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Reaction of 2,2'-Biphenoxyborane in Tetrahydrofuran with Selected Organic Compounds Containing Representative Functional Groups

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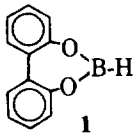
The approximate rates and stoichiometry of the reaction of excess 1,3,2-biphenyldioxaborepin [2,2'-biphenoxyborane (BPB)] with selected organic compounds containing representative functional groups under the standardized conditions (tetrahydrofuran, hydride to compound being 4 : 1, room temperature) was examined in order to define the characteristics of the reagent for selective reductions and compare its reducing power with those of other substituted boranes. The results indicate that BPB is unique and the reducing power is much stronger than that of other dialkoxyboranes, such as catecholborane and di-*s*-butoxyborane. BPB reduces aldehydes, ketones, quinones, lactones, tertiary amides, and sulfoxides readily. Carboxylic acids, anhydrides, esters, and nitriles are also reduced slowly. However, the reactions of acid chlorides, epoxides, primary amides, nitro compounds, and disulfides with this reagent proceed only sluggishly.

Introduction

Catecholborane (1,3,2-benzodioxaborole) has appeared to be a very useful hydroborating agent.[1] The usefulness of catecholborane as a hydroborating agent is enhanced by the fact that the reagent can tolerate a number of functional groups under hydroboration conditions, because catecholborane is a mild reducing agent.[1a,b] Similarly, di-*s*-butoxyborane appears to be an extremely mild, even milder than catecholborane, reducing agent.[2] With the exception of simple aldehydes, most functional groups studied are inert toward this reagent.

This uniqueness of stable dialkoxyboranes attracted us. We became to believe that the systematic study on the hydroboration and reduction reactions of various dialkoxyboranes will make a broad spectrum of their reducing and hydroborating properties which, in turn, provide useful applications. Therefore, we decided to explore the reducing characteristics of 1,3,2-biphenyldioxaborepin [2,2'-biphenoxyborane (BPB) **1**], a new stable cyclic dialkoxyborane,[4] systematically.



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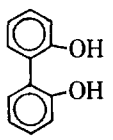
Results and Discussion

Preparation and Stability of the Reagent. 2,2-Biphenoxyborane (BPB), **1**, is readily prepared by the reaction of 2,2'-biphenol and borane in THF at −10℃ (Eq. 1).



$$+ BH_3 \cdot THF \xrightarrow[-10^\circ]{THF} \mathbf{1} + 2H_2\uparrow \quad (1)$$

BPB is quite stable, similar to the stability of catecholborane and 4,4,6-trimethyl-1,3,2-dioxaborinane. We could not detect any significant change in B-11 NMR spectra and in hydride concentration for 6 months at room temperature.

Procedure for Rate and Stoichiometry Studies. The general procedure adopted in this study involved preparation of a reaction mixture of BPB (0.5 M, 0.5 M in hydride) and the compound (0.125 M) under study in THF at room temperature. The solution was maintained at room temperature. In some cases where the hydride-to-compound ratio of 4 : 1 is not adequate for complete reduction, the hydride concentration was maintained constant, but the concentration of compound, was reduced to give a higher ratio. Hydrogen evolution, following addition of the compound to be examined to the reagent, was measured. A blank reaction was run un-

Table 1. Reaction of 2,2'-Biphenoxyborane with Representative "Active Hydrogen Compounds" in Tetrahydrofuran at Room Temperature

Compounds[a]	Time h.	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
1-Hexanol	0.5	1.00	1.00	0.00
	1.0	1.00	1.00	0.00
Benzyl alcohol	0.5	1.00	1.00	0.00
	1.0	1.00	1.00	0.00
3-Hexanol	0.5	0.94	0.94	0.00
	1.0	1.00	1.00	0.00
3-Ethyl-3-pentanol	0.5	0.89	0.89	0.00
	1.0	1.00	1.00	0.00
Phenol	0.5	1.00	1.00	0.00
	1.0	1.00	1.00	0.00
n-Hexylamine	3.0	0.11	0.11	0.00
	24.0	0.16	0.16	0.00
	72.0	0.26	0.26	0.00
1-Hexanethiol	1.0	0.34	0.34	0.00
	3.0	0.44	0.44	0.00
	24.0	0.72	0.72	0.00
	72.0	0.93	0.93	0.00
	96.0	0.99	0.99	0.00
Thiophenol	0.5	0.91	0.91	0.00
	1.0	1.00	1.00	0.00

