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Thexylalkoxyborane as Hydroborating Agent for Alkenes and Alkynes

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In order to elucidate the effect of alkoxy substituent in thexylborane and hence establish their usefulness as hydroborating agent, reactions of alkenes and alkynes with thexylalkoxyborane (ThxBHOR; R=Et, *i*-Pr, *i*-Bu, *sec*-Bu, *t*-Bu, Ph) were investigated in detail. The reagents readily hydroborated alkenes and alkynes of various structural types at 25 °C in excellent regioselectivity. The selectivity increases consistently with increasing steric size of alkoxy substituent. Especially, the selectivity achieved by the *sec*-butoxy derivative is comparable to that previously achieved by thexylhaloborane-methyl sulfide (ThxBHX·SMe₂), the most selective hydroborating agent known.

Introduction

Of the most readily available of the monoalkylboranes, thexylborane (2,3-dimethyl-2-butylborane, ThxBH₂)^{1,2} has been demonstrated to be a highly useful reagent for the cyclic hydroboration of dienes.³⁻⁵ Moreover, the halogen-substituted derivatives of thexylborane, thexylhaloborane-methyl sulfide (ThxBHX·SMe₂; X=Cl, Br, I), are exceptionally valuable reagents for the selective hydroboration of alkenes and alkynes of different structural types.⁶⁻¹⁰ These reagents hydroborate most alkenes and alkynes cleanly with high regio- and stereospecificity to produce isomerically pure thexylalkyl- and thexylalkenylhaloboranes, respectively. These versatile intermediates have been used effectively in organic synthesis.⁸⁻¹¹ In addition to that, ThxBHX·SMe₂ are also

attractive reducing agents,^{9,10,12-14} especially for the conversion of carboxylic acids and their derivatives to the corresponding aldehydes.^{15,16} These results clearly suggest that the halogen substituent in ThxBH₂ enhances the selectivity dramatically both in reduction and hydroboration reactions.

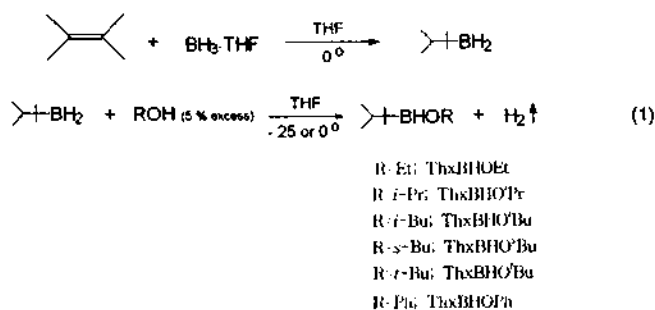
Accordingly, we decided to extend our investigation to the reaction of alkoxy derivatives of ThxBH₂. We prepared a series of thexylalkoxyborane (ThxBHOR; R=Et *i*-Pr, *i*-Bu, *sec*-Bu, *t*-Bu, Ph) and applied them to the hydroboration of alkenes and alkynes to examine the directive effect, in the hope of better understanding the nature of reagents and of exploring their role in organic synthesis. In this article, we describe in full the results of our study on the hydroboration characteristics of thexylalkoxyborane.

Results and Discussion

Preparation of ThxBHOR. The approximate rates and stoichiometry of the reaction of ThxBH₂ with 2 equiv of alcohols at -25 or 0 °C were examined in order to establish the generality of this synthesis of ThxBHOR. The course of the reaction was monitored by calculating the moles of hydrogen evolved. These results are summarized in Table 1.

ThxBH₂ reacted with alcohols examined, except only *t*-butyl alcohol, readily to evolve 1 equiv of hydrogen within 30 min at -25 °C and no further hydrogen evolution even in the presence of excess alcohols was apparent. The evolution of hydrogen in the reaction of *t*-butyl alcohol at -25 °C was relatively slow. However, at the elevated reaction temperature to 0 or 25 °C the reaction was complete within 30 min or 5 min, respectively, with only 1 equiv of hydrogen evolution.

