stirred solution of 2.5 equivalents of LDA in 30mL of dry THF was added 0.33 g(0.0014 mole) of **10** in 5 mL of dry THF at −78°C under nitrogen. After 10 min, 0.22 mL(1.5 eq.) of 1,3-dibromopropane was added to the reaction mixture and stirred overnight at rt. Work-up as usual gave 0.093 g of liquid(24% yield).

^{1}H NMR: δ7.27(5H,br s); 4.60(2H,s); 2.06(4H,m); 1.70(4H,m); 1.50(4H,m).

^{13}C NMR: δ181.7(s),136.3(s),128.6(d),128.2(d),127.7(d), 63.4(s),42.4(t),36.4(t),27.4(t).

MS: 269(M$^+$, base),241,229,213,200,185,172,145,132, 109,91,79,66.

HRMS: Calcd for $C_{17}H_{19}NO_2$: 269.1413. Observed: 269.1403.

IR: 2941,1709(C=O),1399,1353,1147,969,701.

3-(N-Benzyl)-2,4-dioxotricyclo[3.3.2.0]nonane, **12**. 1,2-Dibromoethane(0.9 mL, 1.5 eq.) was used instead of 1,3-dibromopropane as the synthesis of **11** (25% yield).

^{1}H NMR: δ7.6-7.25(5H,m); 4.63(2H,s); 2.32-1.53 (10H,m).

MS: 255(M+,base),227,199,171,150,136,123,108, 91,79,65.

HRMS: Calcd for $C_{16}H_{17}NO_2$: 255,1259, Observed: 255.1254.

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Reaction of Thexylbromoborane-Methyl Sulfide in Methylene Chloride with Selected Organic Compounds Containing Representative Functional Groups†

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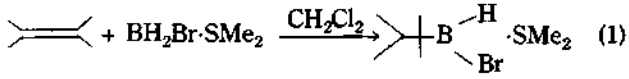
The approximate rate and stoichiometry of the reaction of excess thexylbromoborane-methyl sulfide, ThxBHBr·SMe$_2$, with selected organic compounds containing representative functional groups under standardized conditions (methylene chloride, 0°C) were studied in order to characterize the reducing characteristics of the reagent for selective reductions. The selectivity of the reagent was also compared to the selectivity of thexylchloroborane-methyl sulfide. Thexylbromoborane appears to be a much milder and hence more selective reducing agent than thexylchloroborane. The reagent tolerates many organic functionalities. Thus, the reagent shows very little reactivity or no reactivity toward acid chlorides, esters, epoxides, amides, nitro compounds including simple olefins. However, this reagent can reduce aldehydes, ketones, carboxylic acids, nitriles, and sulfoxides. Especially the reagent reduces carboxylic acids including α,β-unsaturated ones and nitriles to the corresponding aldehydes. In addition to that, thexylbromoborane shows good stereoselectivity toward cyclic ketones, much better than the chloro-derivative.

Thexylchloroborane-methyl sulfide has appeared to be a fascinating reducing agent for the selective reduction of organic functionalities[1], especially for the direct reduction of carboxylic acids to the corresponding aldehydes[2]. It is believed that this unique reducing characteristics is due to the introduction of chlorine atom to thexylborane[3], which provides such fascinating selectivity and specificity. This intrigued us. Consequently, we prepared thexylbromoborane-methyl sulfide, which is analogous to the chloro-derivative in structure but different in electronic and steric effect, and explored the reducing characteristics of the reagent systematically.

Thexybromoborane-methyl sulfide can be prepared readily from the addition of 2,3-dimethyl-2-butene (tetramethylethylene) to monobromoborane-methyl sulfide in methylene chloride (eq.1).



(1)

The reagent, ThxBHBr·SMe$_2$, in methylene chloride is very stable and no disproportionation or loss of hydride is ob-

† Dicated to Professor Nung Min Yoon on the occasion of his 60th birthday.

