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Reaction of Di-*s*-butoxyborane in Tetrahydrofuran with Selected Organic Compounds Containing Representative Functional Groups. Catalytic Effect of Tetraalkoxyborate on the Reaction of Dialkoxyborane †

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The approximate rate and stoichiometry of the reaction of excess di-*s*-butoxyborane with selected organic compounds containing representative functional groups under standardized conditions (tetrahydrofuran, 25°C) was examined in order to define the characteristics of the reagent for selective reductions. And the catalytic effect of lithium tetra-*s*-butoxyborate on the reaction of di-*s*-butoxyborane was also studied in order to increase the utility of this reducing system. Di-*s*-butoxyborane reacts only with simple aldehydes. However the addition of 2.5 mole % of lithium tetra-*s*-butoxyborate shows the tremendous rate enhancement of reaction for aldehydes, ketones, anhydrides, acid chlorides, lactones, and epoxides. This catalytic effect is assumed to *in situ* formation of lithium trialkoxyborohydride.

The alkylboranes[1-3], as substituted boranes, exhibit their own unique reducing characteristics. This uniqueness and hence selectivity on the reduction of organic functionalities is of dependence upon the alkyl-substituents. In the same sense, the reducing properties of dialkoxyboranes should be varied with their alkoxy-substituents.

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

Catecholborane (1,3,2-benzodioxaborole)[4], reported by Kabalka and his coworkers, appears to be a very useful reducing and hydroborating agent. This uniqueness attracted us. Therefore, we decided to explore the reducing characteristics of di-*s*-butoxyborane, a relatively stable acyclic dialkoxyborane, systematically.

Recently Yoon and coworkers[5] reported that dialkoxyborane is believed to react with lithium tetraalkoxyborate to form lithium trialkoxyborohydride, a basic reducing agent, and trialkoxyborane (eq 1).

$$Li(RO)_4B + (RO)_2BH \longrightarrow (RO)_3B + Li(RO)_3BH \quad (1)$$

It seems very interesting, because the addition of small amount of tetraalkoxyborate would catalyze the reaction in which the reduced alkoxy group serves to regenerate tetraalkoxyborate, and hence this catalytic effect might increase the selectivity of dialkoxyborane on the reduction of organic functionalities.

Consequently, we undertook to sutdy the approximate rate and stoichiometry for the reaction of excess di-*s*-butoxyborane in tetrahydrofuran (THF) in the absence or presence of catalytic amount of lithium tetra-*s*-butoxyborate with selected organic compounds containing representative functional groups under standardized conditions (THF, 25°C).

Results and Discussion

Preparation and Stability of the Reagent. Di-*s*-butoxyborane is readily prepared by the reaction of 2 equiv of *s*-butyl alcohol and 1 equiv of boranemethyl sulfide (BMS) in THF (eq 2).

$$2\ s\text{-BuOH} + BH_3{\cdot}SMe_2 \xrightarrow[RT]{THF} (s\text{-BuO})_2 + 2H_2\uparrow \quad (2)$$

Di-*s*-butoxyborane displays remarkable stability when compared with other dialkoxyboranes such as dimethoxyborane[6], di-*n*-butoxyborane, and 1,3,2-dioxaborolane[7] which undergo rapid disproportionation, except for 4,4,6-trimethyl-1,3,2-dioxaborinane[8] and catecholborane[4] which are quite stable.

Pasto and coworkers[9] reported that the dialkoxyboranes undergo slow redistribution reactions to give mixtures of borane and id-and trialkoxyboranes and the rate of attainment of equilibrium is markedly dependent on the structure of the alkoxy group. They observed that primary, straight-chain dialkoxyboranes (*i.e.*, *n*-propoxy and *n*-butoxy) attain equilibrium in approximately 2 days at 25°, whereas the isobutoxy-, *s*-butoxy, and *t*-butoxyborane systems require 7, 18, and 35 days, respectively, to reach equilibrium.

