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ORGANOBORANES FOR SYNTHESIS. 5. STOICHIOMETRICALLY CONTROLLED REACTION OF ORGANOBORANES WITH OXYGEN UNDER MILD CONDITIONS TO ACHIEVE QUANTITATIVE CONVERSION TO ALCOHOLS[1,2]

HERBERT C. BROWN,* M. MARK MIDLAND[3a] and GEORGE W. KABALKA[3b]

Richard B. Wetherill Laboratory, Purdue University
West Lafayette, Indiana 47907 USA

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Abstract - The reaction of organoboranes with oxygen under mild conditions can be controlled to give an essentially quantitative conversion of all three alkyl groups on boron to the corresponding alcohol. The controlled oxidation is a very clean reaction, with only minor amounts of carbonyl and hydrocarbon products formed. All organoboranes react quite rapidly in the initial stages, but vary considerably in the time required to achieve the desired uptake of oxygen. In contrast to oxidation by alkaline hydrogen peroxide, a portion of this reaction proceeds through alkyl radicals, thus resulting in some loss of stereospecificity. Oxidation of mixed organoboranes reveals that the relative rates of oxidation of alkyl groups on boron are consistent with a radical mechanism, with tertiary > secondary > primary in the rate of oxidation. The selective oxidation of one alkyl group in the presence of the other is not possible, due to small differences in relative rates of oxidation. However, thexyl and cyclohexyl groups can be selectively removed from boron in the presence of alkenyl groups. Thus, controlled oxidation of thexyldialkenylborane affords pure dialkenylborinic acid.

Trialkylboranes react readily with oxygen[4] and consequently must be protected under an inert atmosphere for most reactions. The autoxidation of trialkylboranes in dilute solutions has been of considerable theoretical interest.[5] A radical-chain process occurs with an alkyl radical being displaced from boron (eqs 1-3). More recently, it has become apparent that such radical-chain reactions involving organoboranes may be of synthetic interest. Thus, the slow admission of air initiates 1,4-addition of trialkylboranes to inert α,β-unsaturated compounds by a radical process.[6] This oxygen-initiated conjugate addition reaction has opened a new area of considerable synthetic utility.[7]

$$R_3B + O_2 \longrightarrow R\cdot; \quad (1)$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot; \quad (2)$$

$$RO_2\cdot + R_3B \longrightarrow RO_2BR_2 + R\cdot \quad (3)$$

The direct oxidation of trialkylboranes with oxygen, however, has hitherto not been of much synthetic utility. Sufficient oxygen is absorbed by trialkylboranes to oxidize all three carbon-boron bonds, but the reaction is reported to be complex, especially in tetrahydrofuran (THF) solution.[8] Long reaction times and elevated temperatures were employed in an attempt to achieve high conversion to alcohol. Consequently, we undertook to examine in detail the reaction of organoboranes with oxygen with the hope of overcoming some of the difficulties which have been reported.[8] Since THF is a common solvent for hydroboration,[9] it would be particularly convenient if clean oxidations could be achieved with oxygen in this solvent.

A number of organoborane reactions involve the conversion of only one of the alkyl groups of a trialkylborane to the desired product. This difficulty was overcome by the use of a variety of mixed organoboranes, prepared conveniently via hydroboration of alkenes with partially alkylated borane reagents, such as 9-borabicyclo[3.3.1]nonane (9-BBN), dicyclohexylborane, 2,3-dimethyl-2-butylborane (thexylborane) and bis(3-methyl-2-butyl)borane (disiamylborane).[7,9] These reagents

have been proven to be valuable since they permit the economical use of alkyl groups. Therefore, it was of interest to study also the selective oxidation of mixed organoboranes.

RESULTS AND DISCUSSION

Quantitative oxidation of an organoborane to the corresponding alcohol would involve the uptake of 1.5 mol of oxygen per mol of trialkylborane, followed by hydrolysis of the intermediate borate ester (eq 4). The oxidation of trialkylboranes in THF was explored using the automatic gasimeter[10] for generating the oxygen and following the progress of the reaction. Oxygen was produced by the basic manganese dioxide-catalyzed decomposition of hydrogen peroxide. The generator, a 200-mL flask immersed in water bath, was charged with 3 g of manganese dioxide, 5 mL of water, and 2 mL of 3 *N* sodium hydroxide. The tube leading from the generator was fitted with glass wool and the tube to the reaction flask was filled with sodium hydroxide pellets to absorb water. The buret was filled with a standard solution[11] of hydrogen peroxide. The mercury valve maintains a constant pressure as oxygen is absorbed by the organoborane solution. Thus, the reaction may be followed simply from the buret reading.

