

## Selective Reductions. XVII. Reaction of Thexylborane in Tetrahydrofuran with Selected Organic Compounds Containing Representative Functional Groups. Comparison of the Reducing Characteristics of Diborane and Its Alkyl Derivatives

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The approximate rates and the stoichiometry of the reaction of excess thexylborane with 56 selected organic compounds containing representative functional groups under standard conditions (tetrahydrofuran solution, 0°) were determined in order to establish the utility of the reagent as a selective reducing agent and to compare its characteristics with those of diborane and disiamylborane previously studied. Alcohols evolve hydrogen rapidly, phenol only in moderate speed, and benzenethiol slowly. No hydrogen evolution is observed with *n*-hexylamine and 1-hexanethiol. Aldehydes and ketones are reduced rapidly. Among the ketones, 2-heptanone and acetophenone are reduced rapidly, while the reaction with benzophenone is quite sluggish. *p*-Benzoquinone consumes one hydride rapidly, but further reaction becomes very slow. On the other hand, anthraquinone is reduced very sluggishly. Caproic acid liberates hydrogen immediately and is then reduced at a moderate rate, whereas benzoic acid shows practically no reduction at standard conditions. However, both acids afford good yields of the corresponding aldehydes under special conditions. Acid chlorides and anhydrides react sluggishly with the reagent. Ethyl caproate is reduced very slowly, whereas ethyl benzoate, phenyl acetate, and phthalide undergo practically no reductions under standard conditions. However,  $\gamma$ -butyrolactone is reduced at a moderate rate. 1,2-Butylene oxide and cyclohexene oxide react very slowly, while styrene oxide and 1-methyl-1,2-cyclohexene oxide react at a moderate rate, but not in a simple manner. Amides and nitriles are all reduced slowly, indicating the possibility of a potential aldehyde synthesis. 1-Nitropropane is inert, whereas nitrobenzene is reduced at a moderate rate. Azobenzene reacts very slowly. Azoxybenzene is reduced slowly without hydrogen evolution. Cyclohexanone oxime liberates hydrogen, with only very slow reduction thereafter. Pyridine is inert; however, pyridine *N*-oxide is reduced at a moderate rate, consuming three hydrides per mole. Of the sulfur compounds tested, only dimethyl sulfoxide is reduced to dimethyl sulfide at a moderate rate. Thus, under the standard conditions, disulfide, sulfide, sulfone, sulfonic acids, and cyclohexyl tosylate are all inert to this reagent.

Thexylborane<sup>2,3</sup> (2,3-dimethyl-2-butylborane) has been prepared by the hydroboration of 2,3-dimethyl-2-butene with borane in the ratio of 1:1. And it has been demonstrated that thexylborane is a convenient reagent for the cyclic hydroboration of dienes.<sup>4-6</sup> Recently we carried through systematic studies of the approximate rates and stoichiometry of the reaction of diborane<sup>7</sup> and disiamylborane<sup>8</sup> in tetrahydrofuran solution at 0° with a standard list of compounds representative of the more common functional groups. We have observed many differences in reducing characteristics between these two hydrides. Thexylborane carries a bulky alkyl group and has two hydrogens attached to boron. It exists as a dimer in tetrahydrofuran<sup>3</sup> solution. From these structural considerations, we anticipated that there might result unique reducing characteristics for thexylborane different from those of diborane and disiamylborane.

In order to compare the reducing characteristics of thexylborane with those of diborane and disiamylborane, we adopted the same standard conditions, tetrahydrofuran solutions (1.0 *M* in "hydride," 0.25 *M* in organic compound) at 0°.

### Results and Discussion

#### Procedure for Rate and Stoichiometry Studies.—

Thexylborane was prepared by adding diborane to a cooled solution of tetramethylethylene in tetrahydrofuran in the ratio of one borane to one olefin. The reagent was stable at 0°, showing no significant change in hydride concentration for 14 days.

The procedure adopted for the rate and stoichiometric studies was to add 12.5 mmol of the organic compound to 25 mmol of thexylborane in sufficient tetrahydrofuran to give 50 ml of solution. This made the reaction mixture 0.5 *M* in thexylborane (*i.e.*, 1.00 *M* in hydride) and 0.25 *M* in the compound under examination. Thus hydride was present in excess, with a ratio of hydride to compound of 4:1.

The solution was maintained at 0° and aliquots were removed at appropriate time intervals and analyzed for residual hydride. In this manner it was possible to establish both the rate at which the reduction proceeds and the stoichiometry of the reaction, *i.e.*, the number of hydrides utilized per mole of the compound. When the reaction comes to an effective halt, the sample was analyzed for tetramethylethylene in order to make certain that no displacement had taken place. All reductions were carried out under nitrogen atmosphere.

**Alcohols, Phenols, Amines, and Thiols.**—All the alcohols tested liberated hydrogen rapidly and quantitatively. However, phenol liberated hydrogen only at a moderate rate, and *n*-hexylamine was inert. The aliphatic thiol, 1-hexanethiol, was inert to this reagent, whereas the aromatic thiol, benzenethiol, liberated hydrogen slowly, the evolution of hydrogen being almost complete in 24 hr. The results are summarized in Table I.

**Aldehydes and Ketones.**—All of the aldehydes and ketones consumed one hydride, indicating reduction to the corresponding alcohols. The aldehydes were re-

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(2) H. C. Brown and A. W. Moerikofer, *J. Amer. Chem. Soc.*, **84**, 1478 (1962).

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(4) H. C. Brown and C. D. Pfaffenberger, *J. Amer. Chem. Soc.*, **89**, 5475 (1967).

(5) H. C. Brown and E. Negishi, *ibid.*, **89**, 5477 (1967).

(6) H. C. Brown and E. Negishi, *Chem. Commun.*, 594 (1968).

(7) H. C. Brown, P. Heim, and N. M. Yoon, *J. Amer. Chem. Soc.*, **92**, 1637 (1970).

(8) H. C. Brown, D. B. Bigley, S. K. Arora, and N. M. Yoon, *ibid.*, **92**, 7161 (1970). Disiamylborane is bis(3-methyl-2-butyl)borane, prepared in the reaction of 2 mol of 2-methyl-2-butene with 1 mol of borane in THF.

TABLE I  
REACTION OF THEXYLBORANE WITH REPRESENTATIVE  
"ACTIVE HYDROGEN" COMPOUNDS IN TETRAHYDROFURAN AT 0°

Compound <sup>a</sup>	Time, hr	Hydrogen evolved <sup>b</sup>	Hydride used <sup>b</sup>	Hydride used for reduction <sup>b</sup>
1-Hexanol	0.25	0.99	0.99	0.00
	0.5	1.00	1.00	0.00
Benzyl alcohol	0.25	0.98	0.98	0.00
	0.5	1.00	1.00	0.00
3-Hexanol	0.25	0.97	0.97	0.00
	0.5	1.00	1.00	0.00
3-Ethyl-3-pentanol	0.25	0.92	0.92	0.00
	0.5	0.98	0.98	0.00
	1.00	1.00	1.00	0.00
Phenol	0.25	0.30	0.30	0.00
	0.5	0.44	0.44	0.00
	1.0	0.63	0.63	0.00
	3.0	0.94	0.94	0.00
	6.0	1.00	1.00	0.00
<i>n</i> -Hexylamine	14.0	0.00	0.00	0.00
1-Hexanethiol	10.0	0.00	0.00	0.00
Benzenethiol	1.0	0.13	0.13	0.00
	3.0	0.38	0.38	0.00
	6.0	0.65	0.65	0.00
	12.0	0.82	0.82	0.00
	24.0	0.92	0.92	0.00

<sup>a</sup> 12.5 mmol of a compound to 25 mmol of thexyborane (50 mmol of hydride) in 50 ml of solution; 0.25 *M* in compound and 1.00 *M* in hydride. <sup>b</sup> Millimoles/millimole of compound.

duced very rapidly, with the reaction being over in 15 min. Benzophenone was reduced at a much slower rate than the corresponding rates exhibited by 2-heptanone and acetophenone.<sup>9</sup> A similar trend is observed with diborane and disiamylborane. Cinnamaldehyde consumed one hydride rapidly, while the rate of uptake of a second hydride was moderate. An experiment, carried out in the ratio of 1 equivalent of hydride per mole of compound, established that the aldehyde group was attached faster than the double bond. The stoichiometry also established that almost no elimination<sup>10</sup> occurred following hydroboration. The stereochemistry of the reduction of norcamphor is very similar to that observed in the reduction with disiamylborane,<sup>8</sup> showing 91% *endo*- and 9% *exo*-norbornanol. The results are summarized in Table II.

