction mixture and it was stirred for 0.2-2 h (-20°C). A solution of 10% K_2CO_3 (3 ml) was added and stirred for an additional 15 min and after usual work up the alcohol was obtained in very good yields.

Reaction of Alkenes with Ti $(BH_4)_3$

Entry	Substrate	t/h	Product [a]	Yield [b] %
1		0.2		93
2	$CH_3(CH_2)_{13}CH=CH_2$	0.3	$CH_3(CH_2)_{14}CH_2OH$	94
3	 $Ph-\overset{Me}{C}=CH_2$	0.5	 $Ph-\overset{CH_3}{CH}\,CH_2OH$	83
4	$Ph-CH=CH_2$	0.5	$Ph-CH_2CH_2OH$	77
5			 1 : 1.2	82
6		0.5	 1 : 1.5	95
7		0.8	 1 : 8	90
8		0.8	 1 : 4	72
9		0.8		64
10		2.0		89

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[a] All the products were identified by direct comparison of physical data with those of authentic samples.

[b] Yields refer to purified products after chromatography.

Acknowledgement:

One of the authors (KSR) wishes to thank the Management of **IDL CHEMICALS LIMITED** and Dr. G.D. Prasad, Chief Executive, INBRI division for sponsorship to the Ph.D Programme and Dr.G. Om Reddy for help in the initial stages of work.

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(Received in UK 21 October 1992)