$$R_3B + 1.5\ O_2 \longrightarrow (RO)_3B \xrightarrow{3\ H_2O} 3\ ROH + (HO)_3B \quad (4)$$

Using a 0.5 *M* solution of tri-*n*-butylborane in THF, it was found that the reaction with air was rapid at first, but soon became slow and failed to reach completion in a reasonable time. However, the use of pure oxygen produced a rapid reaction.[12] The rate of stirring was important for an efficient absorption of oxygen. For maximum efficiency, a magnetic stirring bar fitted with a Teflon collar was used.[10] With the present apparatus, the course of the reaction is readily followed and the reaction can be stopped at precisely 100% oxygen absorption. Treatment with aqueous alkali provides a nearly quantitative yield of alcohol.

Since the oxidation is very rapid during the initial stages, the apparatus must be carefully flushed with oxygen without significant absorption of the gas prior to stirring the reaction mixture. This is achieved by flushing the apparatus with an empty flask attached in place of the usual reaction flask. This empty flask is then replaced by the reaction flask and the remaining nitrogen carefully flushed in one of two ways. The first proved satisfactory for the highly reactive secondary organoboranes in small scale reactions. It consists of removing a known volume (usually 50 mL) of nitrogen from above the THF solution with a syringe while generating oxygen at such a rate as to keep the system at atmospheric pressure. The second method, used for the less reactive primary alkylboranes, or for large scale reactions, involves carefully and quickly flushing the system by injecting 2 mL of 30% hydrogen peroxide into the generator once the reaction flask is in place on the flushed apparatus. Stirring then initiates a rapid reaction.

The initial reaction could be moderated by changing the oxygen-nitrogen ratio above the solution. However, this causes other problems. For example, in the latter stages of oxidation, the reaction becomes very sluggish and fails to reach completion. A possible explanation is that the concentration of oxygen in the solution is too low to give a satisfactory rate. Other reactions, such as the intermolecular redox reaction,[8] may occur during this long reaction time. The problem is solved by using a 100% oxygen atmosphere. The first boron-carbon bond is oxidized very rapidly by a radical-chain process (eqs 1-3).[13] This initial oxidation produces a peroxide which may either react with a second mole of oxygen, or may undergo an intermolecular redox reaction (eqs 5 and 6).[8] The resulting borinate ester may be further oxidized (eq 7). Thus, the final reaction mixture may contain a mixture of several types of borate esters. Regardless of the mixture, when enough oxygen is present, addition of sodium hydroxide causes a reduction of the peroxide linkage and oxidation of the remaining boron-carbon bonds. This may involve either a rearrangement with displacement of the alkyl group from boron to oxygen (eq 7),[14] or hydrolysis of the alkyl peroxide (eq 8), followed by base-catalyzed oxidation of the boron-carbon bond by the peroxide anion, as with hydrogen peroxide. Both would presumably go through the same $HOB^-(OOR)R_2$ intermediate.

$$RO_2BR_2 + O_2 \longrightarrow (RO_2)_2BR; \quad (5)$$

$$RO_2BR_2 + R_3B \longrightarrow 2\ ROBR_2; \quad (6)$$

$$ROBR_2 + O_2 \longrightarrow RO\text{–}\overset{\overset{R}{\curvearrowright}}{B}\text{–}O\text{–}OR \longrightarrow (RO)_3B \quad (7)$$

$$HO^- + R_2BOOR \longrightarrow HOB^-(OOR)R_2 \longrightarrow HOB(OR)R + {}^-OR \quad (8)$$

Effect of Oxygen Concentration. The above oxidation was very rapid with oxygen being absorbed even before stirring was started. This causes problems when the system is flushed with oxygen since an

unknown quantity of oxygen is absorbed. Several methods of controlling the oxidation were studied.

It was hoped that a partial atmosphere of oxygen over the solution would moderate the reaction. The oxygen-nitrogen ratio was varied by partially evacuating the system, then refilling with oxygen. With lower percentages of oxygen, the reaction was moderated. However, the reaction became very sluggish in the latter stages and oxygen absorption was incomplete. The results are shown graphically in Figure 1.