On the basis of the results in Table 1, we utilized a slight excess alcohols (5% excess) in the reaction with ThxBH₂ under the practical conditions¹⁷ (Eq. 1). The solution of ThxBH₂ in THF can be readily prepared by the monohydroboration of 2,3-dimethyl-2-butene with BH₃·THF.^{1,2}



The ¹¹B NMR spectra of the resulting ThxBHOR solution in THF so prepared exhibited a clean doublet centered at δ 51.1 ppm (*J*_{BH} = 127 Hz) for ThxBHOEt, δ 50.4 (*J*_{BH} = 126 Hz) for ThxBHO*i*Pr, δ 50.9 (*J*_{BH} = 121 Hz) for ThxBHO*t*Bu, δ 50.2 (*J*_{BH} = 125 Hz) for ThxBHO*s*Bu, δ 48.2 (*J*_{BH} = 126 Hz) for ThxBHO*r*Bu, and δ 50.9 (*J*_{BH} = 128 Hz) for ThxBHOPh. All the reagents were stable when stored under a static pressure of dry nitrogen at 0 °C.

Hydroboration of Representative Alkenes. We examined the reaction of ThxBHOR with alkenes of different structural types under the standardized reaction conditions (10% excess reagent, 25 °C, tetrahydrofuran) to determine the time required for complete hydroboration. However, the reaction with ThxBHOEt was so relatively fast that the reaction temperature was kept at 0 °C, whereas the reaction with ThxBHO*t*Bu was so sluggish that 100% excess reagent was utilized at 25 °C. The approximate rate of hydroboration was monitored by hydrolyzing aliquots with a mixture of methanol-glycerine-water (1:1:1), followed by measurement of hydrogen evolved.

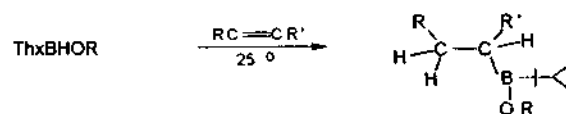
The relative rate of hydroboration with ThxBHOR toward alkenes appears to be essentially dependent upon the steric size of alkoxy group. Thus, the rate is in order of ThxBHOEt > ThxBHO*s*Bu >> ThxBHO*i*Pr > ThxBHO*t*Bu >> ThxBHO*r*Bu. The rate of ThxBHOPh is somewhere between ThxBHOEt and ThxBHO*t*Bu. Especially noteworthy is the reac-

Table 1. Reaction of Thexylborane with Excess Alcohols^a in Tetrahydrofuran

Alcohol	Temp, °C	Time, min	Hydrogen evolution ^b
ethanol	-25	1	0.65
		5	0.95
		15	1.01
		60	1.01
isopropyl alcohol	-25	1	0.32
		5	0.58
		15	0.82
		30	1.00
		60	1.00
isobutyl alcohol	-25	1	0.45
		5	0.94
		15	0.99
		30	1.01
		60	1.01
<i>sec</i> -butyl alcohol	-25	1	0.30
		5	0.45
		15	0.78
		30	1.00
		60	1.00
<i>tert</i> -butyl alcohol	0	1	0.56
		5	0.89
		15	0.91
		30	1.00
		60	1.00
phenol	-25	1	0.37
		5	0.91
		15	0.97
		30	1.01
		60	1.01

^aAlcohol : reagent = 2 : 1. ^bMmol per mmol of reagent.

tivity of ThxBHO*t*Bu: the reagent was absolutely inert toward all the alkenes examined under the experimental reaction conditions. Consequently, all the alkenes examined undergo the hydroboration readily with these reagents, except ThxBHO*t*Bu, under the experimental conditions. The results are summarized in Table 2.



The directive effects in the hydroboration of alkenes with ThxBHOR were next investigated. After standard hydroboration with the reagents under the standardized conditions (ThxBHOEt at 0 °C; the others at 25 °C), the corresponding intermediate of thexylalkylborinate in each case was oxidized with alkaline hydrogen peroxide, and the oxygenated produ-

Table 2. Reaction of Representative Alkenes with Thexylalkoxyborane in Tetrahydrofuran at 25 °C^a