Table 1. Reaction of Thexylbromoborane-Methyl sulfide with Representative Active Hydrogen Compounds in Methylene Chloride at 0°C

compound[a]	time (hr)	hydrogen evolved[b,c]	hydride used[b,c]	hydride used for reduction[b,c]
1-hexanol	0.5	0.97	0.97	0.00
	1.0	0.97	0.97	0.00
benzyl alcohol	0.5	1.06	1.06	0.00
	1.0	1.08	1.08	0.00
3-hexanol	0.5	0.95	0.95	0.00
	1.0	0.95	0.95	0.00
3-ethyl-3-pentanol	0.5	0.97	0.97	0.00
	1.0	0.98	0.98	0.00
phenol	0.25	0.93	0.93	0.00
	0.5	0.97	0.97	0.00
	1.0	1.01	1.01	0.00
n-hexylamine	12.0	0.00	0.00	0.00
1-hexanethiol	12.0	0.00	0.00	0.00

[a] 3.0 Mmole of compound to 12 mmole of ThxBHBr·SMe_2(12 mmole of hydride) in 12.0 m*l* of solution; 0.25 M in compound and 1.0 M in hydride. [b] Mmole/mmole of compound. [c] Hydrogen evolved from blank minus the hydrogen evolved on hydrolysis of the reaction mixture after the indicated reaction period.

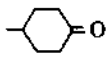
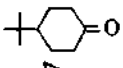
Table 2. Reaction of Thexylbromoborane-Methyl Sulfide with Representative Aldehydes and Ketones in Methylene Chloride at 0°C

compound[a]	time (hr)	hydrogen evolved[b,c]	hydride used[b,c]	hydride used for reduction[b,c]
caproaldehyde	0.5	0.00	0.90	0.90
	1.0	0.00	1.01	1.01
benzaldehyde	0.5	0.00	0.84	0.84
	1.0	0.00	0.96	0.96
	3.0	0.00	1.01	1.01
2-heptanone	1.0	0.00	0.60	0.60
	3.0	0.00	0.99	0.99
	6.0	0.00	0.99	0.99
norcamphor	1.0	0.00	0.90	0.90
	3.0	0.00	1.01	1.01
	6.0	0.00	1.01	1.01
acetophenone	0.5	0.00	0.98	0.98
	1.0	0.00	1.02	1.02
benzophenone	9.0	0.00	0.44	0.44
	12.0	0.00	0.58	0.58
	36.0	0.00	0.78	0.78
	48.0	0.00	0.78	0.78
	72.0	0.00	0.98	0.98
cinnamaldehyde	0.5	0.00	1.04	1.04
	1.0	0.00	1.24	1.24
	3.0	0.00	1.40	1.40

[a~c] See corresponding footnote in Table 1.

served while the reagent is kept at 0°C. In order to investigate the reducing characteristics of the reagent, we undertook the systematic study on the approximate rate and stoichiometry for the reaction of excess thexylbromoborane-methyl sulfide in methylene chloride with 55 compounds containing representative functional groups under standardized conditions (methylene chloride, 0°C).

Table 3. Stereochemistry of Cyclic Ketone Reduction with $ThxBH_2$, ThxBHCl, ThxBHBr in Methylene Chloride

compound	Reduction Temperature	Less Stable Isomer(%)[a,b]		
		$ThxBH_2$[c]	ThxBHCl[c]	ThxBHBr[d]
	0	47-50	94.5	97.5
	-23		96.5	98.5
	0		68.5	80.5
	-23		69.5	86
	0		56.5	77
	-23		58	79
	0		65.5	78.5
	-23		66	86
	0	92	98.5	99
	-23		99.9	99.6

[a] H^-/Ketone = 2:1. [b] Quantitative Yields. [c] In THF. [d] In CH_2Cl_2.

