Reaction of Thexylalkoxyboranes with Selected Organic Compounds Containing Representative Functional Groups Comparison of Reducing Characteristics of the Alkoxy Derivatives

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The reaction of alcohol with a solution of thexylborane ($ThxBH_2$) in tetrahydrofuran (THF) provides a new class of mild and selective reducing agents, thexylalkoxyboranes (ThxBHOR: R=Et, *i*-Pr, *i*-Bu, *s*-Bu, *t*-Bu, Ph). In order to elucidate the effect of the alkoxy group in reduction reactions, the reducing power of ThxBHOR toward selected organic compounds containing representative functional groups under practical conditions (THF, 25°, the quantitative amount of reagent to compound) has been investigated. Generally, the reactivity of ThxBHOR is largely dependent upon the alkoxy substituent. ThxBHOR can be synthesized from a variety of alcohols, thus allowing control of the steric and electronic environment of these reagents.

Introduction

The introduction of halo group into thexylborane ($ThxBH_2$) provides exceptionally valuable derivatives, thexylhaloborane-methyl sulfide ($ThxBHX \cdot SMe_2$: X=Cl, Br, I). The reagents hydroborate most alkenes and alkynes cleanly with high regio- and stereospecificity to produce isomerically pure thexylalkyl- and thexylalkenylhaloboranes, respectively.[1-5] These versatile intermediates have been used effectively in organic synthesis.[3-6] In addition to that, $ThxBHX \cdot SMe_2$ are also very attractive reducing agents,[4,5,7-9] especially for the transformation of carboxylic acids and their derivatives to the corresponding aldehydes.[10,11] These results clearly suggest that the halo derivatives of $ThxBH_2$ show a dramatic selectivity enhancement both in reduction and hydroboration reactions, compared to that achieved by $ThxBH_2$ itself.[12,13]

Similarly, the introduction of alkoxy group into $ThxBH_2$ provides another class of useful derivatives, thexylalkoxyboranes (ThxBHOR: R=Et, *i*-Pr, *i*-Bu, *s*-Bu, *t*-Bu, Ph) (Eq. 1).[14]

$$\rangle\!+\!BH_2 + ROH \xrightarrow[-25\ ^\circ C \text{ or } 0\ ^\circ C]{THF} \rangle\!+\!BHOR + H_2\uparrow \quad (1)$$

R=Et: ThxBHOEt
R=*i*-Pr: ThxBHO^{i}Pr
R=*i*-Bu: ThxBHO^{i}Bu
R=*s*-Bu: ThxBHO^{s}Bu
R=*t*-Bu: ThxBHO^{t}Bu
R=Ph: ThxBHOPh

These derivatives readily hydroborate alkenes and alkynes of various structural types at 25° in excellent regioselectivity.[14] The selectivity increases consistently with increasing steric size of alkoxy substituent. Especially, the selectivity achieved by the *s*-butoxy derivative (ThxBHO^{s}Bu) is comparable to that previously achieved by $ThxBHX \cdot SMe_2$,[1-5] the most selective hydroborating agent known. These derivatives also show a very similar trend presented by $ThxBHX \cdot SMe_2$ (X=Cl, Br)[10,11] in the reduction of carboxylic acids to aldehydes: among them, ThxBHO^{i}Pr and ThxBHO^{s}Bu efficiently reduced various carboxylic acids to aldehydes in good yields.[15] Such unique reducing action intrigued us, because the alkoxy derivatives seem to be a new class of selective reducing agents. Accordingly, we began a systematic study of their reducing properties. We examined the possibility for selective reductions of representative organic compounds with use of the reagents in a limiting amount.

A portion of our results has appeared in the form of preliminary communications.[16] We now describe in full the result of our study on the reduction characteristics of thexylalkoxyboranes toward representative organic functionalities under practical conditions (THF, 25°, the quantitative amount of reagent to compound).