Alkene	Time, h	Hydride used for hydroboration ^b					
		R in ThxBHOR					
		Et	<i>i</i> -Bu	<i>i</i> -Pr	<i>s</i> -Bu ^d	<i>t</i> -Bu	Ph
1-octene	1.0	0.93,1.00 ^c	0.93	0.38	0.20,0.40		0.96
	3.0	1.00	1.00	0.57	0.29,0.61	0.00	1.00
	6.0			0.72	0.38,0.78		
	12.0			0.84	0.48,0.91		
	24.0			1.00	0.60,1.00		
	72.0				0.97 ^e		
1-decene	1.0	0.92,1.00 ^c	0.90	0.35	0.39		0.96
	3.0	1.00	0.98	0.47	0.58	0.00	1.00
	6.0		1.00	0.63	0.76		
	12.0			0.79	0.93		
	24.0			1.00	1.00		
3,3-dimethyl-1-butene	1.0	0.69	0.61	0.27	0.35		0.88
	3.0	0.88	0.82	0.41	0.48	0.00	0.96
	6.0	0.95	0.90	0.60	0.67		1.00
	12.0	1.00	0.97	0.84	0.88		
	24.0		1.00	1.00	1.00		
2,4,4-trimethyl-2-pentene	1.0	0.54	0.50	0.20	0.27		0.70
	3.0	0.81	0.71	0.39	0.43		0.84
	6.0	0.93	0.86	0.61	0.63	0.00	0.96
	12.0	1.00	0.94	0.81	0.84		1.00
	24.0		1.00	1.00	1.00		
1-methylcyclohexene	1.0	0.57	0.52	0.27	0.31		0.79
	3.0	0.84	0.76	0.40	0.41	0.00	0.91
	6.0	0.95	0.88	0.61	0.62		0.97
	12.0	1.00	0.94	0.82	0.83		1.00
	24.0		1.00	1.00	1.00		
α -methylstyrene	1.0	0.95	0.91	0.43	0.47		0.94
	3.0	1.01	0.97	0.71	0.71	0.01	1.00
	6.0		1.00	0.84	0.85		
	12.0			0.97	1.00		
	24.0			1.00			

^aTen % excess reagent was utilized, except where otherwise indicated. ^bMmol per mmol of alkene. ^cAt 0 °C. ^dTwo equivalents of reagent was used, except where marked 'd' on the data obtained with ThxBHO^tBu. ^eTen % excess reagent was used. ^fat 25 °C.

cts were analyzed by GC. The results are summarized in Table 3.

Essentially quantitative conversions of alkenes to the corresponding alcohols with an excellent regioselectivity in placing the boron atom exclusively at the less hindered carbon atom were observed in every case. Simple straight-chain terminal olefins, such as 1-octene and 1-decene, gave predominant addition of the boron atom to the terminal carbon atom in 94-96% selectivity. However, branching of the *tert*-butyl group adjacent to the double bond influences the direction of addition. Thus, 3,3-dimethyl-1-butene gave 3,3-dimethyl-1-butanol in 99-100% ratio. In the case of disubstituted terminal olefins, the directive effect of the two substituent is overwhelming and results in the almost complete addition of the boron atom to the terminal carbon atom. Thus, α -methylstyrene gave 99.2-100% of the primary alkylborane. In

the case of trisubstituted internal olefins, the boron atom also approaches to the less hindered carbon atom to give the secondary derivatives exclusively. Thus, 1-methylcyclohexene and 2,4,4-trimethyl-2-pentene underwent hydroboration to give more than 99.5% of the secondary derivative.

The selectivity achieved by all these reagents appears excellent. Inspection of the data for product distribution, however, reveals that the steric size of alkoxy substituent in thexylborane influences the regioselectivity in the hydroboration of alkenes. The relative selectivity is in order of ThxBHO^tBu > ThxBHOⁱPr > ThxBHO^sBu > ThxBHO^tPh > ThxBHOEt (at 0 °C). Especially, the selectivity achieved by ThxBHO^tBu reaches essentially 100%, except the case of straight-chain terminal olefins. The selectivity matches that displayed by ThxBHI·SMe₂,¹⁰ the most selective hydroborating agent known as seen in the comparison data of Table 4.