Effect of Temperature. With an aim to moderate the initial reaction, the temperature was lowered. However, even at -78°C in THF, the absorption of oxygen was very fast. A detailed study of this reaction revealed some interesting results, which are discussed elsewhere.[15]

Stoichiometry. Using the above method, the oxygen absorption could easily be followed. In an uncontrolled reaction, more than a theoretical amount of oxygen was absorbed. To see what effect the oxygen stoichiometry had on the yield of alcohol, samples were removed at various levels of oxygen absorption and added to 3 *N* sodium hydroxide and analyzed for alcohol. Tris(2,4,4-trimethyl-1-pentyl)borane was chosen for study because the oxidation of this borane was slow in the latter stages. The results are given in Table 1. The best yield was obtained when 1.5 mol of oxygen was absorbed per mol of R_3B.

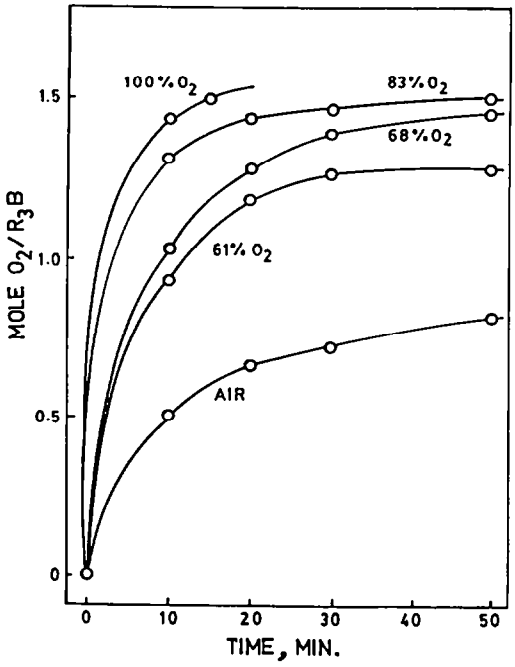


Figure 1. The effect of oxygen concentration on the autoxidation of tri-*n*-butylborane

When less than the stoichiometric amount of oxygen is absorbed, boron-carbon bonds remain.

Table 1. Formation of Alcohol at Various Oxygen Stoichiometries[a]

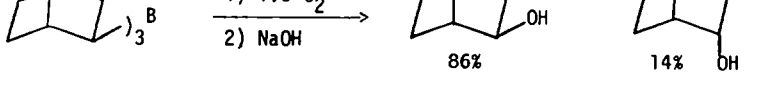
% oxygen[b]	66	74.5	81.4	86.8	94.3	100	110
% alcohol[c]	66.0	70.5	77.3	83.0	90.7	96.3	74.5

[a]Tris(2,4,4-trimethyl-1-pentyl)borane was used in these experiments. [b]Based on a stoichiometry of 1.5 O_2/R_3B. [c]Analyzed by GC following treatment with sodium hydroxide.

When more than the stoichiometric amount of oxygen is absorbed, an equivalent amount of the product remains as the peroxide (eq 9). Thus, it is important to stop the reaction when the precise amount of oxygen is absorbed. This is easily done using the automatic gas generator.

$$(RO_2)_2BR + {}^-OH \longrightarrow 2\ ROH + RO_2^- \qquad (9)$$

Stereochemistry. The alkaline hydrogen peroxide oxidation of organoboranes proceeds with the retention of configuration in the alkyl group. Thus, the hydroboration-oxidation of norbornene and 1-methylcyclopentene afford 99.5% *exo*-norbornanol and 100% *trans*-2-methylcyclopentanol respectively.[9,16] However, the free-radical nature of autoxidation reaction leads to the loss of stereochemistry (eqs 10 and 11). We investigated the stereochemistry of the present reaction using the organ-



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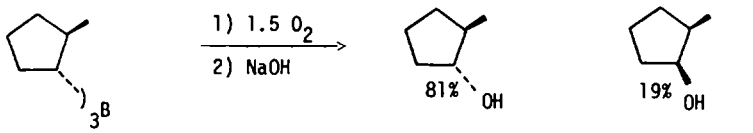


(11)

oboranes from norbornene and 1-methylcyclopentene. In both cases a loss of stereochemistry was found.