Results and Discussion

Procedure for Rate and Stoichiometry Studies. Thexylbromoborane-methyl sulfide was prepared from the hydroboration of 2,3-dimethyl-2-butene (tetramethylethylene) with monobromoborane-methyl sulfide, which was prepared by reaction of borane-methyl sulfide (BMS) with a half equiv of bromine[4], in methylene chloride. The reagent was stable at 0°C at least for 3 months. The procedure for the systematic study involved preparation of a reaction mixture of the reagent (1.0M in hydride) and the compound examined (0.25 M) under study in methylene chloride at 0°C. Hydrogen evolution during the reaction was measured by using a gas-buret. A blank test under identical conditions, but without the compound, was accompanied. At the appropriate reaction intervals, aliquots were withdrawn from the reaction mixture and analyzed for residual hydride by hydrolysis[5]. From the difference in the volume of hydrogen evolution in the two cases, the hydride used by the compound for reduction was calculated. In this way, it was possible to calculate a value for the number of moles of the hydride consumed by the compound to evolve hydrogen and the number of moles of hydride utilized for the reduction[5].

Alcohols, Amines, and Thiols (Active Hydrogen Compounds) Of those active hydrogen compounds examined, alcohols evolved 1 equiv of hydrogen rapidly and quantitatively in less than 1 h. However, n-hexylamine and 1-hexanethiol did not evolve any hydrogen under these conditions. The rate of reaction of ThxBHBr·SMe_2 with active hydrogen compounds studied is a little slower than that of ThxBHCl·SMe_2[1]. These results are summarized in Table 1.

Aldehyde and Ketones. Of those aldehydes and ketones studied, the less hindered compounds consumed 1 equiv of hydride for reduction rapidly within 1 or 3 h, whereas the more hindered ketones such as benzophenone required 3 days for complete reduction. This also indicates that thexylbromoborane is a much weaker reducing agent than the chloro-derivative. For example, benzophenone is reduced with ThxBHCl·SMe_2 in less than 12 h. Cinnamaldehyde consumed one hydride rapidly, while the second hydride consumption was relatively slow. The results are summarized in

Table 4. Reaction of Thexylbromoborane-Methyl Sulfide with Representative Quinones in Methylene Chloride at 0°C

compound[a]	time (hr)	hydrogen evolved[b,c]	hydride used[b,c]	hydride used for reduction[b,c]
p-benzoquinone	1.0	1.00	1.90	0.90
	12.0	1.00	1.91	0.91
anthraquinone	24.0	0.00	0.00	0.00

[a–c] see corresponding footnote in Table 1.

Table 5. Reaction of Thexylbromoborane-Methyl Sulfide with Representative Carboxylic acids and Acyl Derivatives in Methylene Chloride at 0°C

compound[a]	time (hr)	hydrogen evolved[b,c]	hydride used[b,c]	hydride used for reduction[b,c]
caproic acid	0.25	1.03	1.57	0.54
	0.5	1.03	1.75	0.72
	1.0	1.03	1.94	0.91
	12.0	1.03	2.07	1.04
benzoic acid	0.25	1.02	1.47	0.45
	0.5	1.02	1.67	0.65
	1.0	1.02	1.75	0.73
	3.0	1.02	1.84	0.82
	6.0	1.02	1.94	0.92
	12.0	1.02	1.98	0.96
	24.0	1.02	1.98	0.96
acetic anhyride	1.0	0.00	0.92	0.92
	12.0	0.00	2.00	2.00
	24.0	0.00	2.83	2.83
	72.0[d]	0.00	2.95	2.95
succinic anhydride	1.0	0.00	0.24	0.24
	6.0	0.00	1.10	1.10
phthalic anhydride	1.0	0.00	0.41	0.41
	3.0	0.00	0.59	0.59
	6.0	0.00	0.80	0.80
	12.0	0.00	0.88	0.88
	24.0	0.00	0.90	0.90
caproyl chloride	6.0	0.00	0.10	0.10
	12.0	0.00	0.16	0.16
benzoyl chloride	12.0	0.00	0.12	0.12
	24.0	0.00	0.15	0.15

[a–c] See corresponding footnote in Table 1. [d] Room temperature after 24 hr.

Table 2.