Table 3. Directive Effects in the Hydroboration of Alkenes with Thexylalkoxyborane in Tetrahydrofuran at 25 °C^a

Alkene	Products	Product distribution, % ^{b,c}				
		ThxBHOEt ^d	ThxBHO ^t Bu	ThxBHO ⁱ Pr	ThxBHO ^t Bu ^r	ThxBHO ^t Ph
1-octene	1-octanol	94	94	95	96	94
	2-octanol	6	6	5	4	6
1-decene	1-decanol	94	94	95	96	94
	2-decanol	6	6	5	4	6
3,3-dimethyl-1-butene	3,3-dimethyl-1-butanol	99.3	99.4	99.7	>99.9	99.0
	3,3-dimethyl-2-butanol	0.7	0.6	0.3	trace	1.0
2,4,4-trimethyl-2-pentene	2,4,4-trimethyl-3-pentanol	99.7	>99.9	>99.9	>99.9	99.6
	2,4,4-trimethyl-2-pentanol	0.3	trace	trace	trace	0.4
1-methylcyclohexene	2-methylcyclohexanol	99.4	99.4	99.6	>99.9	96
	1-methylcyclohexanol	0.6	0.6	0.4	trace	4
α -methylstyrene	2-phenyl-1-propanol	99.3	99.4	99.7	>99.9	99.2
	2-phenyl-2-propanol	0.7	0.6	0.3	trace	0.8

^aTen % excess reagent was utilized, except where otherwise indicated. ^bThe distribution is deduced by GC analysis from the oxygenated products of the intermediate Thx(R)BOR. ^cTotal yields are 94±5%. ^dReacted at 0 °C. ^eTwo equivalents of reagent was used.

Table 4. Directive Effects (% Substitution) in Alkenes with Various Hydroborating Agents^a

Alkene	Products	Product distribution, % ^{b,c}			
		BH ₃ ·THF ^b	ThxBHI·SMe ₂ ^c	ThxBHO ⁱ Pr	ThxBHO ^t Bu
1-decene	1-decanol	94	>99.9	95	96
	2-decanol	6	trace	5	4
2,4,4-trimethyl-2-pentene	2,4,4-trimethyl-3-pentanol	98	99.8	>99.9	>99.9
	2,4,4-trimethyl-2-pentanol	2	0.2	trace	trace
1-methylcyclohexene	2-methylcyclohexanol	97.2	>99.9	99.6	>99.9
	1-methylcyclohexanol	2.8	trace	0.4	trace
α -methylstyrene	2-phenyl-1-propanol	100	>99.9	99.7	>99.9
	2-phenyl-2-propanol	trace	trace	0.3	trace

^aat 25 °C, except where otherwise indicated. ^bAt 0 °C; ref. 18. ^cAt 25 °C; ref. 10.

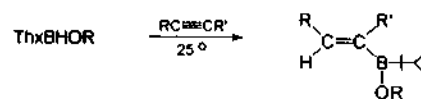
	CH ₃ (CH ₂) ₃ CH=CH ₂		CH ₃ C(CH ₂) ₂ CH=C(CH ₃) ₂		Ph(CH ₂)C=CH ₂	
	t	i	t	i	t	i
ThxBHO ^t Bu	6	94	tr.	>99.9	0.6	99.4
ThxBHO ⁱ Pr	5	95	tr.	>99.9	0.3	99.7
ThxBHO ^t Bu	4	96	tr.	>99.9	tr.	>99.9

Hydroborating of Representative Alkynes. Initially, the rate and stoichiometry of the reaction of ThxBHOR with representative terminal and internal alkynes were investigated. First, two equivalents of the reagents were employed to 1-hexyne, as representative of simple terminal alkynes, at 25 °C in order to determine the stoichiometry of the reaction of alkynes. 1-Hexyne utilized only 1 equiv of reagent for hydroboration: all the reagents in an excess amount undergo a clean monohydroboration with either internal or terminal alkynes at 25 °C, with one exception of the case of ThxBHO^tBu. ThxBHO^tBu was absolutely inert toward alkynes. Therefore, 10% excess reagents were applied to all the alkynes examined to determine the time required for complete monohydroboration, and the results are summarized in Table 5.

Whereas each reagent is rather insensitive to the position of triple bond in alkynes in the hydroboration reaction, the relative reactivity of the reagents toward alkynes depends

upon the steric size of alkoxy substituent.