[a] 5.0 Mmol of compound was added to 20 mmol of BPB (0.125 M in compound and 0.5 M in hydride). [b] Mmol/mmol of compound.

der identical conditions, but without addition of the compound. Periodically, aliquots were taken from the reaction mixture and analyzed for residual hydride by hydrolysis. From the difference in yields of hydrogen in the two cases, the hydride used by the compound for reductions was calculated. In this manner it was possible both to establish the rate at which reduction proceeds and the stoichiometry of the reaction, *i.e.*, the number of hydrides utilized per mole of compound when the reaction comes to an effective halt.

Alcohols, Phenols, Amines, and Thiols (Active Hydrogen Compounds). Surprisingly, primary, secondary, and tertiary alcohols all liberated hydrogen quantitatively within 1 h at room temperature. Phenol, thiophenol, and benzyl alcohol also evolved hydrogen readily. Only *n*-hexylamine and l-hexanethiol evolved hydrgen slowly. This remarkable fast reaction is a contrast to the reactions of di-*s*-butoxyborane and catecholborane[3] which show, in general, resistance to alcohols. The results are summarized in Table 1.

Aldehydes and Ketones. Aldehydes examined, shch as caproaldehyde and benzaldehyde, took up 1 equiv of hydride readily to be reduced to the corresponding alcohols cleanly. The reaction of simple ketons, such as 2-heptanone and norcamphor, was completed within 1 h at room temperature. However, the reaction of hindered ketones, such as acetophenone and benzophenone, slowed down, requiring 3 h and 12 h for complete reduction, respectively. Unexpectedly, cinnamaldehyde reacted rapidly with 2 equiv of hydride to provide hydrocinnamyl alcohol cleanly. The experimental

Table 2. Reaction of 2,2'-Biphenoxyborane with Representative Aldehydes and Ketones in Tetrahydrofuran at Room Temperature

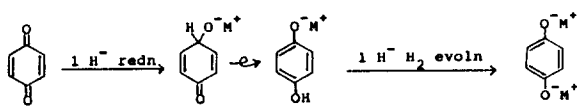
Compounds[a]	Time h.	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Caproaldehyde	0.5	0.02	0.91	0.89
	1.0	0.02	1.02	1.00
	3.0	0.02	1.02	1.00
Benzaldehyde	0.5	0.00	0.87	0.87
	1.0	0.00	0.95	0.95
	3.0	0.00	1.00	1.00
2-Heptanone	0.5	0.00	0.91	0.91
	1.0	0.00	1.03	1.03
Norcamphor	0.5	0.00	1.00	1.00
	1.0	0.00	1.00	1.00
Acetophenone	0.5	0.00	0.86	0.86
	1.0	0.00	0.93	0.93
	3.0	0.00	1.00	1.00
Benzophenone	0.5	0.00	0.32	0.32
	1.0	0.00	0.42	0.42
	3.0	0.00	0.69	0.69
	6.0	0.00	0.91	0.91
	12.0	0.00	1.01	1.01
Cinnamaldehyde	0.5	0.02	2.02	2.00
	1.0	0.02	2.02	2.00

[a,b] See corresponding footnotes in Table 1.

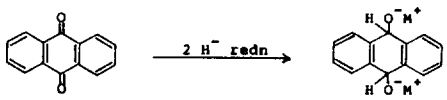
data are summarized in Table 2.

The stereochemistry in the reduction of cyclic ketones with BPB is summarized in Table 3. The stereochemical outcome appears to be similar to that of simple boranes.