Our study on the stability of di-*s*-butoxyborane agrees with the Pasto's result[9]. However, the rate of redistribution was so slow that we could not detect any significant change in ^{11}B NMR spectra for 5 days (this period is our primary concern for the reduction of organic compounds) within experimental error. Furthermore, the stability of di-*s*-butoxyborane was confirmed by the reaction of di-*s*-butoxyborane with excess *s*-butyl alcohol at room temperature, and the results are summarized in Table 1.

As shown in Table 1, di-*s*-butoxyborane is very inert to excess *s*-butyl alcohol. This means that di-*s*-butoxyborane is quite resistant toward disproportionation, and hence no difficulty is expected to use this reagent for our purpose.

Table 1. Reaction of excess *s*-Butyl Alcohol with Dialkoxyborane at Room Temperature in Tetrahydrofuran[a]

Reaction time (h.)	6	24	72	120	168
Evolution of hydrogen[b]	0.00	0.00	0.01	0.06	0.12

[a] 1 Equiv of *s*-butyl alcohol and 1 equiv of dialkoxyborane (1M). [b] Mmoles of hydride used per mmole of dialkoxyborane.

Table 2. Reaction of Di-*s*-butoxyborane with Representative "Active Hydrogen" Compounds in Tetrahydrofuran at Room Temperature

Compounds[a]	Time, hr.	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
1-Hexanol	0.5	0.00	0.00	0.00
	12.0	0.01	0.01	0.00
	48.0	0.05	0.05	0.00
Benzyl	0.5	0.96	0.96	0.00
alcohol	1.0	1.00	1.00	0.00
3-Hexanol	0.5	0.00	0.00	0.00
	48.0	0.00	0.00	0.00
3-Ethyl-3-	0.5	0.00	0.00	0.00
pentanol	48.0	0.00	0.00	0.00
Phenol	0.5	0.00	0.00	0.00
	12.0	0.05	0.05	0.00
	48.0	0.10	0.10	0.00
n-Hexyl	0.5	1.00	1.00	0.00
amine	24.0	1.00	1.00	0.00
1-Hexane-	0.5	0.00	0.00	0.00
thiol	48.0	0.00	0.00	0.00
Benzene-	0.5	0.00	0.00	0.00
thiol	12.0	0.03	0.03	0.00
	48.0	0.08	0.08	0.00

[a] 5.0 Mmoles of compound, except where otherwise indicated, to 20.0 mmoles of hydride. [b] Millimoles/mole of compound.

Procedure for Rate and Stoichiometry Studies. Di-*s*-butoxyborane was prepared by adding 2 equiv of *s*-butyl alcohol to a solution of 1 equiv of borane-methyl sulfide (BMS) in THF.

The procedure used in this study involved preparation of a reaction mixture of di-*s*-butoxyborane (1.0 M, 1.0 M in hydride) and the compound (0.25 M) under study in THF at room temperature. The solution was maintained at room temperature. Hydrogen evolution, following addition of the compound to the reagent, was measured. A blank reaction was run under identical conditions, but without addition of the compound. Periodically, aliquots were taken from the reaction mixture and analyzed for residual hydride by hydrolysis[10]. From the difference in yields of hydrogen 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 used by the compound to evolve hydrogen and the number of moles of hydride utilized for the reduction process[10].

Alcohols, Phenols, Amines, and Thiols (Active Hydrogen Compounds). Primary, secondary, and tertiary alcohols all failed to react with di-*s*-butoxyborane, and phenol

Table 3-a. Reaction of Di-*s*-butoxyborane with Representative Aldehydes and Ketones in Tetrahydrofuran at Room Temperature

Compounds[a]	Time, hr.	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Capro-	0.5	0.00	0.25	0.25
aldehyde	6.0	0.00	0.48	0.48
	24.0	0.00	0.65	0.65
	72.0	0.00	1.00	1.00
Benz-	0.5	0.00	0.15	0.15
aldehyde	12.0	0.00	0.55	0.55
	48.0	0.00	0.75	0.75
	96.0	0.00	1.00	1.00
2-Heptanone	0.5	0.00	0.08	0.08
	12.0	0.00	0.36	0.36
	48.0	0.00	0.50	0.50
Norcamphor	0.5	0.01	0.08	0.07
	12.0	0.01	0.38	0.37
	48.0	0.01	0.55	0.54
Aceto-	0.5	0.02	0.04	0.02
phenone	12.0	0.02	0.36	0.34
	48.0	0.02	0.49	0.47
Benzo-	0.5	0.00	0.01	0.01
phenone	12.0	0.00	0.22	0.22
	48.0	0.00	0.41	0.41
Cinnam-	0.5	0.04	0.13	0.09
aldehyde	12.0	0.04	0.40	0.36
	48.0	0.04	0.65	0.61

[a,b] See corresponding footnotes in Table 2.