Results and Discussion

Preparation of a solution of thexylalkoxyborane (ThxBHOR). Thexylborane ($ThxBH_2$) reacted with primary and secondary alcohols, such as ethanol, isopropyl alcohol, isobutyl alcohol, *sec*-butyl alcohol, and with phenol readily to evolve 1 equiv of hydrogen within 30 min at −25° and no further hydrogen was evolved even in the presence of excess alcohols. However, practically the reaction of *tert*-butyl alcohol with $ThxBH_2$ needed an elevated temperature to 0 or 25° to complete the quantitative hydrogen evolution. The detailed reaction procedure for the preparation of ThxBHOR and ^{11}B NMR spectra of the resultant solution have already been described in the previous article.[14]

Alcohols, phenols, amines, and thiols. The alcohols, phenols, and primary amines listed in Table 1 evolved hydrogen incompletely with stoichiometric amounts of ThxBHOR. After initial rapid evolution of some hydrogen, no further release of gas was apparent. However, it is best to defer for the present consideration of the reason why the hydrogen evolution stops beneath the stoichiometric point. Virtually no hydrogen evolution was noticed with thiols.

Table 1. Reaction of thexylalkoxyborane with representative "active hydrogen compounds" in tetrahydrofuran at 25℃[a]

Compound	Time (h)	Ratio of rgt/compd	Hydride used for hydrogen evolution[b,c] R in ThxBHOR					
			Et	*i*-Bu	*i*-Pr	*s*-Bu	*t*-Bu	Ph
1-Hexanol	0.5	1.0	0.69	0.62	0.54	0.46	0.32	0.50
	1	1.0	0.69	0.62	0.55	0.48	0.39	0.51
	3	1.0	0.69	0.62	0.55	0.48	0.39	0.51
Benzyl alcohol	0.5	1.0	0.84	0.82	0.63	0.61	0.55	0.72
	1	1.0	0.84	0.82	0.64	0.61	0.56	0.72
Phenol	0.5	1.0	0.52	0.43	0.34	0.24	0.14	0.48
	1	1.0	0.52	0.43	0.35	0.25	0.15	0.48
	3	1.0	0.52	0.43	0.35	0.25	0.15	0.48
n-Hexylamine	0.5	1.0	0.31	0.24	0.23	0.03	0.01	0.31
	1	1.0	0.31	0.24	0.23	0.03	0.01	0.31
1-Hexanethiol	0.5	1.0	0.00	0.00	0.00	0.00	0.00	0.00
	1	1.0	0.00	0.00	0.00	0.00	0.00	0.00
Benzenethiol	0.5	1.0	0.11	0.08	0.00	0.00	0.00	0.10
	1	1.0	0.11	0.08	0.00	0.00	0.00	0.10

[a]Solutions being 0.8 M in reagent and 2.0 M in compound examined both in THF were utilized for reactions. [b]Mmoles of reagent per mmole of compound. [c]Determined gasometrically.

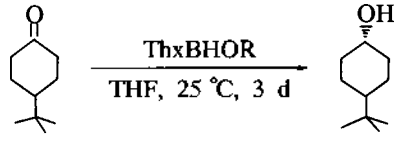
None of these compounds underwent reduction by these reagents.

It is noteworthy to mention that the relative amount of hydrogen evolved in the reaction of such active hydrogen compounds with ThxBHOR appears to be essentially dependent upon the steric size of alkoxy group. Thus, the amount of hydrogen evolved is in order of ThxBHOEt>ThxBHO^{i}Bu> ThxBHO^{i}Pr>ThxBHO^{s}Bu>ThxBHO^{t}Bu. The position of ThxBHOPh is somewhere between ThxBHOEt and ThxBHO^{i}Pr.

Aldehydes and ketones. All of the alkoxy derivatives in a theoretical amount, with the exception of ThxBHO^{t}Bu, reduced aldehydes examined cleanly to the corresponding alcohols in 48 or 72 h at 25°. The reduction with ThxBHO^{t}Bu was very sluggish, showing only approximately 60% completion in 72 h. The rate difference in the reduction of ketones with ThxBHOR appears to be much sharper than that in the reduction of aldehydes: ThxBHOEt, ThxBHO^{t}Bu and ThxBHOPh showed only the acceptable reduction rate under these reaction conditions. Especially, ThxBHO^{t}Bu exhibited almost no reactivity toward some ketones. In the case of ThxBHO^{t}Bu, the rate difference between aldehydes and ketones is quite remarkable: aldehydes were cleanly reduced to alcohols with theoretical amounts of ThxBHO^{t}Bu at a relatively fast rate, whereas the reduction of ketones was quite sluggish and incomplete. Even after 120 h at 25°, a maximum of only approximately 80% of the theoretical amounts of alcohol was produced. These results suggest this reagent possesses interesting possibility for the chemoselective reduction of aldehydes in the presence of ketones. We plan to explore this area in greater detail.