Quinones. Two examples for quinones were examined and the results are summarized in Table 4. Both quinones consumed 2 equiv of hydride at a relatively fast rate. Thus, *p*-benzoquinone rapidly utilized 2 equiv of hydride per mole of compound, of which approximately 1 for hydrogen evolution and 1 for reduction. This value indicates that the reduction of *p*-benzoquinone proceeded to give hydroquinone exclusively (Eq. 2). However, anthraquinone consumed 2 equiv of hydride for reduction without evolution of any hydrogen to indicate a clean reduction to 9,10-dihydro-9,10-anthracenediol (Eq. 3). In fact, we isolated the hydroquinone and the diol in yields of 78 and 76%, respectively.



(2)



(3)

Carboxylic Acids and Derivatives. Carboxylic acids were reduced at a moderate rate after immediate hydrogen evolution to the corresponding alcohols cleanly, similar to the case of catecholborane. This phenomenon is a sharp contrast to the case of di-*s*-butoxyborane, which shows an abso-

Table 3. Stereochemistry in the Reduction of Representative Cyclic Ketones with 2,2'-Biphenoxyborane in Tetrahydrofuran at Room Temperature[a,b]

Ketone	Less stable isomer	Yield (%)[c]
2-Methylcyclohexane	*cis*	13 (13)[d]
3-Methylcyclohexane	*trans*	14
4-Methylcyclohexane	*cis*	8
4-*t*-Butylcyclohexane	*cis*	11
3,3,5-Trimethylcyclohexanone	*trans*	62
Norcamphor	*endo*	95 (96)[d]
Camphor	*exo*	73

[a] A 2 : 1 reagent : ketone ratio was used. [b] The yields of alcohols were more than 95%. [c] A normalized yield. [d] At 0℃.

Table 4. Reaction of 2,2'-Biphenoxyborane with Representative Quinones in Tetrahydrofuran at Room Temperature

Compounds[a]	Time h.	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
p-Benzoquinone	0.5	0.85	1.83	0.98
	1.0	0.92	1.96	1.04
	3.0	0.95	2.00	1.05
Anthraquinone[c]	0.5	0.00	0.73	0.73
	1.0	0.00	0.99	0.99
	3.0	0.00	1.84	1.84
	6.0	0.00	2.02	2.02

[a,b] See corresponding footnotes in Table 1. [c] Yellow precipitate.

Table 5. Reaction of 2,2'-Biphenoxyborane with Representative Carboxylic Acids and Acyl Derivatives in Tetrahydrofuran at Room Temperature

Compounds[a]	Time h.	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Caproic acid	0.5	1.03	1.11	0.08
	1.0	1.03	1.41	0.38
	3.0	1.03	2.10	1.07
	6.0	1.03	2.96	1.93
	12.0	1.03	3.04	2.01
Benzoic acid	0.5	1.02	1.05	0.03
	3.0	1.02	1.22	0.20
	12.0	1.02	1.98	0.96
	24.0	1.02	2.86	1.84
	48.0	1.02	3.01	1.99
	72.0	1.02	3.02	2.00
Acetic anhydride[c]	0.5	0.00	1.26	1.26
	1.0	0.00	1.87	1.87
	3.0	0.00	2.99	2.99
	6.0	0.00	3.32	3.32
	12.0	0.00	3.65	3.65
	24.0	0.00	4.03	4.03
Succinic anhydride[c]	1.0	0.02	0.56	0.54
	6.0	0.02	1.35	1.33
	12.0	0.02	2.02	2.00
	24.0	0.02	2.94	2.92
	48.0	0.02	3.67	3.65
	72.0	0.02	4.03	4.01
Phthalic anhydride[c]	1.0	0.04	0.20	0.16
	6.0	0.04	0.57	0.53
	24.0	0.04	1.61	1.57
	72.0	0.04	3.40	3.36
	96.0	0.04	4.06	4.02
Caproyl chloride	1.0	0.00	0.06	0.06
	6.0	0.00	0.44	0.44
	12.0	0.00	0.86	0.86
	24.0	0.00	1.36	1.36
	96.0	0.00	2.00	2.00
Benzoyl chloride	1.0	0.00	0.01	0.01
	12.0	0.00	0.68	0.68
	24.0	0.00	0.75	0.75
	72.0	0.00	1.14	1.14
	144.0	0.00	2.00	2.00