**Quinones.**—*p*-Benzoquinone consumed rapidly approximately one hydride per mole of compound, of which 43% was utilized for hydrogen evolution and the remaining 57% for reduction. Afterward the reaction became very sluggish, showing a total of 1.12 mmol of hydride consumption after 12 hr, a value which did not increase over 24 hr. The reaction of the reagent with anthraquinone was very sluggish. These results are similar to the reactions observed with disiamylborane, and further study is required before any sound interpretation can be given to the reaction involving *p*-benzoquinone. The results are summarized in Table III.

**Carboxylic Acids and Derivatives.**—Both caproic acid and benzoic acid liberated hydrogen rapidly and quantitatively. The reaction with caproic acid then proceeded at a moderate rate to achieve reduction, whereas

(9) In contrast to this reagent, lithium tetrakis(*N*-dihydropyridyl)-aluminate is reported to reduce benzophenone remarkably rapidly (95% in 5 min) compared with the corresponding reduction of acetophenone (32% in 12 hr). P. T. Lansbury and J. O. Peterson, *J. Amer. Chem. Soc.*, **85**, 2236 (1963).

(10) K. Kratze and P. Claus, *Monatsh. Chem.*, **94**, 1140 (1963).

TABLE II  
REACTION OF THEXYLBORANE WITH REPRESENTATIVE  
ALDEHYDES AND KETONES IN TETRAHYDROFURAN AT 0°

Compound <sup>a</sup>	Time, hr	Hydrogen evolved <sup>b</sup>	Hydride used <sup>b</sup>	Hydride used for reduction <sup>b</sup>
Caproaldehyde	0.25	0.00	0.99	0.99
	0.5	0.00	0.99	0.99
Benzaldehyde	0.25	0.00	1.05	1.05
	0.5	0.00	1.05	1.05
2-Heptanone	0.25	0.00	0.70	0.70
	0.5	0.00	0.83	0.83
	1.0	0.00	0.93	0.93
	3.0	0.00	0.99	0.99
	6.0	0.00	1.05	1.05
Norcamphor	0.5	0.03	0.97	0.94
	1.0	0.03	1.01	0.98
	3.0	0.03		
Acetophenone	0.25	0.00	0.58	0.58
	0.5	0.00	0.77	0.77
	1.0	0.00	0.90	0.90
Benzophenone	3.0	0.00	0.97	0.97
	6.0	0.00	0.97	0.97
	1.0	0.00	0.13	0.13
	3.0	0.00	0.26	0.26
	6.0	0.00	0.45	0.45
	48.0	0.00	0.96	0.96
Cinnamaldehyde	0.25	0.00	1.24	1.24
	0.5	0.00	1.36	1.36
	1.0	0.00	1.50	1.50
	3.0	0.00	1.94	1.94
	6.0	0.00	2.00	2.00

<sup>a, b</sup> See corresponding footnotes in Table I.

TABLE III  
REACTION OF THEXYLBORANE WITH REPRESENTATIVE  
QUINONES IN TETRAHYDROFURAN AT 0°

Compound <sup>a</sup>	Time, hr	Hydrogen evolved <sup>b</sup>	Hydride used <sup>b</sup>	Hydride used for reduction <sup>b</sup>
<i>p</i> -Benzoquinone	0.5	0.33	0.90	0.57
	1.0	0.36	0.94	0.58
	3.0	0.43	1.00	0.57
	6.0	0.46	1.09	0.66
	12.0	0.46	1.12	0.66
	24.0	0.46	1.13	0.67
Anthraquinone	3.0	0.00	0.16	0.16
	24.0	0.00	0.23	0.23
	48.0	0.00	0.28	0.28
	72.0	0.00	0.32	0.32

<sup>a, b</sup> See corresponding footnotes in Table I.

practically no reduction of benzoic acid was observed under the same conditions. However, using 2.5 mol of thexyborane per mole of acid, addition of acid at -20°, followed by refluxing of the THF solution, it was possible to obtain a 98% yield of caproaldehyde from caproic acid and a 82% yield of benzaldehyde from benzoic acid, both after extended refluxing (36 hr). (The yields were determined by analysis for aldehyde with 2,4-dinitrophenylhydrazine.) This simple reduction of carboxylic acids to aldehydes is a promising development, and we plan to undertake research to improve the procedure and to examine the scope of the reaction.

Acetic anhydride consumed two hydrides very rapidly, with only a slow reduction thereafter. However, no aldehyde could be detected. The two cyclic anhydrides and the two acid chlorides reacted only very sluggishly. No aldehydes could be detected in the acid

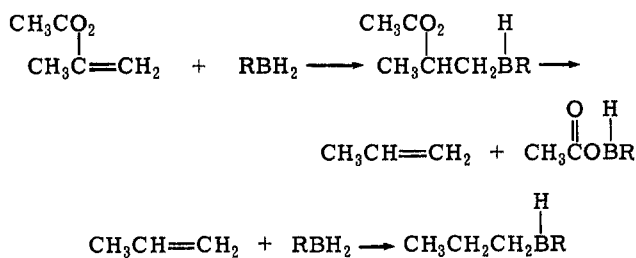
chloride reactions. The results are summarized in Table IV.

TABLE IV  
REACTION OF THEXYLBORANE WITH REPRESENTATIVE  
CARBOXYLIC ACIDS AND ACYL DERIVATIVES IN  
TETRAHYDROFURAN AT 0°

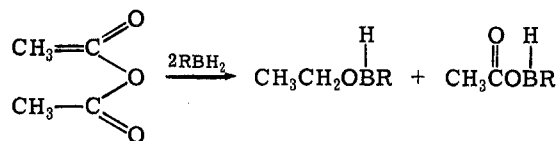
Compound <sup>a</sup>	Time, hr	Hydrogen evolved <sup>b</sup>	Hydride used <sup>b</sup>	Hydride used for reduction <sup>b</sup>
Caproic acid	0.5	1.00	1.27	0.27
	1.0	1.00	1.55	0.55
	3.0	1.00	1.85	0.85
	6.0	1.00	2.12	1.12
	12.0	1.00	2.40	1.40
Benzoic acid	0.5	1.00	1.00	0.00
	6.0	1.00	1.08	0.08
	48.0	1.00	1.08	0.08
Acetic anhydride	0.5	0.00	2.00	2.00
	6.0	0.00	2.12	2.12
	24.0	0.00	2.50	2.50
Succinic anhydride	0.5	0.00	0.10	0.10
	1.0	0.00	0.12	0.12
	3.0	0.00	0.21	0.21
	6.0	0.00	0.25	0.25
	12.0	0.00	0.32	0.32
Phthalic anhydride	0.5	0.00	0.12	0.12
	1.0	0.00	0.16	0.16
	6.0	0.00	0.35	0.35
	12.0	0.00	0.41	0.41
	24.0	0.00	0.46	0.46
Caproyl chloride	12.0	0.00	0.05	0.05
	24.0	0.00	0.10	0.10
	48.0	0.00	0.20	0.20
Benzoyl chloride	12.0	0.00	0.20	0.20
	24.0	0.00	0.35	0.35
	48.0	0.00	0.55	0.55

<sup>a, b</sup> See corresponding footnotes in Table I.