Again, the relative rate of reduction with ThxBHOR toward aldehydes and ketones appears to be essentially dependent upon the steric size of alkoxy group, as the relative amount of hydrogen evolved in the reaction of alcohols is. The results are summarized in Table 2.

The stereochemistry of ThxBHOR in the reduction of representative substituted cycloalkanones was also examined. The stereoselectivity presented in Table 3 indicates that the ThxBHORs behave like unhindered hydride reagents to produce the thermodynamically more stable alcohol epimers preferentially. For example, the reduction of 4-*tert*-butylcyclohexanone using 2 equiv of ThxBHOR gave 90-97% *trans*-4-*tert*-butylcyclohexanol in 7 days at 25° (Eq. 2). It is interesting to note that there appears no significant effect of the alkoxy group of ThxBHOR upon the ratio of alcohol epimers produced in the reduction of cycloalkanones: the isomer distribution in this reduction seems not to be dependent upon the steric size of alkoxy group.



(2)

Carboxylic acids. Carboxylic acids were examined with 2 or 3 equiv of ThxBHOR at 25°. With the exception of the *t*-butoxy derivative, all of the derivatives reacted with both hexanoic acid and benzoic acid to evolve 1 equiv of hydrogen instantly and quantitatively, and the concurrent hydride consumption for reduction reached 1 equiv slowly but further hydride uptake was very sluggish to indicate the possibility of the formation of aldehyde intermediate. In fact, the reaction of hexanoic acid with 2 or 3 equiv of ThxBHOR provided hexanal in 80-93% yield within 4 days at 25° (Eq. 3). However, the reaction of benzoic acid gave significantly lower yields of benzaldehyde (45-65%), as given in Table 4.

$$CH_3(CH_2)_4COOH \xrightarrow[\text{THF, 25 ℃, 3-4 d}]{\text{ThxBHOR}} \underset{80\text{-}90\%}{CH_3(CH_2)CHO} \quad (3)$$

It is necessary to point out that both ThxBHO^{i}Pr and ThxBHO^{s}Bu are reagents of choice for converting carboxylic acids to aldehydes. The yields of aldehydes are

Table 2. Reaction of thexylalkoxyborane with representative aldehydes and ketones in tetrahydrofuran at 25℃[a]

Compound	Time (h)	Ratio of rgt/compd	Product	Yield (%)[b]					
				R in ThxBHOR					
				Et	*i*-Bu	*i*-Pr	*s*-Bu	*t*-Bu	Ph
Hexanal	1	1.0	1-hexanol	81	77	75	65	38	71
	6	1.0	1-hexanol	98	88	81	73	46	85
	12	1.0	1-hexanol	100					
	24	1.0	1-hexanol		96	97	89	57	92
	48	1.0	1-hexanol		100	100	98	62	100
	72	1.0	1-hexanol				100	65	
Benzaldehyde	1	1.0	benzyl alcohol	80	79	70	62	34	69
	6	1.0	benzyl alcohol	97	92	85	78	42	77
	12	1.0	benzyl alcohol	100	98				
	24	1.0	benzyl alcohol		100	98	95	47	86
	48	1.0	benzyl alcohol			100	100	51	94
	72	1.0	benzyl alcohol					54	100
2-Heptanone	24	1.0	2-heptanol	98					92
	48	1.0	2-heptanol	100	96	83	50	10	100
	72	1.0	2-heptanol		100	97			
	96	1.0	2-heptanol			100			
	120	1.0	2-heptanol				79	40	
Norcamphor	48	1.0	norborneol	85	69	52	32	0	79
	72	1.0	norborneol	100				0	93
	96	1.0	norborneol					0	100
	120	1.0	norborneol		97			0	
	168	1.0	norborneol		100	83	74	0	
Acetophenone	24	1.0	1-phenylethanol	92	78	69	38		
	48	1.0	1-phenylethanol	100	83	76	41	15	95
	72	1.0	1-phenylethanol		94	85	48	22	100
	96	1.0	1-phenylethanol		100	93	54		
	120	1.0	1-phenylethanol			100	65	42	
Benzophenone	48	1.0	diphenylmethanol	97	84	73	42	0	90
	72	1.0	diphenylmethanol	100	72	80		0	98
	96	1.0	diphenylmethanol		99			0	100
	120	1.0	diphenylmethanol		100	95	60	0	