Table 3-b. Reaction of Di-*s*-butoxyborane in the Presence of Lithium Tetra-*s*-butoxyborate (1:0.025) with Representative Aldehydes and Ketones in Tetrahydrofuran at Room Temperature

Compounds[a]	Time, hr.	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Capro-	0.5	0.00	1.00	1.00
aldehyde	3.0	0.00	1.00	1.00
Benz-	0.5	0.00	0.97	0.97
aldehyde	1.0	0.00	1.00	1.00
2-Heptanone	0.5	0.00	0.89	0.89
	1.0	0.00	1.00	1.00
Norcamphor	0.5	0.01	0.91	0.90
	1.0	0.01	1.01	1.00
Aceto-	0.5	0.02	0.90	0.88
phenone	3.0	0.02	1.02	1.00
Benzo-	0.5	0.00	0.85	0.85
phenone	3.0	0.00	1.00	1.00
Cinnam-	0.5	0.04	1.00	0.96
aldehyde	1.0	0.04	1.04	1.00

[a,b] See corresponding footnotes in Table 2.

evolved hydrogen only very slowly. However, benzyl alcohol evolved hydrogen rapidly and quantitatively. Surprisingly, *n*-hexylamine also reacted with this reagent at a fast rate and evolved 1 equiv of hydrogen in less than 0.5 h. 1-Hexanethiol did not evolve any hydrogen, whereas benzenethiol evolved hydrogen very slowly. These results are summarized in Table 2.

Table 4. Reaction of Di-*s*-butoxyborane with Representative Quinones in Tetrahydrofuran at Room Temperature

Compounds[a]	Time, hr.	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
p-Benzo-	0.5	0.05	0.15	0.10
quinone	6.0	0.14	0.34	0.20
	24.0	0.16	0.49	0.33
	72.0	0.16	0.59	0.43
Anthra-	0.5	0.00	0.03	0.03
quinone[c]	6.0	0.00	0.10	0.10
	24.0	0.00	0.23	0.23
	72.0	0.00	0.30	0.30

[a,b] See corresponding footnotes in Table 2.
[c] Reverse addition(solution of reagent added to suspension of compound).

Aldehydes and Ketones. Of those aldehydes and ketones studied, caproaldehyde and benzaldehyde reacted with di-*s*-butoxyborane slowly to consume 1 equiv of hydride in 3 days and 4 days, respectively. The rate of reduction for all the ketones examined was very slow. These results are summarized in Table 3-a.

On the other hand, the addition of 2.5 mole % of lithium tetra-*s*-butoxyborate enhanced the rate of reduction of aldehydes and ketones tremendously. Thus, all the compounds examined are reduced to the corresponding alcohol stage within 1 or 3 h at room temperature. This catalytic effect is fascinating. This reaction is believed to involve the *in situ* formation of lithium trialkoxyborohydride *via* disproportionation, and then it reduces the carbonyl compounds rapidly, as follows (eq 3-5);

$$Li(RO)_4B + (RO)_2BH \rightleftharpoons (RO)_3B + Li(RO)_3BH \quad (3)$$

$$Li(RO)_3BH + \underset{}{\overset{O}{\overset{\|}{C}}} \longrightarrow Li(RO)_4B \quad (4)$$

$$Li(RO)_4B + (RO)_2BH \rightleftharpoons (RO)_3B + Li(RO)_3BH \quad (5)$$

These results are summarized in Table 3-b.

Quinones. Di-*s*-butoxyborane reacted with both *p*-benzoquinone and anthraquinone slowly with the partial evolution of hydrogen for the case of *p*-benzoquinone. However, the catalytic effect of borate was not significant in this case. These results are summarized in Table 4.