**Esters and Lactones.**—The reduction of esters by thexylborane was sluggish.  $\gamma$ -Butyrolactone underwent a relatively slow reduction. However, no aldehyde could be detected when 1 mol of the lactone was treated with 0.5 mol of thexylborane for 24 hr at 0°. The reduction of phthalide was very slow at 0°. Isopropenyl acetate utilized two hydrides rapidly. However, following the initial reaction, reduction proceeded only slowly. Presumably the reaction involves an initial hydroboration, followed by a rapid elimination and hydroboration of the propylene produced in the elimination step, as shown in the following equations (R = thexyl). The reaction intermediate, thexylacetox-



borane, shown in the above possible mechanism, may also be present in the acetic anhydride reduction. The



reaction is believed to follow the course indicated. The very slow reaction after the uptake of two hydrides in both cases can be correlated with a unique characteristic of this species. It appears that the thexylacetoxyborane moiety undergoes reduction intermolecularly rather than intramolecularly in the reaction of carboxylic acids with thexylborane, resulting in the formation of the aldehyde in high yield. The results are summarized in Table V.

TABLE V  
REACTION OF THEXYLBORANE WITH REPRESENTATIVE  
ESTERS AND LACTONES IN TETRAHYDROFURAN AT 0°

Compound <sup>a</sup>	Time, hr	Hydrogen evolved <sup>b</sup>	Hydride used <sup>b</sup>	Hydride used for reduction <sup>b</sup>
Ethyl caproate	1.0	0.00	0.23	0.23
	3.0	0.00	0.21	0.21
	6.0	0.00	0.25	0.25
	12.0	0.00	0.31	0.31
	24.0	0.00	0.47	0.47
	48.0	0.00	0.65	0.65
Ethyl benzoate	1.0	0.00	0.04	0.04
	3.0	0.00	0.07	0.07
	6.0	0.00	0.12	0.12
	12.0	0.00	0.23	0.23
	24.0	0.00	0.30	0.30
	48.0	0.00	0.34	0.34
Phenyl acetate	1.0	0.00	0.15	0.15
	3.0	0.00	0.20	0.20
	6.0	0.00	0.20	0.20
	12.0	0.00	0.21	0.21
	24.0	0.00	0.22	0.22
	48.0	0.00	0.25	0.25
$\gamma$ -Butyrolactone	1.0	0.00	0.12	0.12
	3.0	0.00	0.32	0.32
	6.0	0.00	0.60	0.60
	12.0	0.00	1.04	1.04
	24.0	0.00	1.50	1.50
Phthalide	1.0	0.00	0.01	0.01
	3.0	0.00	0.03	0.03
	6.0	0.00	0.06	0.06
	12.0	0.00	0.14	0.14
	24.0	0.00	0.25	0.25
Isopropenyl acetate	1.0	0.00	2.02	2.02
	3.0	0.00	2.08	2.08
	6.0	0.00	2.10	2.10
	12.0	0.00	2.20	2.20
	24.0	0.00	2.24	2.24

<sup>a, b</sup> See corresponding footnotes in Table I.

**Epoxides.**—The reactions of the reagent with simple epoxides, 1,2-butylene oxide and cyclohexene oxide, were very sluggish. However, styrene oxide consumed more hydride than expected from the stoichiometric requirement for reduction to the corresponding alcohols. (Reduction to 1- and 2-phenylethanol requires one hydride.) 1-Methyl-1,2-cyclohexene oxide consumed two hydrides, one involving hydrogen evolution and the other involving reduction. These results are very similar to those realized in the corresponding reactions in-

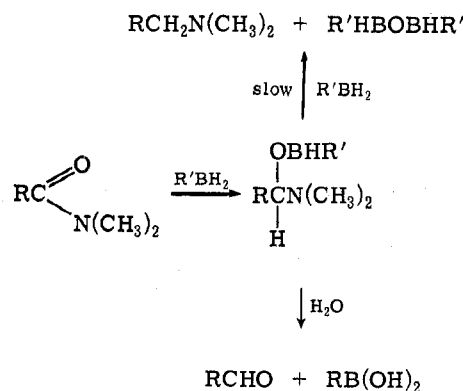
TABLE VI  
REACTION OF HEXYLBORANE WITH REPRESENTATIVE  
EPOXIDES IN TETRAHYDROFURAN AT 0°

Compound <sup>a</sup>	Time, hr	Hydrogen evolved <sup>b</sup>	Hydride used <sup>b</sup>	Hydride used for reduction <sup>b</sup>
1,2-Butylene oxide	1.0	0.00	0.03	0.03
	3.0	0.00	0.08	0.08
	6.0	0.00	0.17	0.17
	12.0	0.00	0.25	0.25
	24.0	0.00	0.37	0.37
Styrene oxide	1.0	0.00	0.16	0.16
	3.0	0.00	0.31	0.31
	6.0	0.00	1.19	1.19
	24.0	0.00	1.68	1.68
	Cyclohexene oxide	1.0	0.00	0.03
6.0		0.00	0.12	0.12
12.0		0.00	0.21	0.21
24.0		0.00	0.31	0.31
48.0		0.00	0.41	0.41
1-Methyl-1,2-cyclohexene oxide	1.0	0.49	0.76	0.27
	3.0	0.84	1.55	0.71
	6.0	0.97	1.34	0.97
	12.0	0.97	2.01	1.04
	24.0	0.97	2.02	1.05

<sup>a, b</sup> See corresponding footnotes in Table I.

volving diborane and disiamylborane. The results are summarized in Table VI.

**Amides and Nitriles.**—Primary amides underwent reduction slowly. Caproamide did not evolve hydrogen, whereas benzamide revealed partial hydrogen evolution (0.9 mol per mole of compound). This difference in behavior is presumably due to the difference in acidity of the amide hydrogen atoms. Tertiary amides were reduced slowly. Even though the rate data do not reveal any indication of a halt at the aldehyde stage (one hydride uptake), we were able to establish the preparation of some aldehydes under these conditions. Thus, a 44% yield of benzaldehyde (2,4-DNP analysis) was realized after 2 hr (0.95 hydride consumed) or after 8 hr (1.5 hydride consumed) in the reaction of hexylborane with *N,N*-dimethylbenzamide. Similarly, a 55% yield of crotonaldehyde was indicated in 4 hr (1.04 hydride consumed) and a 65% yield in 8 hr (1.3 hydride consumed) in the reaction of the reagent with *N,N*-dimethylcaproamide. These data suggest that the tertiary amides are much more easily attacked than the intermediate corresponding to aldehyde.



Since we had previously observed that disiamylborane reacts with tertiary amides even more cleanly to give aldehydes, we did not study this feature further.

Finally, nitriles were reduced very slowly, indicating relatively stable intermediates which can be hydrolyzed to aldehydes. Thus, using 1 mol of hexylborane per mole of nitrile at room temperature, we observed a 40% yield of benzaldehyde after 3 days and a 60% yield of caproaldehyde after 12 hr, as measured with 2,4-DNP. The results are summarized in Table VII.