The stereoselectivity of the reagent on the reduction of cyclic ketones was also studied, and the results and those of ThxBH$_2$ and ThxBHCl·SMe$_2$ for comparison are summarized in Table 3. The introduction of bromine enhances the stereoselectivity to a large extent, compared with the result of the chloro-derivative. For example, 4-*t*-butylcyclohexanone is reduced by ThxBHBr·SMe$_2$ to the corresponding less stable isomer (*cis* alcohol) in a ratio of 86% at -23°C, whereas the ratio by ThxBHCl·SMe$_2$ is 66% at -23°C[1].

Quinones. Interestingly *p*-benzoquinone reacted with ThxBHBr·SMe$_2$ rapidly to evolve 1 equiv of hydrogen and to consume one hydride for reduction. The rate of reaction with ThxBHCl·SMe$_2$ is very slow for both hydrogen evolution and reduction process[1]. Hence, in this case, the reduction goes cleanly to the hydroquinone stage. However, no reaction between anthraquinone and ThxBHBr·SMe$_2$ under these conditions was observed, exactly same as the case of ThxBHCl·SMe$_2$. These results are summarized in Table 4.

Table 6. Reaction of Thexylbromoborane-Methyl Sulfide with Representative Esters and Lactones in Methylene Chloride at 0°C

compound[a]	time (hr)	hydrogen evolved[b,c]	hydride used[b,c]	hydride used for reduction[b,c]
ethyl caproate	12.0	0.00	0.20	0.20
	24.0	0.00	0.23	0.23
ethyl benzoate	1.0	0.00	0.11	0.11
	3.0	0.00	0.23	0.23
	24.0	0.00	0.23	0.23
phenyl acetate	1.0	0.00	0.06	0.06
	6.0	0.00	0.23	0.23
	24.0	0.00	0.25	0.25
r-butyrolactone	0.5	0.00	0.20	0.20
	1.0	0.00	0.31	0.31
	3.0	0.00	0.36	0.36
	9.0	0.00	0.54	0.54
	36.6	0.00	1.14	1.14
	72.0[d]	0.00	1.48	1.48
phthalide	3.0	0.00	0.14	0.14
	24.0	0.00	0.16	0.16
isopropenyl acetate	0.5	0.00	0.68	0.68
	1.0	0.00	0.80	0.80
	3.0	0.00	1.08	1.08
	12.0	0.00	1.25	1.25
	48.0[d]	0.00	2.76	2.76

[a–c] See corresponding footnote in Table 1. [d] Room temperature after 24 hr.

Carboxylic Acids and Acyl Derivatives. Both caproic acid and benzoic acid reacted with this reagent to evolve 1 equiv of hydrogen instantly and quantitatively, and consumed one more equivalent of hydride for the reduction and no further hydride uptake was apparent, similar to the case of the chloro-derivative. In fact, the reaction of caproic acid with ThxBHBr·SMe$_2$ provides caproaldehyde in almost quantitative yield. However, the reaction of benzoic acid is puzzling. Only a 50% yield of benzaldehyde was realized after 24 h by analysis with 2,4-dinitrophenylhydrazine.

This facile reduction of carboxylic acids to the corresponding aldehydes has been published.[6] In this respect, ThxBHBr·SMe$_2$ and ThxBHCl·SMe$_2$ are very promising reagents of reducing carboxylic acids to aldehydes. However, ThxBHBr·SMe$_2$ is a much milder and hence more selective reducing agent than ThxBHCl·SMe$_2$, and simple olefins are resistant to hydroboration with this reagent, whereas the chloro-derivative readily hydroborates double bonds. Thus, thexylbromoborane can reduce α,β-unsaturated carboxylic acids to the corresponding olefinic aldehydes in high yields[6]. The procedure and the method of isolation of products applicable for both reagents are now abailable[7].