[a]See corresponding footnote in Table 1. b Determined by GC analysis with an internal standard and authentic samples.

Table 3. Stereochemistry in the reduction of cyclic ketones with thexylalkoxyborane in tetrahydrofuran at 25℃[a,b]

Compound	Less stable isomer	Ratio of less stable isomer(%)[c]				
		R in ThxBHOR				
		Et	*i*-Bu	*i*-Pr	*s*-Bu	Ph
2-methylcyclohexanone	*cis*-2-methylcyclohexanol	47	49	38	30	33
3-methylcyclohexanone	*trans*-3-methylcyclohexanol	14	14	10	4	11
4-methylcyclohexanone	*cis*-4-methylcyclohexanol	11	10	8	6	12
2-*tert*-methylcyclohexanone	*cis*-2-*tert*-butylcyclohexanol	28	11	5	1	4
4-*tert*-methylcyclohexanone	*cis*-4-*tert*-butylcyclohexanol	9	10	8	7	3
3,3,5-trimethylcyclohexanone	*trans*-3,3,5-trimethylcyclohexanol	45	48	45	44	42
2-methylcyclopentanone	*cis*-2-methylcyclohexanol	49	50	54	59	53
norcamphor	*endo*-norborneol	10	7	5	1	4

[a]See corresponding footnote in Table 1. [b]Two equiv of reagent was utilized: reacted for 7 days. [c]The yields of alcohols were more than 90%.

comparable to those obtained by ThxBHX·SMe_2 (X=Cl, Br).[10,11] Details of such conversion have already been communicated.[15] In this respect, ThxBHOR and ThxBHX·SMe_2 are very promising reagents of reducing carboxylic acids to aldehydes. However, the alkoxy derivatives are much milder and hence more selective reducing agents than the halo derivatives. A simple, convenient procedure for the isolation of the aldehydes applicable for these reagents are now available.[10,15]

Acid chlorides. The reaction of acid chlorides with 2 equiv of ThxBHOR, with the exception of ThxBHO'Bu, utilized 1 equiv of hydride for reduction relatively rapid and

Table 4. Reaction of thexylalkoxyborane with representative carboxylic acids in tetrahydrofuran at 25℃[a]

Compound	Time (h)	Ratio of rgt/ compd	Hydride used for reduction[b,c,d] R in ThxBHOR[e]					
			Et	*i*-Bu	*i*-Pr	*s*-Bu	*t*-Bu	Ph
Hexanoic acid	3	2.0	0.78	0.66	0.62	0.58		0.72
	6	2.0	0.92	0.79	0.77	0.69		0.85
	24	2.0	0.96	0.89	0.84	0.78	0.38	0.93
	48	2.0	1.00(86)	0.97	0.94	0.86	0.41	0.98
	72	2.0		0.99(87)	0.98	0.91	0.41(36)	1.00(82)
	96	2.0			1.00(93)	0.98(90)		
	6	3.0	0.93	0.84	0.79	0.72		0.86
	24	3.0	1.04(81)	0.98(84)	0.97	0.89		1.02(80)
	48	3.0	1.11	1.08	1.03(90)	0.98		1.13
	72	3.0	1.24	1.13	1.09	1.05(93)	0.51	1.20
	96	3.0	1.32	1.22	1.11	1.08	0.52	1.25
	120	3.0	1.34	1.23	1.12	1.08	0.52(38)	1.25
	3	2.0	0.72	0.68	0.60	0.56		0.69
Benzoic acid	6	2.0	0.82	0.77	0.74	0.66		0.85
	24	2.0	0.98	0.82	0.79	0.73	0.42	0.91
	48	2.0	1.00(52)	0.90	0.88	0.81	0.42(30)	0.98
	72	2.0		0.96	0.94	0.88		1.00(45)
	96	2.0		1.00(55)	0.99(65)	0.94(64)		
	6	3.0	0.87	0.82	0.79	0.72		0.84
	24	3.0	1.02(48)	0.94	0.89	0.88	0.48	0.99(45)
	48	3.0	1.15	1.09(56)	0.98(62)	0.95	0.49	1.14
	72	3.0	1.25	1.12	1.05	1.01(68)	0.49(33)	1.24
	96	3.0	1.26	1.19	1.09	1.04		1.24