Carboxylic Acids and Acyl Derivatives. Both caproic acid and benzoic acid reacted with di-*s*-butoxyborane to evolve hydrogen rapidly and quantitatively. However, no reduction was observed. Acetic anhydride slowly consumed 2 equiv of hydride without further hydride uptake, suggesting the reduction to the carboxylic acid and alcohol stage. Cyclic anhydrides, such as succinic and phthalic anhydride, reacted with di-*s*-butoxyborane only slowly. The rate of reduction of both caproyl chloride and benzoyl chloride was also slow. These results are summarized in Table 5-a.

However, in the presence of catalytic amount of the tetraalkoxyborate, all of the carboxylic acids and acyl derivatives

Table 5-a. Reaction of Di-*s*-butoxyborane with Representative Carboxylic Acids and Acyl Derivatives in Tetrahydrofuran at Room Temperature

Compounds[a]	Time, hr.	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Caproic	0.5	1.00	1.00	0.00
acid	24.0	1.00	1.00	0.00
Benzoic	0.5	0.20	0.20	0.00
acid	3.0	1.00	1.00	0.00
	24.0	1.00	1.00	0.00
Acetic	0.5	0.02	0.20	0.18
anhydride[c]	3.0	0.02	0.87	0.85
	12.0	0.02	1.42	1.40
	48.0	0.02	2.02	2.00
Succinic	0.5	0.03	0.15	0.12
anhydride[d]	6.0	0.03	0.50	0.47
	24.0	0.03	0.79	0.76
	72.0	0.03	1.30	1.27
Phthalic	0.5	0.01	0.06	0.05
anhydride[d]	6.0	0.01	0.20	0.19
	24.0	0.01	0.34	0.33
	72.0	0.01	0.41	0.40
Caproyl	0.5	0.00	0.00	0.00
chloride	12.0	0.00	0.06	0.06
	48.0	0.00	0.25	0.25
Benzoyl	0.5	0.00	0.00	0.00
chloride	12.0	0.00	0.09	0.09
	48.0	0.00	0.15	0.15

[a,b] See corresponding footnotes in Table 2. [c] Hydride to compound in the ratio of 6:1 [d] Reverse addition (solution of reagent added to suspension of compound).

Table 5-b. Reaction of Di-*s*-butoxyborane in the Presence of Lithium Tetra-*s*-butoxyborate (1:0.025) with Representative Carboxylic Acids and Acyl Derivatives in Tetrahydrofuran at Room Temperature

Compounds[a]	Time, hr.	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Caproic	0.5	1.00	1.10	0.10
acid	6.0	1.00	1.36	0.36
	24.0	1.00	1.55	0.55
	72.0	1.00	1.73	0.73
Benzoic	0.5	1.00	1.06	0.06
acid	6.0	1.00	1.26	0.26
	24.0	1.00	1.42	0.42
	72.0	1.00	1.59	0.59
Acetic	0.5	0.02	0.62	0.60
anhydride[c]	6.0	0.02	2.33	2.31
	24.0	0.02	3.50	3.48
	72.0	0.02	4.02	4.00
Succinic	0.5	0.03	0.44	0.41
anhydride[d]	6.0	0.03	1.31	1.28
	24.0	0.03	1.76	1.73
	72.0	0.03	2.03	2.00
Phthalic	12.0	0.01	0.87	0.86
anhydride[d]	48.0	0.01	1.24	1.23
	96.0	0.01	1.53	1.52
Caproyl	0.5	0.00	0.40	0.40
chloride	6.0	0.00	0.82	0.82
	24.0	0.00	1.40	1.40
	48.0	0.00	2.00	2.00
Benzoyl	12.0	0.00	0.92	0.92
chloride	48.0	0.00	1.50	1.50
	92.0	0.00	2.00	2.00

[a,b] See corresponding footnotes in Table 2. [c] Hydride to compound in the ratio of 6:1. [d] Reverse addition (solution of reagent added to suspension of compound).

examined was reduced in an extraordinary rate enhancement. Especially, in the case of acetic anhydride and both acid chlorides, the reaction underwent the complete reduction to the alcohol stages within 2 or 4 days at room temperature. Similar considerations adopted for the case of aldehyde and ketones account for this catalytic effect. These results are summarized in Table 5-b.