TABLE VII  
REACTION OF HEXYLBORANE WITH REPRESENTATIVE  
AMIDES AND NITRILES IN TETRAHYDROFURAN AT 0°

Compound <sup>a</sup>	Time, hr	Hydrogen evolved <sup>b</sup>	Hydride used <sup>b</sup>	Hydride used for reduction <sup>b</sup>	
Caproamide <sup>c</sup>	0.5	0.00	0.25	0.25	
	1.0	0.00	0.34	0.34	
	6.0	0.00	0.75	0.75	
	12.0	0.00	1.35	1.35	
	24.0	0.00	1.62	1.62	
	Benzamide <sup>c</sup>	1.0	0.11	0.40	0.30
		3.0	0.30	1.02	0.72
		6.0	0.50	1.57	1.07
12.0		0.73	2.11	1.38	
24.0		0.90	2.58	1.68	
<i>N,N</i> -Dimethyl <sup>d</sup> caproamide		0.5	0.00	0.48	0.48
		1.0	0.00	0.60	0.60
		3.0	0.00	0.93	0.93
	6.0	0.00	1.17	1.17	
	12.0	0.00	1.40	1.40	
	24.0	0.00	1.60	1.60	
	48.0	0.00	1.80	1.80	
	72.0	0.00	1.92	1.92	
<i>N,N</i> -Dimethyl <sup>d</sup> benzamide	0.5	0.00	0.48	0.48	
	1.0	0.00	0.80	0.80	
	3.0	0.00	1.15	1.15	
	6.0	0.00	1.40	1.40	
	12.0	0.00	1.72	1.72	
	24.0	0.00	1.95	1.95	
	48.0	0.00	1.99	1.99	
	Capronitrile <sup>d</sup>	1.0	0.00	0.20	0.20
3.0		0.00	0.25	0.25	
6.0		0.00	0.28	0.28	
12.0		0.00	0.38	0.38	
Benzonitrile <sup>d</sup>	24.0	0.00	0.42	0.42	
	1.0	0.00	0.15	0.15	
	3.0	0.00	0.18	0.18	
	6.0	0.00	0.23	0.23	
	12.0	0.00	0.25	0.25	
	24.0	0.00	0.32	0.32	

<sup>a, b</sup> See corresponding footnotes in Table I. <sup>c</sup> Compound was added as a solid. <sup>d</sup> Hydrolyzed with a mixture of concentrated hydrochloric acid and tetrahydrofuran (2:1).

**Nitro Compounds and Their Derivatives.**—1-Nitropropane was inert to this reagent. However, nitrobenzene was reduced at a moderate rate without hydrogen evolution. Azobenzene was reduced only sluggishly, whereas azoxybenzene underwent slow reduction without hydrogen evolution. The results are summarized in Table VIII.

**Other Nitrogen Compounds.**—Cyclohexanone oxime liberated 0.44 mmol of hydrogen rapidly, but uptake of hydride for reduction was very slow. With diborane also the hydrogen evolution was only partial, but reduction then proceeded at a moderate rate. On the other hand, with disiamylborane, cyclohexanone oxime liberated hydrogen quantitatively, but no reduction was observed. Phenyl isocyanate was slowly reduced,

TABLE VIII  
REACTION OF THEXYLBORANE WITH NITRO COMPOUNDS  
AND THEIR DERIVATIVES IN TETRAHYDROFURAN AT 0°

Compound <sup>a</sup>	Time, hr	Hydrogen evolved <sup>b</sup>	Hydride used <sup>b</sup>	Hydride used for reduction <sup>b</sup>
1-Nitropropane	40.0	0.00	0.00	0.00
Nitrobenzene <sup>c</sup>	0.5	0.00	0.14	0.14
	1.0	0.00	0.23	0.23
	3.0	0.00	0.38	0.38
	6.0	0.00	0.54	0.54
	12.0	0.00	0.92	0.92
	24.0	0.00	1.45	1.45
Azobenzene	48.0	0.00	1.95	1.95
	0.5	0.00	0.01	0.01
	6.0	0.00	0.04	0.04
	12.0	0.00	0.12	0.12
	24.0	0.00	0.18	0.18
	48.0	0.00	0.25	0.25
Azoxybenzene <sup>c</sup>	3.0	0.00	0.30	0.30
	6.0	0.00	0.40	0.40
	24.0	0.00	0.89	0.89
	48.0	0.00	1.54	1.54

<sup>a, b</sup> See corresponding footnotes in Table I. <sup>c</sup> Hydrolyzed with a mixture of concentrated hydrochloric acid and tetrahydrofuran (2:1).

consuming two hydrides in 48 hr, with the consumption of the third hydride very sluggish. Pyridine did not react with this reagent. However, pyridine-*N*-oxide consumed three hydrides in 24 hr. This behavior is similar to that observed with diborane, but the reaction proceeds at a faster rate. The results are summarized in Table IX.

TABLE IX  
REACTION OF THEXYLBORANE WITH OTHER NITROGEN  
COMPOUNDS IN TETRAHYDROFURAN AT 0°

Compound <sup>a</sup>	Time, hr	Hydrogen evolved <sup>b</sup>	Hydride used <sup>b</sup>	Hydride used for reduction <sup>b</sup>
Cyclohexanone <sup>c</sup> oxime	0.5	0.44		
	15.0	0.44	0.62	0.18
	20.0	0.44	0.75	0.31
	120.0	0.44	1.29	0.85
Phenyl isocyanate <sup>c</sup>	144.0	0.44	1.42	0.98
	0.5	0.00	1.31	1.31
	1.0	0.00	1.35	1.35
	6.0	0.00	1.44	1.44
	48.0	0.00	2.03	2.03
Pyridine <sup>c</sup>	168.0	0.00	2.47	2.47
	1.0	0.00	0.00	0.00
	3.0	0.00	0.00	0.00
	6.0	0.00	0.04	0.04
Pyridine <i>N</i> -oxide <sup>c</sup>	0.5	0.00	1.28	1.28
	1.0	0.00	1.78	1.78
	3.0	0.00	2.65	2.65
	6.0	0.00	2.80	2.80
	24.0	0.00	2.90	2.90

<sup>a, b</sup> See corresponding footnotes in Table I. <sup>c</sup> Hydrolyzed with a mixture of concentrated hydrochloric acid and tetrahydrofuran (2:1).

**Sulfur Compounds.**—Of the sulfur compounds tested only dimethyl sulfoxide underwent reduction, forming dimethyl sulfide. Both the sulfonic acids liberated hydrogen quantitatively, but no reduction occurred. Disulfides, sulfide, sulfone, and cyclohexyl tosylate were all inert to the reagent. These results are very similar to those realized with diborane and disiamyl-

borane previously explored. The results are summarized in Table X.

TABLE X  
REACTION OF THEXYLBORANE WITH REPRESENTATIVE  
SULFUR DERIVATIVES IN TETRAHYDROFURAN AT 0°

Compound <sup>a</sup>	Time, hr	Hydrogen evolved <sup>b</sup>	Hydride used <sup>b</sup>	Hydride used for reduction <sup>b</sup>
Di- <i>n</i> -butyl disulfide	20.0	0.00	0.00	0.00
Diphenyl disulfide	20.0	0.00	0.00	0.00
Phenyl <i>n</i> -propyl sulfide <sup>c</sup>	24.0	0.00	0.00	0.00
Dimethyl sulfoxide	0.25	0.23	0.62	0.39
	0.5	0.35	0.95	0.60
	1.0	0.55	1.30	0.75
	3.0	0.93	1.90	0.97
	6.0	1.00	2.00	1.00
	12.0	1.00	2.00	1.00
Diphenyl sulfone	40.0	0.00	0.00	0.00
Methanesulfonic acid	0.25	1.00	1.00	0.00
	0.5	1.00	1.00	0.00
	3.0	1.00	1.00	0.00
	3.0	1.00	1.00	0.00
<i>p</i> -Toluenesulfonic acid monohydrate	0.25	2.96	2.96	0.00
	0.5	3.00	3.00	0.00
	3.0	3.00	3.00	0.00
Cyclohexyl tosylate <sup>c</sup>	24.0	0.00	0.00	0.00

<sup>a, b</sup> See corresponding footnotes in Table I. <sup>c</sup> Hydrolyzed with a mixture of concentrated hydrochloric acid and tetrahydrofuran (2:1).