[a-e]See corresponding footnotes in Table 1. [d]Along with immediate evolution of 1 equiv of hydrogen. [f]Figures in parentheses are yields of aldehydes estimated as the corresponding 2,4-dinitrophenylhydrazones.

Table 5. Reaction of thexylalkoxyborane with representative acid chlorides in tetrahydrofuran at 25℃[a]

Compound	Time (h)	Ratio of rgt/ compd	Hydride used for reduction[b,c] R in ThxBHOR[e]					
			Et	*i*-Bu	*i*-Pr	*s*-Bu	*t*-Bu	Ph
Hexanoyl chloride	3	2.0	0.65	0.64	0.52	0.47	0.15	0.65
	6	2.0	0.88	0.82	0.79	0.58		0.83
	24	2.0	0.98	0.94	0.86	0.72	0.37	0.92
	48	2.0	1.09	1.06	0.96	0.88		0.99
	72	2.0	1.12	1.16	1.04	0.97	0.48	1.09
	96	2.0	1.21	1.17	1.12	0.98	0.48	1.15
Benzoyl chloride	3	2.0	0.66	0.61	0.53	0.43	0.20	0.60
	6	2.0	0.80	0.77	0.65	0.51		0.79
	24	2.0	0.89	0.85	0.73	0.69	0.32	0.88
	48	2.0	0.97	0.94	0.89	0.74		0.95
	72	2.0	1.11	1.06	1.02	0.82	0.33	1.08
	96	2.0	1.15	1.08	1.05	0.87	0.33	1.11
	120	2.0				0.92		

[a-c]See corresponding footnotes in Table 1.

further hydride uptake was relatively slow to indicate the formation of aldehyde intermediate (Table 5). We examined this possibility. As summarized in Table 6, the yields of aldehydes from various aliphatic acid chlorides are variable. Among these, the yields obtained by ThxBHO^{i}Pr and ThxBHO^{s}Bu are quite satisfactory (60-83% yield). α,ω-Diacid chlorides, such as adipoyl chloride and sebacoyl chloride, were also converted to dialdehydes in yields of 61-76%. However, the reaction of aromatic acid chlorides with ThxBHO^{i}Pr and ThxBHO^{s}Bu provided the corresponding aldehydes in yields of only around 50%.

Esters and *N,N*-dimethylcarboxamides. All of the derivatives showed no reactivity toward ethyl benzoate but some reactivity toward ethyl hexanoate under the experimental conditions. The reagents also failed to react with *N,N*-dimethylcarboxamides. The actual data are given in Table 7.

Epoxides and nitriles. As shown in Table 8, all epox-

Table 6. Yields of aldehydes in the reduction of representative acid chlorides with thexylalkoxyborane in tetrahydrofuran at 25 °C[a]

Compound	Ratio of rgt/compd	Product	Yield (%)[b] R in ThxBHOR					
			Et[c]	*i*-Bu[c]	*i*-Pr[d]	*s*-Bu[e]	*t*-Bu[e]	Ph[c]
Hexanoyl chloride	2.0	hexanal	82	79	82	83	36	75
Trimethylacetyl chloride	2.0	trimethylacetaldehyde	45	57	62	60		38
Cyclopropanecarbonyl chloride	2.0	cyclopropanecarboxaldehyde	39	44	64	70		32
Adipoyl chloride	4.0	adipaldehyde	58	57	68	61		44
Sebacoyl chloride	4.0	sebacaldehyde	48	49	69	76		43
Benzoyl chloride	2.0	benzaldehyde	45	52	61	61	21	39
o-Toluoyl chloride	2.0	*o*-tolualdehyde	30	39	42	50		28
m-Toluoy chloride	2.0	*m*-tolualdehyde	45	46	52	56		45
p-Toluoyl chloride	2.0	*p*-tolualdehyde	42	43	53	54		41
Phthaloyl dichloride	4.0	phthalic dicarboxaldehyde	35	38	49	51		36