Thus, the relative rate is in order of ThxBHOEt>ThxBHO^tBu>ThxBHOⁱPr>ThxBHO^tBu>ThxBHO^tBu. The reactivity of ThxBHO^tPh is similar to that of ThxBHOEt. Especially noteworthy is that ThxBHO^tBu was absolutely inert toward all the alkynes examined under the experimental reaction conditions. Consequently, all the terminal and internal alkynes examined undergo the clean monohydroboration readily with ThxBHOR, except the *t*-butoxy derivative, at 25 °C in 10% excess amount (1:1.1).



The direct effect of various unsymmetrically substituted acetylenes toward ThxBHOR was next investigated. The regioselectivity for the addition of B-H bond to alkynes was determined by oxidation of the intermediate alkenylthexylalkoxyboranes with hydrogen peroxide in a buffered solution. The distribution of carbonyl isomers was then quantified by GC analysis. The results are summarized in Table 6.

As is evident from the Table, all the thexylalkoxyboranes

Table 5. Reaction of Representative Alkynes with Thexylalkoxyborane in Tetrahydrofuran at 25 °C

Alkyne	Time, h	Hydride used for hydroboration ^b					
		R in ThxBHOR					
		Et	<i>i</i> -Bu	<i>i</i> -Pr	<i>s</i> -Bu	<i>t</i> -Bu	Ph
1-hexyne	0.5	1.00	0.94	0.78	0.64		0.96
	1.0	1.00	1.00	0.83	0.73		1.00
	3.0	1.00	1.00	0.94	0.85	0.00	1.00
	6.0	1.00	1.00	1.00	0.95		1.00
	12.0	1.00	1.00	1.00	1.00		1.00
	24.0	1.00	1.00	1.00	1.00		1.00
	0.5	1.00	0.88	0.78	0.58		0.96
	1.0		0.96	0.83	0.67		1.00
	3.0		1.00	0.94	0.73		
	6.0			1.00	0.91	0.01	
1-heptyne	0.5	0.93	0.91	0.74	0.66		0.93
	1.0	0.97	0.97	0.81	0.74		1.00
	3.0	1.00	1.00	0.91	0.90	0.00	
	6.0			0.97	0.95		
	12.0			1.00	1.00		
2-hexyne	0.5	0.94	0.92	0.78	0.66		0.93
	1.0	1.00	0.97	0.84	0.73		0.97
	3.0		1.00	0.94	0.89		1.00
	6.0			1.00	0.94	0.01	
	12.0				1.00		
2-octyne	0.5	0.88	0.83	0.71	0.66		0.88
	1.0	0.94	0.90	0.79	0.74		0.94
	3.0	1.00	0.97	0.86	0.85	0.00	1.00
	6.0		1.00	0.95	0.92		
	12.0			1.00	1.00		
3,3-dimethyl-1-butyne	0.5	0.97	0.89	0.86	0.69		0.96
	1.0	1.00	0.95	0.94	0.81		1.00
	3.0		1.00	1.00	0.92	0.00	
	6.0				1.00		
phenylethyne	0.5	0.95	0.94	0.80	0.57		0.96
	1.0	1.00	1.00	0.87	0.69		1.00
	3.0			0.95	0.87	0.01	
	6.0			1.00	0.96		
	12.0				1.00		
1-phenyl-1-propyne	0.5	0.94	0.93	0.80	0.61		0.95
	1.0	0.97	0.95	0.86	0.75		1.00
	3.0	1.00	1.00	0.94	0.84	0.00	
	6.0			1.00	0.95		
	12.0				1.00		

^aTen % excess reagent was utilized, except where otherwise indicated. ^bMmol per mmol of alkyne. ^cTwo equivalents of reagent was used.

achieve the clean monohydroboration of both internal and terminal alkynes and the boron atom places predominantly at the less hindered carbon atom in every case. Simple straight-chain terminal alkynes, such as 1-hexyne and 1-heptyne, gave predominant addition of the boron atom to the terminal carbon atom in 95-97% selectivity. However, branching of the *tert*-butyl group adjacent to the triple bond such as in 3,3-dimethyl-1-butyne pushes the boron atom to the terminal

carbon atom to give 3,3-dimethyl-1-butanal in 97-99% purity. The phenylethyne results indicate that the phenyl group is less effective than the alkyl group in directing the boron atom to the terminal carbon. The similar relative effect of the phenyl and methyl groups is observed for 1-phenylpropyne: 80-86% 1-phenyl-2-propanone and 14-20% 1-phenyl-1-propanone. In the case of straight-chain internal alkynes, such as 2-hexyne and 2-octyne, the directive effect is less