Esters and Lactones. Di-*s*-butoxyborane showed very little reactivity toward all of the esters and lactones examined. Little catalytic effect of the tetraalkoxyborate on the reaction of di-*s*-butoxyborane with esters and lactones was observed, with the exception of γ-butyrolactone which slowly utilized 2 equiv of hydride to proceed to the 1,4-butanediol stage. These results are summarized in Table 6-a,b.

Epoxides. All of the epoxides examined, such as 1,2-butylene oxide, styrene oxide, and cyclohexene oxide, reacted with this reagent very slowly under these reaction conditions. Although these reactions were quite slow, the introduction of a catalytic amount of lithium tetra-*s*-butoxyborate enhanced the rate of the reaction. Thus, in the presence of 2.5 mole % of lithium tetra-*s*-butoxyborate, styrene oxide and cyclohexene oxide were reduced at a comparable rate to the corresponding alcohol stages. These results are summarized in Table 7-a,b.

Amides and Nitriles. Primary amides, such as caproamide and benzamide, reacted with di-*s*-butoxyborane to evolve 2 equiv of hydrogen relatively rapidly, however no reduction was observed. Typical disubstituted amides, such as N,N-dimethylcaproamide and N,N-dimethylbenzamide, were inert to this reagent. However, the reaction of nitriles proceeded relatively fast under these conditions. These results are summarized in Table 8-a.

On the other hand, the addition of a catalytic amount of the tetraalkoxyborate showed an interesting process. Thus, primary amides evolved the partial hydrogen and then the reduction proceeded slowly to consume 1 equiv of hydride, possibly suggesting the formation of aldehyde. Further study of this reaction is under investigation. However, interestingly, the rate of reaction of nitriles was rather diminished by adding the catalyst. These results are summarized in Table 8-b.

Nitro Compounds and Their Derivatives. 1-Nitropropane slowly utilized 2 equiv of hydride to proceed to the amine stage. However, all other nitro compounds and their derivatives studied, such as nitrobenzene, azobenzene, and azoxybenzene, showed very low reactivity toward di-*s*-butoxyborane. Furthermore, no significant catalytic effect was apparent. These results are summarized in Table 9.

Other Nitrogen Compounds. Di-*s*-butoxyborane reacted with cyclohexanone oxime to evolve hydrogen instant-

Table 6-a. Reaction of Di-*s*-butoxyborane with Representative Esters and Lactones in Tetrahydrofuran at Room Temperature

Compounds[a]	Time, hr	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Ethyl caproate	0.5	0.00	0.00	0.00
	12.0	0.00	0.08	0.08
	48.0	0.00	0.14	0.14
Ethyl benzoate	0.5	0.00	0.00	0.00
	12.0	0.00	0.14	0.14
	48.0	0.00	0.22	0.22
Phenyl acetate	0.5	0.01	0.01	0.00
	12.0	0.01	0.13	0.12
	48.0	0.01	0.16	0.15
γ-Butyro-lactone	0.5	0.00	0.09	0.09
	12.0	0.00	0.31	0.31
	48.0	0.00	0.54	0.54
Phthalide	0.5	0.00	0.00	0.00
	12.0	0.00	0.07	0.07
	48.0	0.00	0.15	0.15
Isopropenyl acetate	0.5	0.00	0.00	0.00
	12.0	0.00	0.09	0.09
	48.0	0.00	0.16	0.16

[a,b] See corresponding footnotes in Table 2.