[a]See corresponding footnote in Table 1. [b]Estimated as the corresponding 2,4-dinitrophenylhydrazones. [c]Reacted for 48 h. [d]Reacted for 72 h. [e]Reacted for 96 h.

Table 7. Reaction of thexylalkoxyborane with representative esters and *N,N*-dimethylcarboxamides in tetrahydrofuran at 25 °C[a]

Compound	Time (h)	Ratio of rgt/compd	Product	Yield (%)[b] R in ThxBHOr					
				Et	*i*-Bu	*i*-Pr	*s*-Bu	*t*-Bu	Ph
Ethylbenzoate	96	2.0	c	0	0	0	0	0	0
Ethylhexanoate	24	2.0	1-hexanol	55					
	48	2.0	1-hexanol	57	41				
	72	2.0	1-hexanol	57	41				
	96	2.0	1-hexanol			29	27	0	42
N,N-Dimethylbenzamide	96	2.0	c	0	0	0	0	0	0
N,N-Dimethylhexanoamide	96	2.0	c	0	0	0	0	0	0

[a]See corresponding footnote in Table 1. [b]GC yields. [c]No reduction product was detected.

Table 8. Reaction of thexylalkoxyborane with representative epoxides and nitriles in tetrahydrofuran at 25 °C[a]

Compound	Time (h)	Ratio of rgt/compd	Yield (%) of reduction product[b] R in ThxBHOR					
			Et	*i*-Bu	*i*-Pr	*s*-Bu	*t*-Bu	Ph
1,2-Butylene oxide	96	1.0	0	0	0	0	0	0
Cyclohexene oxide	96	1.0	0	0	0	0	0	0
Styrene oxide	96	1.0	0	0	0	0	0	0
Hexanenitrile	96	2.0	0	0	0	0	0	0
Benzonitrile	96	2.0	0	0	0	0	0	0

[a]See corresponding footnote in Table 1. [b]Analyzed by GC.

ides and nitriles examined were totally inert to all of ThxBHOR by gas chromatographic analysis.

Nitrogen and sulfur compounds. The nitro compounds, disulfides and sulfones listed in Table 9 all failed to indicate any reaction with ThxBHOR, but somewhat to our surprise, dimethyl sulfoxide was reduced to dimethyl sulfide quantitatively at a relatively rapid rate. Slow hydrogen evolution was also observed as reduction proceeded, perhaps the hydrogen being evolved from the boronic acid intermediate.[17] The relatively rapid reduction of dimethyl sulfoxide with ThxBHOR and the relative inertness of the reagents towards many other functional group suggests the possibility of the selective deoxygenation of sulfoxides to sulfides under mild conditions. The results are summarized in Table 9.

Conclusion

From the survey of chemistry of ThxBHOR presented in a series of articles,[14-16] we can provide a new class of mild agents possessing high selectivity both in hydroboration and reduction reactions. The reactivity of ThxBHOR is much milder than that of ThxBHX·SMe_2, but ThxBHOR can achieve the conversion of carboxylic acids to aldehydes successfully as ThxBHX·SMe_2 does. Moreover, the reactivity of ThxBHOR can be sterically modified by altering the alkoxy moiety, a feature that enhances the versatility of ThxBHOR. Consequently, by appropriate choice of derivative and reaction conditions it should be possible successfully to apply these reagents for selective reductions of specific organic functionalities.