Table 6. Directive Effects in the Monohydroboration of Alkynes with Thexylalkoxyborane in Tetrahydrofuran at 25 °C^a

Alkyne	Products	Product distribution, % ^{b,c}				
		ThxBHOEt	ThxBHO ⁱ Bu	ThxBHO ⁱ Pr	ThxBHO ⁱ Bu	ThxBHO ⁱ Ph
1-hexyne	hexanal	95	95	96	97	94
	2-hexanone	5	5	4	3	6
1-heptyne	heptanal	95	95	96	97	94
	2-heptanone	5	5	4	3	6
2-hexyne	2-hexanone	61	62	68	89	61
	3-hexanone	39	38	32	11	39
2-octyne	2-octanone	62	62	65	84	63
	3-octanone	38	38	35	16	37
3,3-dimethyl-1-butyne	3,3-dimethylbutanal	97	97	98	99	94
	3,3-dimethyl-2-butanone	3	3	2	1	6
phenylethyne	phenylacetaldehyde	84	84	86	88	80
	acetophenone	16	16	14	12	20
1-phenyl-1-propyne	1-phenyl-2-propanone	83	83	84	86	80
	1-phenyl-1-propanone	17	17	16	14	20

^aTen % excess reagent was utilized. ^bThe distribution is deduced by GC analysis from the oxygenated products of the intermediate alkenylboranes. ^cTotal yields are 90±5%.

significant.

The results for product distribution clearly indicate that the regioselectivity is largely dependent upon the steric size of alkoxy substituent in the xylborane. The relative selectivity is in order of ThxBHOⁱBu > ThxBHOⁱPr > ThxBHOⁱBu > ThxBHOEt > ThxBHOⁱPh, similar to the case of hydroboration of alkenes.

	<i>n</i> -Bu-C≡C-H	<i>n</i> -Pr-C≡C-CH ₃	(CH ₃) ₂ C=C=C-H
	↑ ↑	↑ ↑	↑ ↑
ThxBHO ⁱ Bu	3 97	11 89	1 99
ThxBHO ⁱ Bu	4 96	32 68	2 98

Results for 2-hexyne and 1-phenyl-1-propyne, representative 1-substituted propyne derivatives, are presented in Table 7 along with directive effects for several other hydroborating agents for comparison. Both ThxBHOⁱPr and ThxBHOⁱBu show relatively high regioselectivity but do not approach the selectivities achieved by ThxBHX·SMe₂ and IpcBHX·SMe₂.

Conclusion

It is evident from this study ThxBHOR (R = Et, *i*-Pr, *i*-Bu, *t*-Bu, Ph) is a new class of selective hydroborating agent with high regioselectivity. The selectivity increases consistently with increasing steric size of the alkoxy substituent. Especially, the *s*-butoxy derivative (ThxBHOⁱBu) monohydroborates alkenes and alkynes in excellent regioselectivity. In addition to that, ThxBHOR possesses a potential for a selective reduction of organic functionalities. A detailed study for this possibility is in progress.

Experimental Section

All glassware required for the experiments were predried at 140 °C for several hours, assembled hot cooled to room temperature under a stream of dry nitrogen. Syringes fitted

Table 7. Directive Effects (% Substitution) in 1-Substituted Propynes with Various Hydroborating Agents^a

Hydroborating reagent	R			
	<i>n</i> -Pr		Ph	
	b	a	b	a
B ₂ H ₆ in dylme ^{b,c}	40	60	74	26
ThxBH ₂ ^{b,c}	39	61	43	57
HBBR ₂ ·SMe ₂ ^d	25	75	64	36
Catecholborane ^e	40	60	27	73
2,2'-biphenoxyborane ^f	39	61	16	84
9-BBN ^g	22	78	65	35
CHex ₂ BH ^h	33	67	29	71
Si ₂ BH ⁱ	39	61	19	81
ThxBHCl·SMe ₂ ^j	2	98	3	97
ThxBHBr·SMe ₂ ^j	1.5	98.5	1	99
ThxBHI·SMe ₂ ^j	1	99	1	99
ThxBHO ⁱ Pr	32	68	16	84
ThxBHO ⁱ Bu	11	89	14	86
IpcBHCl·SMe ₂ ^k	8	92	1	99
IpcBHBr·SMe ₂ ^k	4	96	0.5	99.5
IpcBHI·SMe ₂ ^k	2	98	trace	>99.9