**Comparison of the Reducing Characteristics of Diborane, Thexylborane, and Disiamylborane.**—Diborane was first applied for the reduction of organic compounds<sup>11</sup> some 30 years ago. A valuable feature proved to be its characteristics as an electrophilic or acid-type reducing agent,<sup>12</sup> in contrast to the nucleophilic reducing characteristics of sodium borohydride and lithium aluminum hydride.

The introduction of bulky alkyl groups into diborane produces borane-reducing agents which retain the acidic characteristics of the parent system, but exhibit numerous differences in reducing behavior, especially demonstrating a far greater selectivity.

In the hope of systematizing our knowledge of the reducing characteristics of the various hydridic reagents now available and ultimately arriving at simple generalizations governing their behavior, we initiated some time ago a program to examine the rate and stoichiometry of the reaction of these hydrides with a representative list of derivatives. We have previously achieved a comparison of the four aluminohydride reagents.<sup>13</sup> It appears appropriate for the objectives of this program to analyze our findings on diborane, thexylborane, and disiamylborane and point out the relative advantages of each of the reagents for specific reductions.<sup>14</sup>

**I. Active Hydrogen Compounds.**—Changes in the nature of the organic grouping attached to the hydroxyl

(11) H. C. Brown, H. I. Schlesinger, and A. B. Burg, *J. Amer. Chem. Soc.*, **61**, 673 (1939).

(12) H. C. Brown and B. C. Subba Rao, *ibid.*, **82**, 681 (1960).

(13) H. C. Brown and N. M. Yoon, *ibid.*, **88**, 1464 (1966).

(14) Unless specific mention of other conditions is made, it should be understood that these conclusions reached are based on comparative data for tetrahydrofuran solution at 0°. We shall attempt to generalize on the basis of the data obtained with the standard list, as well as such other data that may be available in the literature. While the conclusion should be valid for the average derivatives, it should be recognized that the rich variations possible in organic chemistry will doubtless result in the need to apply the generalizations cautiously to new systems which are quite different chemically from the model compounds.

group of alcohols result in major changes in the rate of hydrogen evolution observed with diborane ( $\text{BH}_3$ ) but not with thexylborane ( $\text{ThBH}_2$ ). However, disiamylborane ( $\text{Si}_2\text{BH}$ ) liberates 1 mol of hydrogen instantly with primary and secondary alcohols but fails to react with 3-ethyl-3-pentanol, a hindered tertiary alcohol. Phenol evolves hydrogen with  $\text{Si}_2\text{BH}$  rapidly. However,  $\text{ThBH}_2$  and  $\text{BH}_3$  require 6 and 12 hr, respectively, for complete hydrogen evolution. *n*-Hexylamine evolves hydrogen only very slowly with  $\text{BH}_3$ , but fails to react with  $\text{ThBH}_2$  and  $\text{Si}_2\text{BH}$ .

Thiols exhibit major differences between these reagents. There is also a considerable difference between the reactivity of an aliphatic and aromatic thiol. Thus,  $\text{BH}_3$  evolves one hydrogen in 1 hr with benzenethiol, but requires 12 hr with 1-hexanethiol, whereas  $\text{ThBH}_2$  gives 0.92 hydrogen in 24 hr with benzenethiol, but is inert to 1-hexanethiol. Finally  $\text{Si}_2\text{BH}$  does not evolve hydrogen with either of these thiols. These results indicate that hydrogen evolution in the reaction of these boranes with active hydrogen compounds is dependent upon two factors: the ease of coordination (between boron atom of the hydride and the electron donor atom to which the active hydrogen atom is attached in the substrate) and the acidity of the active hydrogen.

An alcohol such as 3-ethyl-3-pentanol requires prior coordination between the oxygen and boron atoms in order to react with liberation of hydrogen. Consequently, no reaction occurs with  $\text{Si}_2\text{BH}$ . On the other hand, an acidic molecule such as phenol does not require prior coordination. Thus,  $\text{Si}_2\text{BH}$  reacts rapidly with phenol to liberate hydrogen.

**II. Aldehydes and Ketones.**—All of the aldehydes and ketones included in the list, except benzophenone, are reduced rapidly by all three reagents. Benzophenone is reduced only at a moderate rate. The stereochemistry of reduction of norcamphor is quite interesting. Thus,  $\text{BH}_3$  gives good stereospecificity (98% *endo*-norbornanol and 2% *exo*-norbornanol), whereas both  $\text{ThBH}_2$  and  $\text{Si}_2\text{BH}$  achieve less stereospecificity (91% *endo* and 9% *exo*).

The reduction of the aldehyde group in cinnamaldehyde with excess  $\text{BH}_3$  is accompanied by hydroboration of the double bond and some elimination. However, the more bulky alkyl-substituted boranes do not exhibit such elimination, providing a route to good yields of 1,3-diols from  $\alpha,\beta$ -unsaturated aldehydes.<sup>15</sup>

**III. Quinones.**—The reduction of *p*-benzoquinone with  $\text{BH}_3$  gives hydroquinone exclusively, consuming two hydrides per mole, one for hydrogen evolution and the other for reduction. However, both the  $\text{ThBH}_2$  and  $\text{Si}_2\text{BH}$  consume approximately one hydride rapidly, but subsequent utilization of hydride is sluggish. These reactions require further study. The reduction of anthraquinone is very slow with all three reagents.

**IV. Carboxylic Acids and Acyl Derivatives.**—Carboxylic acids are reduced with  $\text{BH}_3$  with remarkable speed. With  $\text{ThBH}_2$  and  $\text{Si}_2\text{BH}$  hydrogen evolution is rapid, but reduction is very slow. Thus the carboxylic acid group can be reduced preferentially with  $\text{BH}_3$  in the presence of many other functional groups, such as

ester, nitro, disulfide, and tosylate. On the other hand, with  $\text{Si}_2\text{BH}$  it is possible to reduce many functional groups such as carbonyl, *tert*-amide (to aldehydes), and azoxy groups without reducing the carboxylic acid group. The formation of aldehydes in excellent yields from reaction in refluxing THF of carboxylic acids with  $\text{ThBH}_2$ , observed in the present study, should find major application in organic synthesis. The reduction of cyclic anhydrides and acyl chlorides is very slow with  $\text{BH}_3$ , still slower with  $\text{ThBH}_2$ , and essentially absent with  $\text{Si}_2\text{BH}$ .

**V. Esters and Lactones.**—Toward the esters the order of reactivity follows the order  $\text{BH}_3 > \text{ThBH}_2 > \text{Si}_2\text{BH}$ . Lactones are readily reduced to hydroxy-aldehydes with  $\text{Si}_2\text{BH}$ .<sup>8</sup> Aromatic esters and lactones are more inert than aliphatic esters and lactones toward all these hydrides.