Table 6-b. Reaction of Di-*s*-butoxyborane in the Presence of Lithium Tetra-*s*-butoxyborate (1:0.025) with Representative Esters and Lactones in Tetrahydrofuran at Room Temperature

Compounds[a]	Time, hr.	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Ethyl caproate	0.5	0.00	0.01	0.01
	12.0	0.00	0.15	0.15
	48.0	0.00	0.21	0.21
Ethyl benzoate	0.5	0.00	0.00	0.00
	12.0	0.00	0.15	0.15
	48.0	0.00	0.23	0.23
Phenyl acetate	0.5	0.01	0.01	0.00
	12.0	0.01	0.20	0.19
	48.0	0.01	0.24	0.23
γ-Butyro-lactone	0.25	0.00	0.18	0.18
	6.0	0.00	1.23	1.23
	24.0	0.00	1.56	1.56
	72.0	0.00	2.00	2.00
Phthalide	0.5	0.00	0.00	0.00
	12.0	0.00	0.11	0.11
	48.0	0.00	0.16	0.16
Isopropenyl actate	0.5	0.00	0.00	0.00
	12.0	0.00	0.10	0.10
	48.0	0.00	0.18	0.18

[a,b] See corresponding footnotes in Table 2.

ly, but no further reduction of the compound was observed. Pyridine reacted with this reagent to consume 1 equiv of hydride, whereas phenyl isocyanate and pyridine N-oxide showed very little reactivity. Similarly, the catalytic effect of borate was insignificant. These results are summarized in

Table 7-a. Reaction of Di-*s*-butoxyborane with Representative Epoxides in Tetrahydrofuran at Room Temperature

Compounds[a]	Time, hr.	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
1,2-Butylene oxide	0.5	0.00	0.01	0.01
	12.0	0.00	0.15	0.15
	48.0	0.00	0.18	0.18
Styrene oxide	0.5	0.01	0.10	0.09
	12.0	0.01	0.39	0.38
	48.0	0.01	0.51	0.50
Cyclohexene oxide	0.5	0.00	0.02	0.02
	12.0	0.00	0.20	0.20
	48.0	0.00	0.25	0.25

[a,b] See corresponding footnotes in Table 2.

Table 7-b. Reaction of Di-*s*-butoxyborane in the Presence of Lithium Tetra-*s*-butoxyborate (1:0.025) with Representative Epoxides in Tetrahydrofuran at Room Temperature

Compounds[a]	Time, hr.	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
1,2-Butylene oxide	0.5	0.00	0.15	0.15
	12.0	0.00	0.35	0.35
	48.0	0.00	0.58	0.58
Styrene oxide	0.5	0.01	0.19	0.18
	6.0	0.01	0.56	0.55
	24.0	0.01	1.32	1.31
Cyclohexene oxide	0.5	0.00	0.11	0.11
	12.0	0.00	0.73	0.73
	48.0	0.00	1.00	1.00

[a,b] See corresponding footnotes in Table 2.

Table 8-a. Reaction of Di-*s*-butoxyborane with Representative Amides and Nitriles in Tetrahydrofuran at Room Temperature

Compounds[a]	Time, hr.	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Caproamide	0.5	0.19	0.19	0.00
	6.0	2.00	2.00	0.00
	24.0	2.00	2.00	0.00
Benzamide	0.5	0.15	0.15	0.00
	3.0	0.55	0.55	0.00
	24.0	2.00	2.00	0.00
	48.0	2.00	2.00	0.00
N,N-Dimethyl-caproamide	0.5	0.00	0.00	0.00
	24.0	0.00	0.00	0.00
N,N-Dimethyl-benzamide	0.5	0.00	0.00	0.00
	24.0	0.00	0.00	0.00
Capronitrile	0.5	0.00	0.14	0.14
	12.0	0.00	0.55	0.55
	48.0	0.00	0.86	0.86
Benzonitrile	0.5	0.00	0.15	0.15
	12.0	0.00	0.55	0.55
	48.0	0.00	0.82	0.82

[a,b] See corresponding footnotes in Table 2.

Table 8-b. Reaction of Di-*s*-butoxyborane in the Presence of Lithium Tetra-*s*-butoxyborate (1:0.025) with Representative Amides and Nitriles in Tetrahydrofuran at Room Temperature

Compounds[a]	Time, hr.	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Caproamide	0.5	1.01	1.02	0.01
	6.0	1.31	1.75	0.44
	12.0	1.35	2.05	0.70
	24.0	1.36	2.36	1.00
Benzamide	0.5	0.95	1.33	0.38
	3.0	1.12	1.74	0.62
	6.0	1.18	2.08	0.90
	12.0	1.24	2.24	1.00
Capronitrile	0.5	0.00	0.09	0.09
	12.0	0.00	0.40	0.40
	48.0	0.00	0.61	0.61
Benzonitrile	0.5	0.00	0.13	0.13
	12.0	0.00	0.43	0.43
	48.0	0.00	0.68	0.68

[a,b] See corresponding footnotes in Table 2.