[a,b] See corresponding footnotes in Table 1. [c] Hydride/compd. = 6/1.

lute inertness. Acetic anhydride was also reduced readily to the corresponding alcohol after utilizing 4 equiv of hydride within 24 h at room temperature. However, cyclic anhydrides, such as succinic and phthalic anhydrides, reacted with BPB slowly but still faster than that of di-*s*-butoxyborane.[2] The rate of reduction of both caproyl chloride and benzoyl chloride was also slow, requiring 4 and 6 days, respectively, to be reduced to the corresponding alcohols. The results are summarized in Table 5.

Esters and Lactones. Esters examined were all reduced slowly to the corresponding alcohols in 48 or 96 h at room temperature. However, in the case of isoprophenyl acetate the reaction of BPB utilized 2 equiv of hydride rapidly and the further hydride utilization was also completed readily within 6 h. This indicates that the reduction was occurred rapidly, and followed by the concurrent hydroboration, elimination, and rehydroboration successively. The reaction of γ-butyrolactone proceeded relatively fast to the corresponding diol, whereas phthalide utilized 2 equiv of hydride slowly. The results are summatized in Table 6.

Epoxides. 1,2-Butylene oxide and cyclohexene oxide reacted with this reagent very slowly under these reaction conditions. The reaction required 7 to 8 days for complete ring opening. On the other hand, the reaction of styrene oxide consumed 1 equiv of hydride relatively fast and the further reduction was followed slowly. These results are summarized in Table 7.

Amides and Nitriles. Primary amides, such as caproamide and benzamide, liberated 1 equiv of hydrogen relatively repidly, but no further hydrogen evolution was realized. Hydride utilization for reduction was also very slow, taking up approximately only 1 equiv of hydride in 2 or 4 days at room temperature. In these cases, however, no aldehyde product was detected. On the other hand, the reduction of typical disubstituted amides, such as N,N-dimethylcaproamide and N,N-dimethylbenzamide, proceeded readily to afford the corresponding tertiary amines. Likewise, the reaction of nitiles proceeded also relatively fast to give the corresponding amines. These results are summarized in Table 8.

Table 6. Reaction of 2,2'-Biphenoxyborane with Representative Esters and Lactones in Tetrahydrofuran at Room Temperature

Compounds[a]	Time h.	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Ethyl caproate	1.0	0.00	0.28	0.28
	6.0	0.00	0.97	0.97
	12.0	0.00	1.19	1.19
	24.0	0.00	1.60	1.60
	48.0	0.00	2.02	2.02
Ethyl benzoate	1.0	0.00	0.15	0.15
	12.0	0.00	0.58	0.58
	24.0	0.00	1.00	1.00
	72.0	0.00	1.72	1.72
	96.0	0.00	2.01	2.01
Phenyl acetate	1.0	0.00	0.30	0.36
	3.0	0.00	0.56	0.56
	12.0	0.00	0.89	0.89
	24.0	0.00	1.49	1.49
	48.0	0.00	2.00	2.00
γ-Butyrolactone	0.5	0.02	0.42	0.40
	1.0	0.02	0.81	0.79
	3.0	0.02	1.20	1.18
	6.0	0.02	1.69	1.67
	12.0	0.02	2.04	2.02
Phthalide	1.0	0.01	0.40	0.39
	3.0	0.01	0.79	0.78
	12.0	0.01	1.42	1.41
	24.0	0.01	1.67	1.66
	48.0	0.01	1.88	1.87
	72.0	0.01	2.00	1.99
Isopropenyl acetate	0.5	0.02	2.36	2.34
	1.0	0.02	3.27	3.25
	3.0	0.02	4.00	3.98
	6.0	0.02	4.03	4.01

[a,b] See corresponding footnotes in Table 1.