Davies has reported that three epimeric trinorbornylboranes, all give a 76/24 ratio of exo/endo product when dilute solutions (0.01-0.05 *M*) of the boranes are oxidized.[5a] We found that in dilute solution (0.05 *M*) oxidation of the organoborane from 1-methylcyclopentene gave a mixture of 36.6% cis and 63.4% trans product. The oxidation to alcohols in more concentrated solutions (0.5 *M*) gives a higher retention of configuration. When the borane is oxidized to the alcohol, only about one-half of the product results from radical intermediates. The remainder of the boron-carbon bonds are oxidized with retention, either by the intermolecular-redox reaction, or by the base-induced reaction, similar to hydrogen peroxide oxidation.

When one wishes to utilize the stereochemistry of the hydroboration reaction, the organoborane must be protected from air. The hydrogen peroxide-sodium hydroxide oxidation must be used in this case to retain the stereochemistry.

Preparation of Alcohols From Representative Organoboranes. Once the conditions for maximum alcohol production were established, the reaction was applied to a representative series of organoboranes. The results are given in Table 2.

Table 2. The Controlled Reaction of Organoboranes With Oxygen to Form Alcohols

Alkene for R_3B[a]	Time[b] min	Yield[c] %	Isomer Distribution[d]
1-butene	5	94	95% p, 5% s
1-octene	5	96	95% p, 5% s
isobutene	75	98	100% p
2-methyl-1-pentene	75	96	
2,4,4-trimethyl-1-pentene	75	96(88)	
2-butene	5	95	
cyclopentene	5	95	
cyclohexene	6	98(80)	
norbornene	6	91	14% endo
1-methylcyclopentene	7.5	99	19% cis

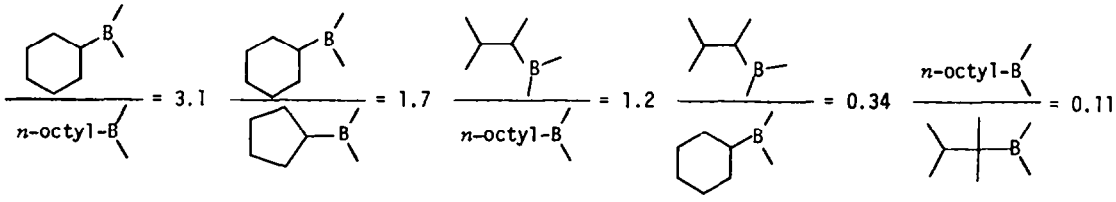
[a] 10 mmol of R_3B in 20 mL of tetrahydrofuran at 0°C. [b] Time for absorption of 1.5 mol of O_2/mol of R_3B. [c] By GC (isolated yields in parentheses). [d] p = primary; s = secondary.

All organoboranes initially absorb oxygen very rapidly, 1-2 min being required for absorption of the first 0.5 mol. However, a beta-methyl substituent on a primary alkylborane, as in triisobutylborane, greatly decreases the rate of oxygen absorption after the initial stage. Rapid stirring was important in the latter stages. The reactions were very clean, with only traces of ketone and hydrocarbon products detected in all cases.

Relative Reactivities of Alkyl Groups. Little is known about the relative reactivities of various alkyl groups on boron in free-radical reactions, except that *t*-butyl groups oxidize 4.5 times faster than *i*-butyl groups.[17] The relative reactivities of some alkyl groups in the 1,4-addition of mixed organoboranes to α,β-unsaturated carbonyl compounds have been determined more recently.[18] Cyclohexyl groups added to acrolein 10.6 times faster than *n*-butyl groups. Now that a wide variety of mixed organoboranes is available, it is desirable to know the relative rates of oxidation of various alkyl groups.

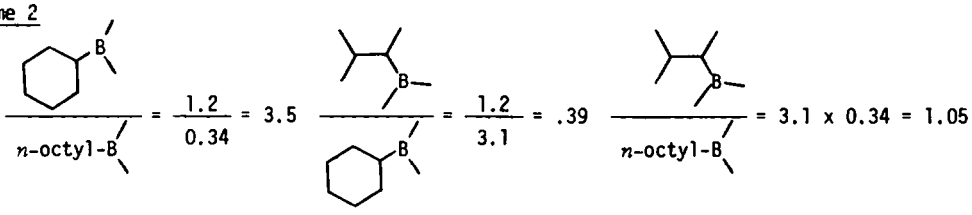
The relative reactivities of a number of mixed trialkylboranes were determined by partial oxidation in tetrahydrofuran at 0°C (0.5 mol oxygen). The oxidized product was reduced with lithium aluminum hydride to destroy any peroxide, then analyzed by GC for the alcohol distribution. The relative reactivities were then calculated taking into account any statistical factor. The results for an average of two runs are listed in Scheme 1.