These results are in marked contrast with the rapid reduction of these functional groups with lithium aluminum hydride and related aluminohydrides.<sup>13</sup>

**VI. Epoxides.**—Simple epoxides such as 1,2-butylene oxide and cyclohexene oxide react very slowly with each of these three hydrides. Therefore, many other more reactive functional groups should be reduced selectively by these reagents without significant attack of the epoxide ring. However, these epoxide rings can be reduced rapidly by diborane by using sodium borohydride in catalytic amounts in  $\text{BH}_3$  solution. When one of the carbon atoms of epoxide ring is either benzylic or tertiary, the addition of borohydride is recommended for simple reductions leading to the corresponding alcohols, preferentially in the anti-Markovnikov fashion.<sup>16</sup> Styrene oxide gives almost exclusively  $\alpha$ -phenylethanol with lithium aluminum hydride. However, we could obtain 2-phenylethanol almost exclusively by the addition of boron trifluoride to the  $\text{BH}_3$  solution.<sup>17</sup>

**VII. Amides and Nitriles.**— $\text{BH}_3$  reduces primary and tertiary amides to the corresponding amines in excellent yield.<sup>18</sup>  $\text{Si}_2\text{BH}$  does not reduce primary amides. However, *tert*-amides are reduced to the corresponding aldehydes with this reagent. Since these hydrides can tolerate many other groups, such as halogen, nitro, and disulfide, the application of this reagent should have advantages in some instances over aluminum hydride<sup>19</sup> for the selective conversion of tertiary amides to amines and over lithium diethoxyaluminumhydride<sup>20</sup> for the conversion of such amides to aldehydes.

**VIII. Nitro Compounds and Derivatives.**—1-Nitropropane is not reduced by any of the three reagents under the standard conditions. However,  $\text{ThBH}_2$  and  $\text{Si}_2\text{BH}$  react slowly with nitrobenzene, whereas  $\text{BH}_3$  is inert. Therefore,  $\text{BH}_3$  is the reagent of choice for the selective reduction of other groups in the presence of an aromatic nitro substituent. Azobenzene is reduced to aniline with  $\text{BH}_3$ , but azoxybenzene is not reduced. This behavior contrasts with that of  $\text{Si}_2\text{BH}$ , which

(15) H. C. Brown and R. M. Gallivan, *J. Amer. Chem. Soc.*, **90**, 2906 (1968).

(16) The reaction of 1-methylcycloalkene oxides with diborane results in 1-methylol-2-cycloalkanols (after oxidation of the intermediate). However, in the presence of borohydrides, *cis*-2-methylcycloalkanols are the major products, with a minor amount of some 1-methylcycloalkanol formed. H. C. Brown and N. M. Yoon, *J. Amer. Chem. Soc.*, **90**, 2656 (1968).

(17) H. C. Brown and N. M. Yoon, *Chem. Commun.*, 1549 (1968).

(18) H. C. Brown and P. Heim, *J. Amer. Chem. Soc.*, **86**, 3566 (1964).

(19) N. M. Yoon and H. C. Brown, *ibid.*, **90**, 2927 (1968).

(20) H. C. Brown and A. Tsukamoto, *ibid.*, **86**, 1089 (1964).

TABLE XI  
REACTION OF REPRESENTATIVE ORGANIC DERIVATIVES WITH EXCESS DIBORANE, THEXYLBORANE, AND  
DISIAMYLBORANE IN TETRAHYDROFURAN AT 0°

Compound <sup>a</sup>	Diborane <sup>b</sup>			Thexylborane <sup>c</sup>			Disiamylborane <sup>d</sup>		
	Hydride used— Evoln	Redn	Time, hr	Hydride used— Evoln	Redn	Time, hr	Hydride used— Evoln	Redn	Time, hr
I. Active Hydrogen									
1-Hexanol	1.00	0	0.5	1.00	0	0.5	1.07	0	0.5
Benzyl alcohol	0.98	0	0.5	1.00	0	0.5	0.99	0.04	0.5
3-Hexanol	0.98	0	1.0	1.00	0	0.5	0.99	0.04	0.5
3-Ethyl-3-pentanol	1.00	0	12.0	0.98	0	0.5	0.00	0	1.0
Phenol	1.00	0	12.0	1.00	0	6.0	1.05	0.01	0.5
<i>n</i> -Hexylamine	0.13	0	20.0	0.00	0	14.0	0.00	0	1.0
1-Hexanethiol	1.00	0	12.0	0.00	0	10.0	0.00	0	1.0
Benzenethiol	1.00	0	1.0	0.92	0	24.0	0.00	0	1.0
II. Aldehydes and Ketones									
Caproaldehyde	0	1.00	2.0	0	0.99	0.5	0	0.97	3.0
Benzaldehyde	0	1.00	0.5	0	1.05	0.5	0	1.00	3.0
2-Heptanone	0	1.00	1.0	0	1.05	6.0	0	1.00	3.0
Norcamphor	0.03	0.96	1.0	0.03	0.99	3.0	0.04	0.97	1.0
Acetophenone	0	1.00	2.0	0	0.97	3.0	0	1.03	6.0
Benzophenone	0	1.00	24.0	0	0.96	48.0	0	0.98	24.0
Cinnamaldehyde	0	2.10	1.0	0	2.00	6.0	0	1.98	24.0
III. Quinones									
<i>p</i> -Benzoquinone	0.90	1.05	6.0	0.46	0.66	12.0	0.71	0.27	3.0
Anthraquinone	0	0.95	1680	0	0.32	72.0	0.11	0.34	24.0
IV. Carboxylic Acids and Acyl Derivatives									
Caproic acid	1.00	1.96	0.5	1.00	1.40	12.0	1.00	0.06	3.0
Benzoic acid	1.00	2.00	24.0	1.00	0.08	48.0	1.03	0	3.0
Acetic anhydride	0	3.82	24.0	0	2.00	0.5	0	1.97	0.5
Succinic anhydride	0	1.32	48.0	0	0.75	48.0	0	0.04	3.0
Phthalic anhydride	0	0.87	48.0	0	0.52	48.0	0	0.02	3.0
Caproyl chloride	0	1.13	48.0	0	0.20	48.0	0	0	3.0
Benzoyl chloride	0	0.98	48.0	0	0.55	48.0	0	0.03	3.0
V. Esters and Lactones									
Ethyl caproate	0	2.00	24.0	0	0.65	48.0	0	0	3.0
Ethyl benzoate	0	0.18	24.0	0	0.34	48.0	0.02	0.03	3.0
Phenyl acetate	0	1.67	24.0	0	0.25	48.0	0.03	0.02	3.0
$\gamma$ -Butyrolactone	0	2.00	24.0	0	1.50	24.0	0	1.02	1.0
Phthalide	0	0.13	24.0	0	0.34	48.0	0	0.05	3.0
Isopropenyl acetate	0	3.95	24.0	0	2.02	1.0	0	2.01	6.0
VI. Epoxides									
1,2-Butylene oxide	0.04	0.99	72.0	0	0.55	48.0	0	0.07	3.0
Styrene oxide	0.04	1.85	24.0	0	1.68	24.0	0.05	2.56	72.0
Cyclohexene oxide	0	0.94	48.0 <sup>e</sup>	0	0.41	48.0	0	0.04	3.0
1-Methyl-1,2-cyclohexene oxide	0.96	0.96	24.0 <sup>e</sup>	0.97	1.04	12.0	0.85	1.11	48.0
VII. Amides and Nitriles									
Caproamide	1.10	1.00	48.0	0	1.62	24.0	1.96	0	24.0
Benzamide	1.38	1.20	48.0	0.90	1.68	24.0	1.99	0	24.0
Dimethylcaproamide	0	2.00	12.0	0	1.92	72.0	0	1.01	6.0
Dimethylbenzamide	0	2.00	24.0	0	1.99	48.0	0	1.01	3.0
Capronitrile	0	1.94	120.0	0	0.42	24.0	0.05	1.29	72.0
Benzonitrile	0	1.97	80.0	0	0.32	24.0	0.04	1.85	72.0
VIII. Nitro Compounds and Derivatives									
1-Nitropropane	0	0	96.0	0	0	40.0	0	0	24.0
Nitrobenzene	0	0	20.0	0	1.95	48.0	0.39	1.27	72.0
Azobenzene	0	2.00	48.0	0	0.25	48.0	0	0.01	3.0
Azoxybenzene	0	0.05	24.0	0	0.89	24.0	0.97	1.00	24.0
IX. Other Nitrogen Compounds									
Cyclohexanone oxime	0.56	1.22	48.0	0.44	0.98	144.0 <sup>c</sup>	1.02	0.01	6.0
Phenyl isocyanate	0	2.05	24.0	0	2.03	48.0	0	1.98	24.0
Pyridine	0	0	48.0	0	0.04	6.0	0.05	0.03	24.0
Pyridine <i>N</i> -oxide	0	2.76	48.0	0	2.90	24.0	0.97	1.03	24.0
X. Sulfur Compounds									
Di- <i>n</i> -butyl disulfide	0	0	24.0	0	0	20.0	0	0.07	3.0
Diphenyl disulfide	0	0	72.0	0	0	20.0	0	0.04	3.0
Phenyl <i>n</i> -propyl sulfide	0	0	40.0	0	0	24.0	0	0	3.0 <sup>o</sup>