Table 7. Reaction of 2,2'-Biphenoxyborane with Representative Epoxides in Tetrahydrofuran at Room Temperature

Compounds[a]	Time h.	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
1,2-Butylene oxide	3.0	0.00	0.02	0.02
	12.0	0.00	0.08	0.08
	24.0	0.00	0.13	0.13
	72.0	0.00	0.33	0.33
	168.0[c]	0.00	1.00	1.00[c]
Styrene oxide	1.0	0.04	0.66	0.62
	3.0	0.04	0.74	0.70
	12.0	0.04	0.89	0.85
	24.0	0.04	1.12	1.08
	72.0	0.04	1.61	1.57
	144.0	0.04	2.02	1.98
Cyclohexene oxide	3.0	0.00	0.04	0.04
	12.0	0.00	0.21	0.21
	24.0	0.00	0.30	0.30
	72.0	0.00	0.48	0.48
	192.0	0.00	1.00	1.00

[a,b] See corresponding footnotes in Table 1. [c] 98% of 2-butanol was realized by GC analysis.

Table 8. Reaction of 2,2'-Biphenoxyborane with Representative Amides and Nitriles in Tetrahydrofuran at Room Temperature

Compounds[a]	Time h.	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Caproamide	0.5	0.30	0.38	0.08
	3.0	0.91	1.11	0.20
	6.0	0.98	1.58	0.60
	24.0	0.98	1.70	0.72
	48.0	0.98	1.97	0.99
Benzamide	1.0	0.80	0.83	0.03
	3.0	0.97	1.08	0.11
	6.0	1.00	1.22	0.22
	24.0	1.00	1.51	0.51
	72.0	1.00	1.83	0.83
	96.0	1.00	2.04	1.04
N,N-Dimethyl benzamide	0.5	0.05	1.46	1.41
	1.0	0.05	1.93	1.88
	3.0	0.05	2.05	2.00
N,N-Dimethyl carproamide	0.5	0.02	1.30	1.28
	1.0	0.02	1.55	1.53
	3.0	0.02	1.77	1.75
	6.0	0.02	2.00	1.98
Capronitrile	1.0	0.00	0.49	0.49
	3.0	0.00	1.04	1.04
	6.0	0.00	1.55	1.55
	12.0	0.00	1.74	1.74
	24.0	0.00	2.04	2.04
Benzonitrile	0.5	0.00	0.65	0.65
	1.0	0.00	1.01	1.01
	3.0	0.00	1.89	1.89
	6.0	0.00	1.92	1.92
	12.0	0.00	2.02	2.02

[a,b] See corresponding footnotes in Table 1.

Nitro Compounds and Their Derivatives. Both aliphatic and aromatic nitro compounds examined, such as 1-nitropropane and nitrobenzene showed very low reactivity toward BPB. However, unexpectedly, azobenzene was reduced to aniline, utilizing 2 equiv of hydride without hydrogen evolution at a moderate rate. On the other hand, azoxybenzene showed very low reactivity toward this reagent. The results are summarized in Table 9.

Other Nitrogen Compounds. Cyclohexanone oxime liberated 1 equiv of hydrogen slowly and utilized 1 equiv of hydride for reduction readily, however no further reduction was apparent. This indicates that the reaction afforded the corresponding N-hydroxylamine derivative. Phenyl isocyanate utilized 2 equiv of hydride relatively rapidly and the third slowly, requiring 5 days for complete reduction corresponding to N-methylaniline. Pyridine and 4-picoline N-oxide were also readily attacked by this raeagent. The results are

Table 9. Reaction of 2,2'-Biphenoxyborane with Representative Nitro Compounds and Their Derivatives in Tetrahydrofuran at Room Temperature

Compounds[a]	Time h.	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
1-Nitropropane	3.0	0.00	0.00	0.00
	24.0	0.00	0.28	0.28
	72.0	0.00	0.54	0.54
Nitrobenzene	0.5	0.00	0.00	0.00
	3.0	0.00	0.07	0.07
	24.0	0.00	0.19	0.19
	72.0	0.00	0.49	0.49
Azobenzene[c]	0.5	0.04	0.50	0.46
	1.0	0.04	0.56	0.52
	3.0	0.04	1.16	1.12
	6.0	0.04	1.42	1.38
	12.0	0.04	1.94	1.90
	24.0	0.04	2.02	1.98
Azoxybenzene	1.0	0.01	0.03	0.02
	24.0	0.01	0.13	0.12

[a,b] See corresponding footnotes in Table 1. [c] Orange precipitate formed immediately and then turned to yellow.