Table 9. Reaction of thexylalkoxyborane with nitrogen and sulfur compounds in tetrahydrofuran at 25 ℃[a]

Compound	Time (h)	Ratio of rgt/compd	Product	Yield (%)[b] R in ThxBHOr					
				Et	*i*-Bu	*i*-Pr	*s*-Bu	*t*-Bu	Ph
1-Nitropropane	48	2.0	c	0	0	0	0	0	0
Nitrobenzene	48	2.0	c	0	0	0	0	0	0
Di-*n*-butyl disulfide	72	2.0	c	0	0	0	0	0	0
Diphenyl disulfide	72	2.0	c	0	0	0	0	0	0
Dimethyl sulfoxide	3	2.0	dimethyl sulfide	73	68				
	6	2.0	dimethyl sulfide	93	83				86
	12	2.0	dimethyl sulfide	100	92	78	73		98
	24	2.0	dimethyl sulfide		100	89	86	66	100
	48	2.0	dimethyl sulfide			100	100	72	
	72	2.0	dimethyl sulfide					85	
Diphenyl sulfone	48	2.0	c	0	0	0	0	0	0

[a]See corresponding footnote in Table 1. [b]Analyzed by GC. [c]No reduction product was detected.

Experimental Section

All operations were carried out under a dry nitrogen atmosphere. All glassware, syringes, and needles were oven-dried at 140° and cooled to room temperature with nitrogen gas before use. All the compounds examined were commercial products of the highest purity which were further purified by standard methods before use. Tetrahydrofuran (THF) was freshly distilled from sodium and benzophenone ketyl. 2,3-Dimethyl-2-butene (tetramethylethylene) was purchased from the Aldrich Chemical Co. and distilled from lithium aluminum hydride. Sodium borohydride was also purchased from the Aldrich Chemical Co. and dried in a hot desiccator under reduced pressure before use. Dimethyl sulfate was freshly distilled. ^{11}B NMR spectra were obtained on a Bruker AMX 300 spectrometer; the chemical shifts are in δ relative to $BF_3 \cdot OEt_2$ with downfield assigned as positive. Gas chromatographic analyses were carried out with Donam DS 6200 and Varian 3300 FID chromatographs using Carbowax 20 M and Methylsilicone 3300 capillary columns.

Preparation of thexylborane ($ThxBH_2$) in THF.[13] The following procedure for the preparation of a 0.9 M THF solution of $ThxBH_2$ is representative. An oven-dried, 1-L round-bottom flask equipped with a magnetic stirring bar and fitted a rubber-capped side-arm was charged by cannula with 454.5 mL of a 1.1 M solution of $BH_3 \cdot THF$[18] (500 mmol) in THF, and the flask was immersed in an ice-salt bath under nitrogen. 2,3-Dimethyl-2-butene (44.2 g, 525 mmol) was added dropwise with stirring, keeping the temperature below 0°. The reaction mixture was stirred for an additional 3 h at that temperature. An aliquot of the $ThxBH_2$ solution in THF so prepared was quenched in a glycerol-water hydrolyzing mixture and the hydrogen gas evolved was measured volumetrically to indicate the concentration of the $ThxBH_2$ solution being 0.90 M. The solution was further utilized for preparation of ThxBHOR.

Preparation of thexylalkoxyborane (ThxBHOR) in THF. The procedure for the preparation of ThxBHO-^{s}Bu is representative. A 250-mL round-bottom flask equipped with a magnetic stirring bar and fitted with a rubber septum was charged by cannula with 110 mL of a 0.90 M solution of $ThxBH_2$ (99 mmol) in THF and cooled under nitrogen to −25° with use of a cooling bath. *s*-Butyl alcohol (7.8 g, 105 mmol) was added dropwise with vigorous stirring. After the hydrogen evolution ceased, the reaction mixture was stirred for an additional 1 h at 0° to afford a 0.8 M of ThxBHO^{s}Bu solution. ^{11}B NMR (THF): δ 50 (d, J =125 Hz). The solution of ThxBHO^{s}Bu thus prepared was stable when stored under a static pressure of dry nitrogen at 0°.

In the same way, the other solution of ThxBHOR were prepared: ThxBHOEt, 0.8 M, δ 51 (d, J=127 Hz); ThxBHO^{t}Bu, 0.8 M, δ 51 (d, J=121 Hz); ThxBHO^{i}Pr, 0.83 M, δ 50 (d, J=126 Hz); ThxBHO^{n}Bu, 0.82 M, δ 48 (d, J=126 Hz); ThxBHOPh, 0.83 M, δ 51 (d, J=128 Hz).