Table 9. Reaction of Di-*s*-butoxyborane with Representative Nitro Compounds and Their Derivatives in Tetrahydrofuran at Room Temperature

Compounds[a]	Time, hr.	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
1-Nitro-	0.5	0.00	0.06	0.06
propane	12.0	0.00	0.77	0.77
	48.0	0.00	2.00	2.00
Nitro-	0.5	0.00	0.09	0.09
benzene	12.0	0.00	0.22	0.22
	48.0	0.00	0.34	0.34
Azobenzene	0.5	0.00	0.02	0.02
	12.0	0.00	0.28	0.28
	48.0	0.00	0.41	0.41
Azoxy-	0.5	0.00	0.00	0.00
benzene	12.0	0.00	0.09	0.09
	48.0	0.00	0.23	0.23

[a,b] See corresponding footnotes in Table 2.

Table 10.

Sulfur Derivatives. All the sulfur compounds examined, such as disulfides, sulfide, sulfoxide, and sulfone, were inert to di-*s*-butoxyborane. And no catalytic effect of the tetraalkoxyborate was observed. These results are summarized in Table 11.

Conclusion

The reducing properties of di-*s*-butoxyborane are now fully characterized. The reagent appears to be an extremely mild reducing agent. With the exception of simple aldehydes, most functional groups studied were inert toward this reagent. However, the addition of a small amount of lithium tetra-*s*-butoxyborate enhances the rate of reduction of aldehydes, ketones, anhydrides, acid chlorides, lactones, and epoxides. This catalytic effect is assumed due to *in situ* formation of lithium trialkoxyborohydride. These reducing systems possess their own unique reducing characteristics, and are complementary each other. Therefore, the combined system should find valuable applications in organic synthesis.

Table 10. Reaction of Di-*s*-butoxyborane with Representative Other Nitrogen Compounds in Tetrahydrofuran at Room Temperature

Compounds[a]	Time, hr.	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Cyclohexanone	0.5	1.01	1.01	0.00
oxime	24.0	1.01	1.01	0.00
Phenyl	0.5	0.00	0.00	0.00
isocyanate	12.0	0.00	0.04	0.04
	48.0	0.00	0.18	0.18
Pyridine	0.5	0.01	0.15	0.14
	3.0	0.01	0.46	0.45
	12.0	0.01	0.83	0.82
	48.0	0.01	1.01	1.00
Pyridine-N-	0.5	0.00	0.08	0.08
oxide	12.0	0.00	0.16	0.16
	48.0	0.00	0.20	0.20

[a,b] See corresponding footnotes in Table 2.

Table 11. Reaction of Di-*s*-butoxyborane with Representative Sulfur Derivatives in Tetrahydrofuran at Room Temperature

Compounds[a]	Time, hr.	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Di-*n*-butyl	0.5	0.00	0.00	0.00
disulfide	24.0	0.00	0.00	0.00
Diphenyl	0.5	0.00	0.00	0.00
disulfide	24.0	0.00	0.00	0.00
Phenyl *n*-propyl	0.5	0.00	0.00	0.00
sulfide	24.0	0.00	0.00	0.00
Dimethyl	0.5	0.00	0.00	0.00
sulfoxide	24.0	0.00	0.00	0.00
Diphenyl	0.5	0.00	0.00	0.00
sulfone	24.0	0.00	0.00	0.00

[a,b] See corresponding footnotes in Table 2.