Acetic anhydride consumed almost 3 equiv of hydride slowly. Apparently, like ThxBHCl·SMe$_2$, this reagent reduces acetic anhydride to acetaldehyde and ethyl alcohol segment[1]. Succinic and phthalic anhydrides reacted with ThxBHBr·SMe$_2$ at a slow rate. The rate of reaction of

Table 7. Reaction of Thexylbromoborane-Methyl Sulfide with Representative Epoxides in Methylene Chloride at 0°C

compound[a]	time (hr)	hydrogen evolved[b,c]	hydride used[b,c]	hydride used for reduction[b,c]
1,2-butyrene oxide	12.0	0.00	0.15	0.15
styrene oxide	24.0	0.00	0.00	0.00
cyclohexene oxide	24.0	0.00	0.00	0.00
2-methylcyclohex-	2.0	0.00	0.00	0.00

[a~c] See corresponding footnote in Table 1.

Table 8. Reaction of Thexylbromoborane-Methyl Sulfide with Representative Nitriles and Amides in Methylene Chloride at 0°C

compound[a]	time (hr)	hydrogen evolved[b,c]	hydride used[b,c]	hydride used for reduction[b,c]
caproamide	1.0	0.06	—	—
	3.0	0.16	—	—
	6.0	0.28	0.43	0.15
	12.0	0.48	0.79	0.31
	48.0[d]	1.25	1.72	0.47
benzamide	1.0	0.06	—	—
	3.0	0.23	0.59	0.36
	6.0	0.40	0.88	0.48
	12.0	0.52	1.18	0.66
	48.0	1.40	2.18	0.78
N,N-dimethyl-	1.0	0.00	0.02	0.02
caproamide	12.0	0.00	0.05	0.05
	24.0	0.00	0.08	0.08
N,N-dimethyl-	1.0	0.00	0.01	0.01
benzamide	12.0	0.00	0.03	0.03
	24.0	0.00	0.05	0.05
capronitrile	1.0	0.00	0.34	0.34
	3.0	0.00	0.84	0.84
	12.0	0.00	1.77	1.77
	24.0	0.00	2.00	2.00
benzonitrile	1.0	0.00	0.26	0.26
	3.0	0.00	0.59	0.59
	12.0	0.00	0.90	0.90
	24.0	0.00	1.33	1.33

[a~c] See corresponding footnote in Table 1. [d] Room temperature after 24 hr.

caproyl chloride and benzoyl chloride was very sluggish. These results are summarized in Table 5.

Esters and Lactones. All of the esters examined reacted with thexylbromoborane-methyl sulfide very slowly. *n*-Butyrolactone reacted with the reagent slowly, while phthalide was actually inert. Isopropenyl acetate, like the case of thexylchloroborane-methyl sulfide, utilized 2 equiv of hydride very slowly, and a third hydride consumption was observed at room temperature. Apparently the reaction involves an slow initial hydroboration, followed by elimination, and finally slow second hydroboration under these conditions. The results are summarized in Table 6.

Epoxide. All of the epoxides examined were actually inert to the reagent. The results are summarized in Table 7.

Amides and Nitriles. Both primary amides examined, such as caproamide and benzamide, evolved hydrogen slowly, and the subsequent reduction was sluggish. Tertiary amides studied are considered to be inert toward this reagent. However, capronitrile reacted with ThxBHBr·SMe_2 relatively fast to use 2 equiv of hydride within 24 h. Apparently, capronitrile is reduced to the amine stage. Benzonitrile, on the other hand, was reduced relatively slowly. These results are summarized in Table 8.

By checking the results for nitriles carefully, we can see the possibility that the reagent reduces nitriles partially to the corresponding aldehydes. Thus, the fact of a first hydride uptake being fast and a subsequent second hydride uptake being relatively slow means that the intermediate (an aldimine) is relatively stable. In fact, the reactions of capronitrile and benzonitrile with a limiting amount of ThxBHBr·SMe_2 under the practical conditions provide caproaldehyde and benzaldehyde in yields of 95% and 73%, respectively. The results for this partial reduction of various nitriles to the corresponding aldehydes have been published[7].

Table 9. Reaction of Thexylbromoborane-Methyl Sulfide with Representative Nitro Compounds in Methylene Chloride at 0°C

compound[a]	time (hr)	hydrogen evolved[b,c]	hydride used[b,c]	hydride used for reduction[b,c]
1-nitropropane	6.0	0.00	0.02	0.02
	24.0	0.00	0.03	0.03
nitrobenzene	6.0	0.00	0.00	0.00
	24.0	0.00	0.00	0.00
azoxybenzene	6.0	0.00	0.03	0.03
	24.0	0.00	0.10	0.10

[a~c] See corresponding footnote in Table 1.