^aAt 25 °C, except where otherwise indicated. ^bAt 0 °C. ^cRef. 19 and 20. ^dRef. 21. ^eAt 70 °C; ref. 22. ^fRef. 23. ^gRef. 24. ^hRef. 25. ⁱRef. 9 and 10. ^jRef. 26 and 27.

with a needle were cooled under a stream of dry nitrogen and assembled. All reactions were carried out under a static pressure of nitrogen in flasks fitted with a septum-covered sidearm using standard techniques for handling air-sensitive materials.²⁸

Materials

All chemicals used were commercial products of the hi-

ghest quality and further purified by standard techniques prior to use. Tetrahydrofuran (THF) was dried over 4 Å molecular sieve and distilled over sodium-benzophenone ketyl prior to use. 2,3-Dimethyl-2-butene (tetramethylethylene) and sodium borohydride were purchased from Aldrich Chemical Co. ^{11}B NMR spectra were recorded on a Bruker AMX 300 spectrometer, and the chemical shifts are reported relative to $\text{BF}_3 \cdot \text{OEt}_2$ with low field assigned as positive.

GC Analysis

GC analyses were performed using Donam DS 6200 and Varian 3300 FID chromatographs equipped with Varian 4400 integrator/plotter. Alcohol or carbonyl compound products were analyzed with use of capillary columns of Carbowax 20 M (15 m) and Methylsilicone 3300 (25 m). All GC yields were determined with use of suitable internal standard and authentic samples.

Preparation of Thexylborane (ThxBH_2) in THF²⁹

The solutions of ThxBH_2 in THF were prepared by the following procedure. In an oven-dried, 1 L-flask equipped with a sidearm, capped by a rubber septum, was placed 454.5 mL of a 1.1 M solution of $\text{BH}_3 \cdot \text{THF}^{30}$ (500 mmol), and the flask was immersed in an ice-salt bath. To this 44.2 g of 2,3-dimethyl-2-butene (525 mmol) was added slowly with stirring, keeping the temperature below 0 °C, and the solution was stirred for 3 h at that temperature. An aliquot of the thexylborane solution in THF so prepared was quenched in a glycerol-water hydrolyzing mixture and the hydrogen evolved was measured volumetrically to indicate the concentration of the ThxBH_2 solution being 0.90 M. The solution was further used for preparation of thexylalkoxyborane.

Preparation of Thexylalkoxyborane (ThxBHOR) in THF

The following reaction is typical of the procedure adopted in the preparation of ThxBHOR . A 100-mL, round-bottomed flask equipped with a magnetic stirring bar, a septum-covered sidearm and connector tube leading to a mercury bubbler, was charged with 110 mL of a 0.90 M solution of ThxBH_2 (99 mmol) in THF and the solution was cooled to -25 °C with use of a cooling bath. To this ThxBH_2 solution, 4.8 g of ethyl alcohol (105 mmol) was added dropwise with vigorous stirring. After the hydrogen evolution ceased, the reaction mixture was stirred for an additional 1 h at that temperature. Some THF was evaporated from the solution under a reduced pressure to give a 1.48 M of ThxBHOEt solution in THF: ^{11}B NMR, δ 51.1 ppm (d, $J_{\text{BH}} = 127$ Hz). The solution of ThxBHOEt thus prepared was stable when stored under a static pressure of dry nitrogen at 0 °C.

In the same way, the other solutions of ThxBHOR were prepared: ThxBHO^iPr , 1.54 M, δ 50.4 ppm ($J_{\text{BH}} = 126$ Hz); ThxBHO^tBu , 1.40 M, δ 50.9 ($J_{\text{BH}} = 121$ Hz); ThxBHO^nBu , 1.41 M, δ 50.2 ($J_{\text{BH}} = 125$ Hz); ThxBHO^sBu , 1.42 M, δ 48.2 ($J_{\text{BH}} = 126$ Hz); ThxBHOPh , 1.45 M, δ 50.9 ($J_{\text{BH}} = 128$ Hz).