Table 10. Reaction of 2,2'-Biphenoxyborane with Other Nitrogen Compounds in Tetrahydrofuran at Room Temperature

Compounds[a]	Time h.	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Cyclohexanone	0.5	0.38	1.23	0.85
oxime[c]	3.0	0.56	1.44	0.88
	6.0	0.63	1.55	0.92
	24.0	0.83	1.84	1.01
	72.0	0.97	2.01	1.04
Phenyl	0.5	0.00	1.36	1.36
isocyanate	1.0	0.00	1.84	1.84
	6.0	0.00	2.19	2.19
	24.0	0.00	2.35	2.35
	72.0	0.00	2.71	2.71
	96.0	0.00	2.94	2.94
Pyridine[c]	0.5	0.00	0.82	0.82
	3.0	0.00	1.43	1.43
	24.0	0.00	1.98	1.98
	72.0	0.00	2.61	2.61
	96.0	0.00	2.73	2.73
4-Picoline	0.5	0.32	1.16	0.84
N-oxide[c]	1.0	0.32	1.77	1.45
	3.0	0.32	2.80	2.48
	6.0	0.32	3.07	2.75
	24.0	0.32	3.34	3.02

[a,b] See corresponding footnotes in Table 1. [c] White precipitate.

summarized in Table 10.

Sulfure Derivatives. The reaction of disulfides and sulfides examined with BPB showed an absolute inertness under these reaction conditions. However, sulfoxides, such as dimethyl sulfoxide, were reduced rapidly to the corresponding sulfides without evolution of hydrogen. Diphenyl sulfone was also slowly reduced. Methanesulfonic acid and *p*-toluenesulfonic acid monohydrate liberated an equivalent of hydrogen rapidly, but no reduction was realized. Finally, cyclohexyl tosylate was also stable under these conditions. The results are summarized in Table 11.

Table 11. Reaction of 2,2'-Biphenoxyborane with Representative Sulfur Derivatives in Tetrahydrofuran at Room Temperature

Compounds[a]	Time h.	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Di-*n*-butyl disulfide	48.0	0.00	0.00	0.00
Diphenyl disulfide	48.0	0.00	0.00	0.00
Penyl *n*-propyl sulfide	48.0	0.00	0.00	0.00
Dimethyl sulfoxide	0.5	0.00	0.80	0.80
	1.0	0.00	0.90	0.90
	3.0	0.00	0.93	0.93
	6.0	0.00	1.00	1.00
Diphenyl sulfone	0.5	0.00	0.20	0.20
	1.0	0.00	0.25	0.25
	24.0	0.00	0.39	0.39
	72.0	0.00	0.59	0.59
	120.0	0.00	0.67	0.67
Methanesulfonic	0.5	1.02	1.02	0.00
acid	1.0	1.02	1.02	0.00
p-Toluenesulfonic	0.5	3.01	3.01	0.00
acid monohydrate	1.0	3.01	3.01	0.00
Cyclohexyl tosylate	1.0	0.00	0.00	0.00

[a,b] See corresponding footnotes in Table 1.

Conclusion

The reducing properties of 2,2'-biphenoxyborane (BPB) in THF are now fully characterized with the standard list of organic compounds containing representative funtional group. The reagent appears to be a mild reducing agent, but stronger than di-*s*-butoxyborane[2] and catecholborane.[3] This systematic study permits not only a ready comparison of rates and stoichiometry of the reaction of BPB to many other reducing systems, but also a useful guide-line to determine which functional groups to be incorporated into the molecules *via* hydroboration of substituted alkenes and alkynes. Consequently, this study enlarges the scope of its applicability as a reducing and hydroborating agent.