Nitro Compounds and Their Derivatives. Of nitro compounds and their derivatives examined, none showed any reactivity toward this reagent. The results are summarized in Table 9.

Other Nitrogen Compounds. Cyclohexanone oxime underwent partial hydrogen evolution with the reduction process being relatively fast. Phenyl isocyanate consumed one hydride fast and the second hydride uptake was very slow. The reagent did not show any reactivity toward pyridine.

Pyridine N-oxide was reduced very slowly with this reagent, approaching to only one hydride uptake even at room temperature. This is a contrast to that reported for thexylchloroborane-methyl sulfide. ThxBHCl·SMe_2 consumes 3 equiv of hydride in 24 h. This difference in reactivity toward pyridine N-oxide reflects the resistance of ThxBHBr·SMe_2 to hydroboration on double bonds. These results are summarized in Table 10.

Sulfur Compounds. Of the sulfur compounds examined, only dimethyl sulfoxide reacted with thexylbromoborane under these reaction conditions. All of the other organosulfur compounds, such as sulfide, disulfides, and sulfone, were inert toward the reagent. Dimethyl sulfoxide evolved 1 equiv of hydrogen fast and the subsequent one hydride uptake for reduction was completed within 1 h to provide dimethyl sulfide. The reagent reacted with two sulfonic acids to evolve hydrogen quantitatively, however no reduction was observed. Cyclohexyl tosylate was inert toward the reagent. The results of the reaction between thexylbromoborane and sulfur

Table 10. Reaction of Thexylbromoborane-Methyl Sulfide with Representative Nitrogen Compounds in Methylene Chloride at 0°C

compound	time[a] (hr)	hydrogen evolved[b,c]	hydride used[b,c]	hydride used for reduction[b,c]
cyclohexanone	0.5	0.12	0.96	0.84
oxime	1.0	0.12	1.06	0.94
	3.0	0.12	1.15	1.03
phenyl isocyanate	1.0	0.00	1.18	1.18
	3.0	0.00	1.42	1.42
	6.0	0.00	1.51	1.51
	12.0	0.00	1.68	1.68
	24.0	0.00	1.71	1.71
pyridine	48.0[d]	0.00	0.00	0.00
pyridine-N-oxide	3.0	0.00	0.44	0.44
	6.0	0.00	0.50	0.50
	12.0	0.00	0.69	0.69
	24.0	0.00	0.75	0.75
	96.0[d]	0.00	0.93	0.93

[a~c] See corresponding footnote in Table 1. [d] Room temperature after 24 hr.

Table 11. Reaction of Thexylbromoborane-Methyl Sulfide with Representative Sulfur Derivatives in Methylene Chloride at 0°C

compound[a]	time (hr)	hydrogen evolved[b,c]	hydride used[b,c]	hydride used for reduction[b,c]
di-*n*-butyl sulfide	48.0[d]	0.00	0.16	0.16
diphenyl disulfide	1.0	0.00	0.12	0.12
	48.0[d]	0.00	0.29	0.29
di-*n*-butyl disulfide	48.0[d]	0.00	0.00	0.00
dimethyl sulfoxide	0.25	0.92	—	—
	0.5	0.97	1.92	0.95
	1.0	1.00	2.01	1.01
diphenyl sulfone	6.0	0.00	0.00	0.00
	24.0	0.00	0.00	0.00
p-toluenesulfonic-	1.0	2.82	2.82	0.00
acid monohydrate	24.0	2.82	2.86	0.04
methanesulfonic-	0.25	1.00	1.00	0.00
acid	24.0	1.00	1.00	0.00
cyclohexyl tosylate	12.0	0.00	0.00	0.00

[a~c] See corresponding footnote in Table 1. [d] Room temperature after 24 hr.

compounds are summarized in Table 11.