Experimental

All glassware used was predried at 140°C for several hours, assembled hot, and cooled under a stream of nitrogen. All reactions were carried out under a static pressure of nitrogen in flasks fitted with a septum-covered sidearm with use of standard techniques for handling air-sensitive materials[10]. Tetrahydrofuran (THF) was dried over a 4-A molecular sieve and distilled for sodium-benzophenone ketyl prior to use. Most of the organic compounds utilized in this study were commercial products of the highest purity. They were further purified by distillation or recrystallizaition when necessary. Some compounds were synthesized by using standard procedures. In all of the cases, physical constants agreed satisfactorily with constants in the literature. ^{11}B NMR spectra were recorded on a Varian FT-80 spectro-

meter, and all ^{11}B NMR chemical shifts are reported relative to BF_3-OEt_2 with low field assigned as positive.

Preparation of Standard Solution of Di-*s*-butoxyborane. An oven-dried, 500-m*l* round-bottomed flask with a sidearm, equipped with a condenser leading to a mercury bubbler was flushed with dry nitrogen and maintained under a static pressure of nitrogen. To this flask were added 40.0 m*l* of 10 M borane-methyl sulfide (400 mmol) and 86.8 m*l* of THF. The temperature of mixture was kept at 25°C by using a water bath. *s*-Butyl alcohol (59.3g, 800 mmol) was added dropwise to the borane solution with stirring. After the complete addition, the stirring was continued for an additional 3 h to ensure the hydrogen evolution. The ^{11}B NMR spectrum of the reaction mixture showed the formation of a > 99° pure di-*s*-butoxyborane, indicating a doublet at δ26.66 (J_{B-H}= 159.8 Hz). The resulting di-*s*-butoxyborane solution in THF was 2.01 M in hydride content. No significant change in ^{11}B NMR spectra was observed when a solution of di-*s*-butoxyborane was kept at room temperature under a static pressure of nitrogen for 5 days.

General Procedure for Determination of Rate and Stoichiometry. To a 100-m*l* flask fitted with a sidearm and capped by a rubber septum was added 9.95 m*l* of a solution of di-*s*-butoxyborane in THF (20 mmol in hydride). The flask was immersed in a water bath at 25°C. The reaction mixture was diluted with 10.05 m*l* of THF containing 5 mmol of the compound to be reduced. In the case of reaction in the presence of a catalytic amount of lithium tetra-*s*-butoxyborate, 0.5 mmol of the borate (1.0 m*l*) was added instead of the same volume of THF. This makes the mixture 1 M in hydride and 0.25 M in the compound under investigation. At different time intervals, 2 m*l* of samples were withdrawn and quenched in a glycerine-water-methanol hydrolyzing mixture. The hydrgen evolved was measured volumetrically. The reaction was stopped when two or more analyses indicated that no more hydride was taken up. For the reaction of compounds with active hydrogen, the reaction flask was attached to a gas meter to measure the evolved hydrogen.

The reaction of caproaldehyde with di-*s*-butoxyborane is described as a representative. After a 0.5-h reaction time at 25°C, hydrolysis of a 2-m*l* aliquot of the reaction mixture indicated 3.75 mmol of residual hydride, which means that 0.25 mmol of hydride per mmol of caproaldehyde had been consumed. After 72 h, the analysis showed 3.00 mmol of residual hydride, which indicated that the compound had been reduced to the corresponding alcohol. These results are summarized in Table 3-a.

In the case of reaction with di-*s*-butoxyborane in the presence of 2.5 mole % of lithium tetra-*s*-butoxyborate, the hydrolysis of the reaction mixture indicated that 1.00 mmol of hydride was used for reduction at 0.5 h and no more hydride was consumed at 3 h. That means that the reaction was completed within 0.5 h under these conditions. These results are summarized in Table 3-b.

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A Facile Synthesis of Propellanes via Dianion Chemistry

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A dianion-mediated dialkylation reaction provides a variety of propellanes. 12-Thia[4.4.3] propel-3-ene, 3-(N-benzyl)-2,4-dioxotricyclo[3.3.3.0] decane and 3-(N-benzyl)-2,4-dioxotricyclo[3.3.2.0] nonane were prepared by this dianion ring annulation methodology.

Introduction

In the related study of ring annulation using dianion chemistry,[1,2] we would like to report a facile preparation of propellanes. It was postulated that a vicinal ester dianion 1, generated from vicinal a diester might be a legitimate in-