Experimental Section

All glassware used in the experiments was predried thoroughly in a drying oven and cooled under a dry nitrogen stream. Hyperdermic syringes and double-ended needles were utilized to transfer solutions. All reactions were performed under a positive pressure of nitrogen in flasks fitted with septum-covered side arms with use of standard techniques for handling air-sensitive materials.[5]

Materials. Most of the organic compounds utilized in

this suty were commercial products of the highest purity. They were further purified when necessary. Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl and stored under dry nitrogen. Dimethyl sulfate, which was used for the preparation of borane in THF, was distilled under reduced pressure after treatment with a small amount of lithium aluminum hydride.

Instruments. GC analyses were carried out on a Hewlett-Packard Model 5790A FID chromatograph equipped with a Hewlett-Packard 3390A intergrator/plotter, using CW 20 M on 100/120 mesh Supelcoport or 15% THEED on 100/120 mesh Supelcoport (0.125 in.×12 ft. columns). All GC yields were determined with use of a suitable internal standard and authentic samples. NMR spectrometer used was a Bruker WP 80 SY for B-11 NMR spectrum.

Preparation of 2,2'-Biphenoxyborane (BPB) in THF. A 1.2 M solution of borane in THF[5] (250 m*l*, 300 mmol), maintained under nitrogen, was placed in a dry 1 *l* round-bottom flask which was connected to a hood vent through a mercury bubbler. The flask was cooled to −10℃ using on ice-salt bath, and a precooled solution of 2,2-biphenol (57.56 g, 309 mmol) in THF (200 m*l*) was added over 1 h to the borane solution with stirring at −10℃. After completion of the addition the reaction mixture was stirred for an additional 2 h at that temperature. The concentration of 2,2'-biphenoxyborane (BPB) solution in THF thus prepared was 0.65 M. The B-11 NMR spectrum of BPB in THF showed a broad doublet centered at δ9.4 ppm (J_{B-H}=121 Hz) relative to $BF_3 \cdot OEt_2$, and it was found to be more than 95% pure. The reagent is stable at least for 6 months at 0℃ when kept under dry nitrogen.

Procedure for Rates and Stoichiometry. The following procedure was used for quantitative studies. The reduction of caproaldehyde is described as an example of the experimental procedure. A dried, 50 m*l* round-bottom flask fitted with rubber syringe cap on an inlet port, a magnetic stirring bar, and a bent adaptor connected to a gas buret through a reflux condenser, was immersed in a water bath at room temperature. The flask was charged with 30.8 m*l* of 0.65 M BPB solution (20.0 mmol) in THF and 4.2 m*l* of THF. Finally, 5 m*l* of a 1.0 M solution of caproaldehyde in THF was injected into the reaction flask. Now the reaction mixture was 0.5 M in the reagent and 0.125 M in caproaldehyde. The hydrogen evolved was collected in the buret and measured (0.02 mmol). After 30 min, a 8 m*l* aliquot of the reaction mixture (1.0 mmol of the compound) was removed with a hypodermic syringe and injected into a hydrolyzing solution of glycerine-water-methanol. The hydrogen evolved amounted to 3.10 mmol as compound to 4.01 mmol for a blank test. The difference 0.91 mmol represented the number of mmoles of hydride used per 1.0 mmol of compounde examined. Aliquots were also removed and hydrolyzed after 1.0 and 3.0 h of reaction time. Both produced 2.99 and 2.99 mmol of hydrogen, indicating 1 equiv of hydride had been used for reduction.

Stereoselective Reductions. The reaction of norcamphor with BPB is representative. In a 25 m*l* round-bottom flask was placed 4.6 m*l* of a 0.65 M solution of the reagent in THF (3.0 mmol). The flask was maintained at 25℃ with a water bath. To this was added 1.5 m*l* of a 1.0 M solution of norcamphor in THF. The reaction was then quenched by addition of 5 m*l* of 2 N NaOH and the aqueous layer saturated with anhydrous potassium carbonate. The GC analysis of the organic layer revealed the presence of 100% norborneol containing 95% (96% at 0℃) of the *endo* isomer. The results are summarized in Table 3.

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