Scheme 1



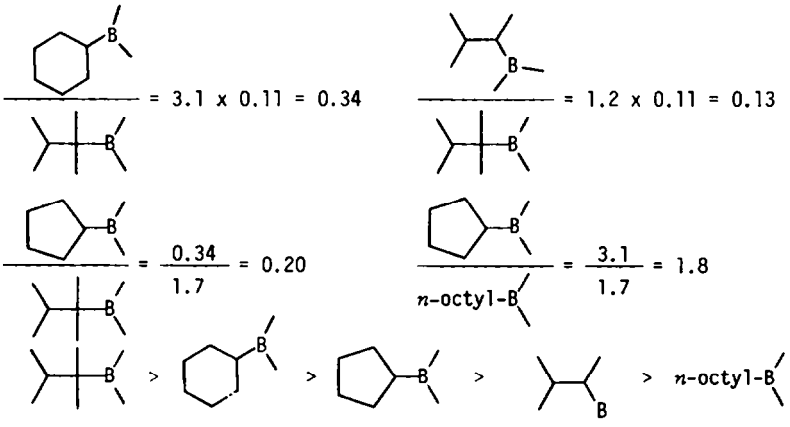
The internal consistency of these results was checked by calculating these ratios from one another. Fairly good results were obtained (Scheme 2).

Scheme 2



With these results, the relative reactivities of other organoboranes not available can be predicted and the relative reactivities of representative alkyl groups can be calculated (Scheme 3).

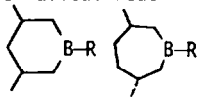
Scheme 3



rel. react. (0°)	9.1	1.8	1.2	1.0

The autoxidation of organoboranes is a free-radical process. Consequently, the relative reactivities of various alkyl groups on boron would be expected to parallel the stability of the intermediate radical. The observed relative rates are consistent with a radical mechanism with 3° > 2° > 1° in rate of oxidation. The differences are slight at 0°C and no selective oxidation is possible with the alkyl systems studied. The ratio does not change appreciably at lower temperature. Apparently there is no great difference in activation energies for the oxidation of various alkyl groups.

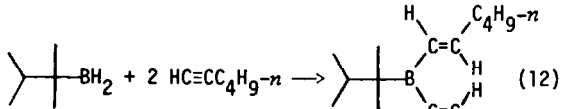
The slower rate for the 3-methyl-2-butyl group, compared to other secondary alkyl groups, is not totally unexpected. It appears to be quite general that an alkyl group with a β-methyl substituent is oxidized at a slower rate. Isobutyl-, 2-methyl-1-pentyl and 2,4,4-trimethyl-1-pentylborane require 75 min for complete oxygen absorption, compared to 5-6 min for other boranes. Such decreased reactivity of a β-methyl substituted alkyl group may be used advantageously in free-radical reactions. Accordingly, 3,5-dimethylborinane and 3,6-dimethylborepane have been used to transfer only the *B*-alkyl groups selective in free radical reactions.[19]

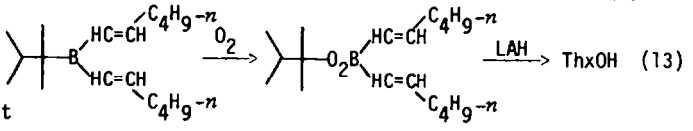


It was hoped that mixed organoboranes could be selectively oxidized, either to remove one group such as a thexyl group, or to transfer one alkyl substituent into an alcohol or peroxide. The mixed organoboranes studied thus far failed to achieve this objective.

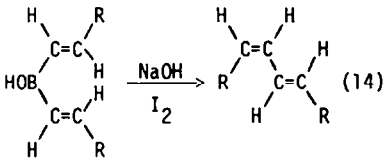
Oxidation of *B*-Alkyl-9-BBN. *B*-Cyclohexyl-9-BBN was oxidized under standard conditions (0°C, tetrahydrofuran). After 8 min, 100% of the theoretical amount of oxygen (1.5 mmol) was absorbed. Hydrolysis with 3 *N* sodium hydroxide gave an 81% yield of cyclohexanol and only a trace of cyclooctane-1,5-diol, plus many other products. However, *B*-*n*-octyl-9-BBN gave a complex mixture of products.