General procedure used for hydride reductions. The following procedure was used for quantitative studies. The reduction of hexanal is described as an example of the experimental procedure. The ThxBHO^{s}Bu solution, 30.0 mL of 0.8 M (24.0 mmol), was introduced into a dried, 100-mL flask fitted with a rubber syringe cap on an inlet port, a magnetic stirring bar, and a bent adapter connected to a gas buret through a reflux condenser and a dry ice vapor trap. The flask was immersed in a temperature-controlled water bath, the stirred solution was maintained at 25°, and 2.40 g of hexanal (24.0 mmol) in 12 mL of THF and dodecane as an internal standard were injected. No hydrogen evolution was apparent. 3.0-mL aliquot of the reaction mixture was removed and injected into a glycerol-water solution to measure residual hydride. The hydrogen evolved amounted to 0.33 mmol, which indicates that 0.67 mmol of hydride was used for reduction per mmol of compound. At the same time, another aliquot of the reaction mixture was also removed and treated with 3 mL of 3 N NaOH and 1.5 mL of 30% H_2O_2. After stirring for 2 hrs at 25°, the mixture was saturated with K_2CO_3. The organic layer was separated, dried with anhydrous $MgSO_4$, and subjected to GC analysis, showing the presence of 1-hexanol in a yield of 65%. Aliquots were also removed and analyzed at specific time intervals listed in Table 2. After 72 h, there was not observed any active hydride remaining in the reaction mixture and the GC analysis also showed 100% 1-hexanol.

Reduction of carboxylic acids. The following pro-

cedure for the reduction of hexanoic acid with ThxBHO^{t}Bu is illustrative. An oven-dried, 50-mL flask, fitted with a side-arm and a reflux condenser connected to a gas buret, was charged with 20.0 mL of a 0.8 M solution of ThxBHO^{t}Bu (16.0 mmol) in THF and immersed in a water bath at 25°, and followed by the dropwise addition, with stirring, of 4 mL of a 2.0 M solution of hexanoic acid (8.0 mmol). One equivalent of hydrogen gas was evolved instantly. The rate of reaction was monitored by measuring periodically the hydride content in a measured aliquot. After 96 h at 25°, the consumption of hydride was complete (Table 4). An aliquot of the reaction mixture (9 mL, 3 mmol) was then withdrawn and subjected to analysis with 2,4-dinitrophenylhydrazine, showing a yield of 90%: mp of the hydrazone 103-105° (lit.[19] mp 104°).

Reduction of acid chlorides. The reduction of hexanoyl chloride with ThxBHO^{t}Bu is described as representative. In the usual setup, 1.62 g of hexanoyl chloride (12.0 mmol) was reduced with 30.0 mL of ThxBHO^{t}Bu (0.8 M, 24.0 mmol) at 25°. The rate of reaction was monitored by measuring the hydride content. After 96 h, there was no significant difference in hydride consumption. Obviously, the reaction was complete in 96 h to indicate the corresponding aldehyde being formed in the reaction mixture. To determine the aldehyde product, an aliquot of the reaction mixture was removed and subjected to analysis with 2,4-dinitrophenylhydrazine, showing a yield of 83%: mp of the hydrazone 104-105°.

General procedure for stereoselectivity studies. The reduction of 2-*tert*-butylcyclohexanone with ThxBHO^{s}Bu is described as representative. In the usual assembly, 0.62 g of 2-*tert*-butylcyclohexanone (4.0 mmol) was reduced with 10.0 mL of ThxBHO^{s}Bu (0.8 M, 8.0 mmol) at 25°. The rate of reaction was monitored as described above. After 7 d, the reaction mixture was treated with 1 mL of 3 N NaOH and 0.5 mL of 30% H_2O_2. The aqueous layer was saturated with anhydrous K_2CO_3, and the organic layer was subjected to GC analysis using a Carbowax 20 M capillary column, showing the presence of of 2-*t*-butylcyclohexanol in a yield of 92% (a 1 : 99 ratio of *cis*- and *trans*-epimers).

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