Conclusion

Thexylbromoborane-methyl sulfide, ThxBHBr·SMe$_2$, appears to be a mild selective reducing agent. The reagent can reduce carboxylic acids including α,β-unsaturated ones to the corresponding aldehydes. This reagent also reduces nitriles to the corresponding aldehydes. This unique reducing characteristics should find very useful applications in organic synthesis.

Experimental

The reaction flasks and other glassware were predried at 140°C for several hours, assembled hot, dried further with a flame, and cooled under a stream of nitrogen. Syringes were assembled and fitted with needles while hot, and then they were cooled. All reactions were carried out under a static pressure of dry nitrogen in flasks fitted with septum-covered sidearms with use a standard techniques for handling air-sensitive materials[5].

Materials. The compounds examined were commercial products of the highest quality. Sepctro-quality methylene chloride was stirred for one day under nitrogen over P_2O_5 and then distilled. Tetrahydrofuran (THF) and methyl sulfide were dried over 4A molecular sieve and distilled over sodium-benzophenone ketyl prior to use. 2,3-Dimethyl-2-butene (tetramethylethylene) synthesized from pinacolone was distilled from lithium aluminum hydride and stored under nitrogen. ^{11}B NMR spectra were recorded on a Bruker FT-80 spectrometer, and the chemical shifts are reported relative to BF_3·OEt_2 with low field assigned as positive.

GC Analysis. GC analyses were performed using a Hewlett-Packard 5790 FID chromatograph equipped with a Hewlett-Packard 3390 A integrator/plotter. Alcohol products were analyzed with use of a 12 ft × 0.125 in. column of 15% THEED on a 100-120 mesh Supelcoport or of 10% Carbowax 20M on 100-120 mesh Supelcoport. All GC yields were determined with use of a suitable internal standard and authentic samples.

Preparation of Monobromoborane-Methyl Sulfide (BH$_2$Br·SMe$_2$) in Methylene Chloride. To an oven-dried, 1-*l* flask equipped with a sidearm, and dry ice-acetone condenser with a stop cock leading to a mercury bubbler was added 150 m*l* (1.5 mole) borane-methyl sulfide (BMS) and 375 m*l* of carbon disulfide. Then to this 38.4 m*l* of bromine (0.75 mole) dissolved in 749 m*l* of carbon disulfide was added using a long double-ended needle dropwise with vigorous stirring. After the complete evolution of hydrogen, carbon disulfide was removed by simple distillation and finally monobromoborane-methyl sulfide was collected by distillation under the reduced pressure. The yield was almost quantitative.

Preparation of Thexylbromoborane-Methyl Sulfide (ThxBHBr·SMe$_2$) in Methylene Chloride. Monobromoborane-methyl sulfide (1.5 mole) in 66 m*l* of methylene chloride and 15 m*l* of methyl sulfide was placed in an oven-dried, 500-m*l* flask fitted with a sidearm a bent-adaptor which was connected to a mercury bubbler. The flask was immersed in an ice-water bath and to this was added 196 m*l* of precooled 2,3-di-methyl-2-butene (1.65 mole) dropwise over a period of 1 h via a double-ended needle. The reaction mixture was stirred for an additional 2 h at 0°C, followed by stirring overnight at room temperature. The resulting thexylbromoborane-methyl sulfide (ThxBHBr·SMe$_2$) solution in methylene chloride was found to be 3.34 M and ^{11}B NMR spectrum showed a clean doublet centered at δ = 5.16 ppm ($J_{B\text{-}H}$ = 123 Hz).

General Procedure for Determination of Rate and Stoichiometry. To a 100-m*l* flask fitted with a sidearm and a condenser leading to a gas-buret was added 6 m*l* of a solution of THxBHBr·SMe$_2$ (3.34 M) in methylene chloride (20 mmol in hydride). The flask was immersed in an ice bath and

the reaction mixture was diluted with 14 m*l* of methylene chloride containing 5 mmol of the compound to be examined. This makes the mixture 1 M in hydride and 0.25 M in the compound under investigation. At appropriate time intervals, 2 m*l* of aliquots were withdrawn and quenched in a THF-glycerin-2 N HCl hydrolyzing mixture. The hydrogen evolved was measured volumetrically. For the reaction of compounds with active hydrogen, the hydrogen evolved was collected in a gas-buret and measured the volume of hydrogen.