TABLE XI (Continued)

Compound <sup>a</sup>	Diborane <sup>b</sup>			Thexylborane <sup>c</sup>			Disiamylborane <sup>d</sup>		
	Hydride used			Hydride used			Hydride used		
	Evoln	Redn	Time, hr	Evoln	Redn	Time, hr	Evoln	Redn	Time, hr
Dimethyl sulfoxide	0.83	0.77	48.0	1.00	1.00	6.0	0.96	1.04	3.0
Diphenyl sulfone	0	0	24.0	0	0	40.0	0	0	3.0
Methanesulfonic acid	1.00	0	0.5	1.00	0	0.5	0.99	0.04	0.5
Toluenesulfonic acid <sup>f</sup>	2.97	0	3.0	3.00	0	0.5	3.06	0.01	0.5
Cyclohexyl tosylate	0	0	40.0	0	0	24.0	0	0	3.0

<sup>a</sup> Hydride to compound ratio, 4:1. <sup>b</sup> 0.33 M BH<sub>3</sub> (1.00 M hydride). <sup>c</sup> 0.50 M RBH<sub>2</sub> (1.00 M hydride). <sup>d</sup> 1.00 M R<sub>2</sub>'BH (1.00 M hydride). <sup>e</sup> At 25°. <sup>f</sup> Monohydrate. <sup>g</sup> Methyl-*p*-tolyl sulfide.

reduces azoxybenzene but not azobenzene. Both of these substrates are reduced slowly by ThBH<sub>2</sub>.

**IX. Other Nitrogen Compounds.**—Cyclohexanone oxime is reduced slowly with BH<sub>3</sub>.<sup>21</sup> However, no significant reductions are observed with ThBH<sub>2</sub> and Sia<sub>2</sub>BH. Phenyl isocyanate undergoes reduction slowly, but only to an intermediate stage, with further reduction being extremely slow. Pyridine is not attacked by any of these three reagents. However, pyridine *N*-oxide reacts at a moderate rate with both BH<sub>3</sub> and ThBH<sub>2</sub>, both without accompanying hydrogen evolution. However, Sia<sub>2</sub>BH apparently reduces this compound cleanly to the pyridine stage, as indicated by the evolution of 1 mol of hydrogen and the uptake of one hydride for reduction.

**X. Sulfur Compounds.**—All of the three reagents react in similar manner with various sulfur functional groups. Of all the sulfur compounds tested, only dimethyl sulfoxide is reduced to dimethyl sulfide. Sulfonic acids evolve hydrogen quantitatively, but no reduction is observed. Thus disulfide, sulfide, sulfone, and tosylate are all inert.

The experimental data supporting these conclusions and generalizations are summarized in Table XI.

In this table are reported the moles of hydrogen evolved and the hydride utilization observed per mole of compound under the standard conditions. In cases where no significant reduction was observed, in spite of the evident possibility for such reduction, the values reported are for the longest period for which the observation was made. Where reaction occurred, the data are for the shortest period, where essentially constant values of hydrogen evolution and hydride uptake were realized. Thus the values do not necessarily give maximum evolution of hydrogen nor the maximum possible utilization of hydride. They merely define the point where further reduction either does not occur or proceeds so slowly as to provide a convenient stopping place for the reaction.

### Experimental Section

**Materials.**—The compounds used were the same collection<sup>7,8</sup> used in the earlier studies. The standard solutions of thexylborane were prepared by the following procedure. In a flask equipped with a thermometer and a side arm, capped by a rubber septum, was placed 100 ml of a solution of tetrahydrofuran containing 25.2 g (0.3 mol) of tetramethylethylene. The reaction flask was immersed in a mixture of Dry Ice-CCl<sub>4</sub>; 74.7 ml of 2.04 M (0.3 mol of borane) diborane solution in THF was added slowly with stirring, keeping the temperature below 0°. The flask was permitted to remain overnight at 0°. The glpc analysis of the thexylborane solution indicated a slight excess (2–5%) of tetramethylethylene.

The thexylborane solution was periodically checked for active hydrogen by standard techniques.<sup>22</sup> No significant change in the hydride concentration was observed when a solution of thexylborane was kept at 0° for 14 days. At room temperature it has been reported that approximately 0.8 M solution of thexylborane did not undergo significant change in the hydride concentration in 16 days. Moreover, oxidation of the thexylborane indicated that isomerization of the tertiary boron to the primary position is very slow, 3% after 8 days and 8–9% after 16 days at room temperature. Even at the refluxing temperature of tetrahydrofuran (65°), the hydride concentration changed only 2% in 24 hr and 8% in 48 hr. However, no 1-butanol could be detected.<sup>23</sup> However, when the THF solution of thexylborane was exposed to the air through a drying tube at room temperature, the hydride concentration decreased to 70% in 48 hr.

**Procedure.**—In a 100-ml flask fitted with a side arm, capped by a rubber septum, 45 ml of a solution of thexylborane in THF (50 mmol in hydride) was placed. The flask was immersed in an ice bath. The reaction mixture was diluted with 5 ml of THF containing 12.5 mmol of the compound to be reduced.

At different time intervals 5-ml samples were withdrawn and quenched in a glycerol-water hydrolyzing mixture (1:3). The hydrogen evolved was measured volumetrically. The reaction was stopped when two or more analyses indicated that no more hydride was taken up. At the end of reduction the sample was analyzed for tetramethylethylene by glpc analysis in order to make certain that no displacement had occurred during the reduction. Solutions were transferred by means of a hypodermic syringe.

The reduction of isopropenyl acetate is described as representative. After 30 min reaction at 0°, the 5-ml aliquot of reaction mixture indicated 2.6 mmol of residual hydride, revealing that 1.85 mmol of hydride per mmole of compound had been consumed. After 1 hr the residual hydride decreased to 2.48 mmol, indicating that 2.02 hydride per mole of compound had been consumed. The reaction then became very slow. Thus, 1.76 mmol of residual hydride was observed after 48 hr, indicating an uptake of 2.4 hydride per mole of compound. Glpc analysis established that no displacement of the alkyl group of thexylborane had taken place during the course of the reaction.

**Quantitative Determination of Aldehydes.**—The following method was used for determination of aldehydes in samples of the reaction mixtures after treating various compounds with thexylborane.