General Procedure for the Determination of the Rate of Reaction of Alkenes and Alkynes

The general procedure was to add 10 mmol of compound to 11 mmol of the reagent taken in sufficient quantity of THF, so that the concentrations were 1 M in compound and

1.1 M in reagent. The reaction mixture was stirred at 25 °C in a temperature-controlled water bath. Aliquots of the reaction mixture were withdrawn at specific time intervals and hydrolyzed with a mixture of glycerol-water (1:1) to measure the residual hydride content. From the amount of hydride remaining, the extent of reaction was calculated.

Regioselectivity in the Hydroboration of Alkenes with ThxBHOR

The regioselectivity in the hydroboration was determined by oxidizing the intermediate alkylthexylalkoxyboranes to the corresponding alcohols with hydrogen peroxide, followed by GC analysis.

The following reaction is typical of the procedure utilized for determining the direct effect. An oven-dried, 50-mL, round-bottomed flask equipped with a sidearm capped with a rubber septum, a magnetic stirring bar, and a connecting tube attached to a mercury bubbler, was flushed with dry nitrogen. The flask, containing 1.122 g of 1-octene (10 mmol) 0.852 g of dodecane (5 mmol) as an internal standard and 1 mL of THF, was immersed into a water bath at 25 °C. The mixture was stirred, and 7.2 mL of a 1.54 M solution of ThxBHO^iPr (11 mmol) in THF was injected into the flask. Stirring was continued for 3 hrs keeping the flask in the water bath for reaction at 25 °C. The alkylthexylisopropoxyborane so formed in the reaction mixture was then oxidized at 0 °C by adding 6 mL of 3 N NaOH and 3 mL of 30% H_2O_2 . After stirring for 2 hrs at 25 °C, the mixture was saturated with K_2CO_3 . The organic layer was separated, dried with anhydrous MgSO_4 , and then analyzed by GC for the amount of 1-octanol and 2-octanol formed in the reaction. The total yield of was 98%, of which 95% 1-octanol and 5% 2-octanol was present. The experiment was repeated for other representative alkenes and the results are summarized in Table 3.

Regioselectivity in the Hydroboration of Unsymmetrically Substituted Alkynes with ThxBHOR

The regioselectivity in the hydroboration was determined by oxidizing the intermediate alkenylthexylalkoxyboranes to the corresponding carbonyl compounds with hydrogen peroxide, followed by GC analysis.

Analysis for Terminal Acetylenes. To a 25 °C solution of 0.825 g of 1-hexyne (10 mmol), 0.852 g of dodecane (5 mmol) and 1 mL of THF was added 7.8 mL of a 1.41 M ThxBHO^iBu solution (11 mmol) in THF. After stirring for 12 hrs at 25 °C, the reaction mixture was cooled to 0 °C, neutralized with 4 mL of 2.5 N NaOH, followed by addition of 10 mL buffer solution (pH 7). The mixture was then oxidized by adding 3 mL of 30% H_2O_2 dropwise at 0 °C and stirred for 2 h. The aqueous layer was saturated with K_2CO_3 and the organic layer was separated. Analysis of the organic layer by GC revealed the presence of 97% hexanal and 3% 2-hexanone in a total yield of 93%.

Analysis for Internal Acetylenes. To a 25 °C solution containing 1.162 g of 1-phenyl-1-propyne (10 mmol), 0.825 g of dodecane (5 mmol) and 1 mL of THF was added 7.8 mL of a 1.41 M ThxBHO^iBu solution (11 mmol) in THF. After stirring for 12 hrs at 25 °C, the reaction mixture was cooled to 0 °C, quenched with 10 mL of 3 N NaOH, and oxidized by adding 5 mL of 30% H_2O_2 . The aqueous layer

was saturated with K_2CO_3 and the organic layer was separated. Analysis of the organic layer by GC showed the presence of 86% 1-phenyl-2-propanone and 14% 1-phenyl-1-propanone in a total yield of 94%.

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