The reaction of 2-heptanone is described as a representative procedure. A 100-m*l* oven-dried flask, equipped with a sidearm and a reflux condenser, connected to a gas-buret *via* a dry ice-acetone trap[5]. The flask was placed in an ice-water bath and cooled down under dry nitrogen. To this flask was added 6 m*l* of 3.34 M ThxBHBr solution in methylene chloride, and followed by addition of 14 m*l* of 2-heptanone (0.57g, 5 mmol) solution in methylene chloride. No hydrogen evolution was observed. After 1 h at 0°C, hydrolysis of a 2-m*l* aliquot of the reaction mixture indicated 1.70 mmol of residual hydride, which means that 0.60 mmol of hydride per mmol of 2-heptanone had been used. After 3 h, the analysis showed 1.505 mmol of residual hydride, which indicates that 0.99 mmol of hydride per mmol of the compound had been consumed. After 6 h, the analysis showed no difference in the residual hydride. These results are summarized in Table 2.

General Procedure for Stereoselectivity Study. The reduction of 2-methylcyclohexanone is described here as representative. To a 25-m*l* vial capped by a rubber septum was added 1.2 m*l* of a solution of ThxBHBr·SMe_2 in methylene chloride (4 mmol in hydride). The vial was kept at -23°C with the aid of a cooling bath. To this was added 1 m*l* of a 2 M 2-methylcyclohexanone solution in methylene chloride (at -23°C). The reaction mixture was kept at -23°C for 6 h. It was then hydrolyzed by the addition of 2 m*l* of methanol, and then treated with 1 m*l* of 3 N NaOH and 0.5 m*l* of 30% H_2O_2. The aqueous layer was saturated with anhydrous potassium carbonate, and the organic layer was subjected to GC analysis. The results are summarized in Table 3.

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Non-Newtonian Intrinsic Viscosities of Biopolymeric and Nonbiopolymeric Solutions (I)

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Experimental results for viscous flow of poly (γ-methyl L-glutamate) solutions have been published elsewhere. The data of $[\eta]^f/[\eta]^o$ are expressed by the following equation, $\frac{[\eta]^f}{[\eta]^o}=1-\frac{A}{[\eta]^o}\{1-\frac{\sinh^{-1}[\beta_2(f/\eta_0)\exp(-c_2f^2/\eta_0^2kT)]}{\beta_2 f/\eta_0}\}$ (A1) where $[\eta]^f$ and $[\eta]^o$ are the intrinsic viscosity at shear stress f and zero, respectively, $A=\lim_{c\to 0}[(1/C)(x_2/\alpha_2)(\beta_2/\eta_0)]$, η_0 viscosity of the solvent, β_2 is the relaxation time of flow unit 2, c_2 is a constant related to the elasticity of flow unit 2. The theoretical derivation of Eq.(A1) is given in the text. The experimental curves of $[\eta]^f/[\eta]^o$ vs. log f are compared with the theoretical curves calculated from Eq.(A1) with good results. Eq.(A1) is also applied to non-biopolymeric solutions, and it was found that in the latter case $c_2=0$. The reason for this is explained in the text. The problems related to non-Newtonian flows are discussed.

Introduction

Some theoretical treatments of the dimensional properties of polypeptides in helix-coil transition region were given in our previous papers,[1,2] and the experimental results on intrinsic viscosities of poly(γ-methyl L-glutamate) (PMLG) solutions were reported elsewhere.[3] In this paper, an equation is derived by using the Ree-Eyring theory of viscosity,[4] which is based on the absolute reaction rate theory, and was successfully applied to polymer solutions, polymer melts,[4] suspension systems,[5] metals, alloys,[6,7] thixotropic and dilatant systems.[8a,b,c] The newly derived equation is applied to