In a 100-ml erlenmeyer flask 0.4 g of 2,4-dinitrophenylhydrazine was dissolved in a mixture of 2 ml of concentrated sulfuric acid and 3 ml of water. To this solution was added 5 ml of methanol, followed by the addition of 1–5 ml of the reaction mixture under investigation. After a short time the expected 2,4-dinitrophenylhydrazone crystallized out. After 15 min, 10 ml of water was added and the mixture was allowed to stand for 1 hr at room temperature. The crystals were separated from the liquid by a glass filter and washed several times with 2 N HCl, followed by a mixture of water-methanol (3:1). The substance was dried over P<sub>2</sub>O<sub>5</sub> under vacuum to constant weight. Test experiments were carried out by using authentic aldehydes, caproaldehyde, and benzaldehyde. In these cases yields of 97–98% of the pure derivatives were realized.

**Reduction of Carboxylic Acids to Aldehydes.**—In a 100-ml flask, equipped with a reflux condenser, magnetic stirring bar, and a thermometer, were placed 22.5 ml of thexylborane solution in THF, containing 25 mmol of hydride. This solution was then

(21) H. Feuer, B. F. Vincent, Jr., and R. S. Bartlett, *J. Org. Chem.*, **30**, 2877 (1965).

(22) H. C. Brown and P. M. Weissmann, *J. Amer. Chem. Soc.*, **87**, 5614 (1965).

(23) Unpublished observation by W. E. Rieder in this laboratory.



allowed to cool to  $-20^{\circ}$  ( $\text{CCl}_4$  + Dry Ice bath). Five millimoles of benzoic acid dissolved in 2.5 ml of THF (cooled to  $-20^{\circ}$ ) was then added slowly under vigorous stirring. After 10 min the mixture was heated up and kept under reflux. After different time intervals the mixture was cooled to  $0^{\circ}$  and 5-ml aliquots were withdrawn and analyzed for aldehyde. After 12 hr 0.197 g of 2,4-DNP derivative was obtained (70%); after 24 hr 0.232

g (82%) was obtained; and this remained constant after 36 hr. From caproic acid, using the same procedure as from benzoic acid, a 68% yield after 12 hr, 88% yield after 24 hr, and 98% yield after 36 hr were realized.

**Registry No.**—Thexylborane, 3688-24-2; diborane, 13283-31-3; disiamylborane, 1069-54-1.

## Nonclassical Oxidation of Aromatics. II. Cobaltic Ion Catalyzed Oxidations of 1,1-Di(*p*-tolyl)ethane and 1,1-Di(3,4-dimethylphenyl)ethane

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$\text{Co}^{\text{III}}$  ion catalyzed oxidation with oxygen in acetic acid has been extended to the 1,1-diarylalkanes. Major and novel products are carboxylic acids in which the bridging ethylidene group survives the oxidation. 1,1-Di(*p*-tolyl)ethane gave 1,1-di(4-carboxyphenyl)ethane (70%) as the major product. 1,1-Di(3,4-dimethylphenyl)ethane afforded isomeric dimethyl, dicarboxylic acids (85%). The products of this oxidation are unexpected, assuming a free-radical pathway. An electron transfer mechanism involving radical cation intermediates is therefore proposed.

Inorganic oxidants including chromic acid, potassium permanganate, and nitric acid are known to oxidize 1,1-diarylalkanes to benzophenone polycarboxylic acids.<sup>1-3</sup> Air oxidation, however, has been limited to di(*p*-tolyl)methane<sup>4,5</sup> and 2,2-diarylalkanes.<sup>6,7</sup> Di(*p*-tolyl)methane was oxidized to a benzophenone dicarboxylic acid. Attempts to oxidize 1,1-di(*p*-tolyl)ethane or 1,1-di(3,4-dimethylphenyl)ethane with oxygen in the liquid phase led to low conversion of almost exclusively nonacidic oxidation products.<sup>8</sup> Similar difficulties were encountered in the attempted oxidation of alkoxytoluenes in acetic acid.<sup>9</sup> In these cases, initially formed hydroperoxide cleaves into phenolic materials which then terminate the reaction. A recent paper describes the synthesis of 1,1-di(*p*-tolyl)ethyl hydroperoxide and its subsequent cleavage to form *p*-cresol and *p*-methylacetophenone.<sup>10</sup>

We have proposed an electron transfer mechanism for the selective oxidation of alkyltoluenes in which methyl groups are preferentially attacked.<sup>11</sup> Extending this work, liquid phase oxidation of 1,1-di(*p*-tolyl)ethane (DTE) and 1,1-di(3,4-dimethylphenyl)ethane (DXE) was examined.

### Results

Oxidations were carried out in acetic acid using cobaltous acetate catalyst and methyl ethyl ketone (MEK)-butane as the promoters. Reactants, experimental conditions, and the results obtained are summarized in Table I.

(1) O. Fischer, *Ber.*, **7**, 1191 (1874).

(2) U. S. Patent 3,479,400 (1964).

(3) U. S. Patent 2,848,486 (1958).

(4) U. S. Patent 2,806,059 (1957).

(5) V. B. Fal'kovskii, R. A. Nurmukhamedova, S. V. L'vov, *Izobret., Prom. Obraztsy, Tovarnye Znaki*, **43** (2), 26 (1966); *Chem. Abstr.*, **64**, 19501 (1966).

(6) U. S. Patent 3,281,459 (1966).

(7) U. S. Patent 3,161,693 (1964).

(8) U. S. Patent 3,424,789 (1969).

(9) G. A. Russell and R. C. Williamson, Jr., *J. Amer. Chem. Soc.*, **86**, 2357 (1964).

(10) G. N. Kirichenko, E. G. Mavlyutova, and T. M. Khannanov, *Neftekhimiya*, **10**, (2), 231 (1970).

(11) A. Onopchenko, J. G. D. Schulz, and R. Seekircher, *J. Org. Chem.*, **37**, 1414 (1972).

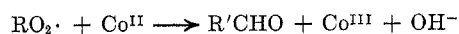
Oxidation of DTE in the presence of cobaltous acetate without a promoter was slow, nonselective, and incomplete, even after 20 hr (expt 1). A mixture of monoacids, including 1-(4-carboxyphenyl)-1-(4-methylphenyl)ethane (I) and 4-methyl-4'-carboxybenzophenone, was isolated (21%) along with 4,4'-dimethylbenzophenone (26%). A similar experiment, but with MEK, afforded I in 45.4% yield (expt 2). Oxidation of DTE in the presence of MEK-butane gave 1,1-di(4-carboxyphenyl)ethane (EDB) and I in yields of 67.3 and 8.3%, respectively (expt 3). Extension of the reaction time beyond a 5-6-hr period did not improve the yields of I or EDB significantly.

Oxidation of DXE under conditions used for DTE gave an isomeric mixture of the corresponding ethylidenedi- and -monocarboxylic acids exclusively (expt 5).

Recovery of products in all experiments was above 85%, whereas cleavage into fragments was between 5 to 10%. Cleavage products from DTE oxidation were (vpc) *p*-acetobenzoic acid, *p*-toluic acid, terephthalic acid, some *p*-methylacetophenone, and traces of *p*-cresol.

### Discussion

Oxidation of 1,1-di(*p*-tolyl)ethane and 1,1-di(3,4-dimethylphenyl)ethane in the system earlier described for alkyltoluenes was investigated.<sup>11</sup> Major and novel products are carboxylic acids in which the bridging ethylidene group remains intact. Large amounts of catalyst in the higher valency state were required to effect selective methyl group oxidation. With  $\text{Co}^{\text{II}}$  ions alone, reaction did not proceed readily and showed no selectivity. Peroxy radicals derived from the substrate were apparently not sufficient to maintain the active  $\text{Co}^{\text{III}}$  species. If the overall rate of reaction is



governed by the reoxidation of  $\text{Co}^{\text{II}}$  to  $\text{Co}^{\text{III}}$ , it should be helped by peroxy radical-forming promoters. Adding for this purpose MEK or cyclohexanone showed an increase in rate and shortening of the induction period. As methylenic ketones are rapidly consumed, precursor