Oxidation of Divinylthexylborane. Thexylborane and 1-hexyne produce the vinylborane (eq 12).[20] This borane was then oxidized under standard conditions. One mol of oxygen was rapidly absorbed. Reduction with lithium aluminum hydride produced a quantitative yield of thexyl alcohol (eq 13). No oxidation of the vinyl group was observed. The selective removal of the thexyl group provides a simple synthesis of divinylborinic acids, which are very important

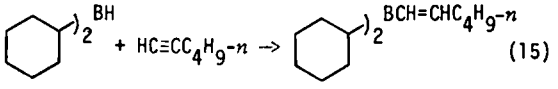




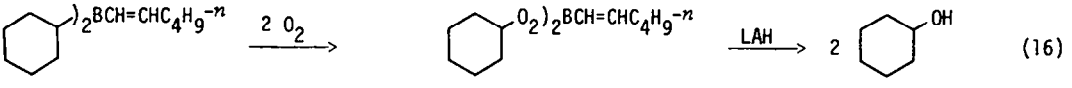
as intermediates in the synthesis of dienes (eq 14).[21]



Oxidation of Dicyclohexylvinylborane. Dicyclohexylborane was reacted with 1-hexyne to produce the corresponding vinylborane (eq 15).[22] This borane was subjected to normal oxidation at 0°C. In 6 min, 2 mol of oxygen were absorbed. At -78°C, 1 mol of oxygen was absorbed in 3 min and 1.5 mol in 60 min. Upon warming to 0°C, the remaining 0.5 mol was absorbed. Upon reduction with lithium aluminum hydride, a 95% yield of cyclohexanol was found. Only traces of the vinyl groups were oxidized.



Both cyclohexyl groups of dicyclohexylvinylborane may be selectively removed. A diperoxide intermediate is formed, as evidenced by analysis after reduction (eq 16). The very low reactivity of



vinylboranes suggests that they may be highly useful in selectively transforming one or two alkyl groups in free-radical reactions. Phenyl substituted organoboranes should also prove valuable in such processes.

The oxidation of vinylboranes has not been studied extensively. It has been stated that vinylboranes oxidize slower than alkylboranes, but no experimental details have been given.[14] The unreactivity of the vinyl group was thought to be due to π overlap of the double bond with boron. However, we find that alkylvinylboranes oxidize fairly rapidly. Overlap here should also slow the reaction. It seems likely that the instability of the vinyl radical is a better explanation for the inertness of trivinylboranes toward free-radical oxidation.

CONCLUSIONS

The present study reveals that the reaction of an organoborane with oxygen can be controlled under very mild conditions to provide a nearly quantitative yield of the corresponding alcohol. The reaction is rapid, even at low temperature.[23] The high yields and remarkable cleanness of this reaction are explained on the basis of the mild conditions employed, which prevent decomposition of the intermediate peroxides.

The reaction of oxygen with mixed organoboranes indicates that relative rates of oxidation of alkyl groups are in the order tertiary > secondary > primary, consistent with the free radical mechanism proposed for such reactions. However, the differences in relative rates of oxidation of various alkyl groups are too small to permit the selective removal of one alkyl group in the presence of the other. Only in the case of alkenyldialkyl- or alkyldialkenylboranes is the selective oxidation of alkyl groups possible, providing the corresponding alkenylboronic or dialkenylborinic acids respectively in good yields.

This study represents a systematic investigation of the autoxidation of organoboranes with oxygen under mild conditions, which enables one to prepare alcohols in nearly quantitative yields. More recently, it has been reported that anodic oxidation of trialkylboranes provides alkyl methyl ethers in methanol solvent and alkyl acetates in acetic acid solvent.[24]

EXPERIMENTAL SECTION

Materials. All glassware was dried in an oven at 135°C and cooled under a stream of nitrogen. All liquids were transferred under nitrogen using dry syringes.[25] Tetrahydrofuran (Mallinckrodt) and all liquid alkenes were distilled from lithium aluminum hydride (Alfa Inorganics) and stored under nitrogen. Diglyme (Ansul Chemical Co.) was dried over calcium hydride, then distilled from lithium aluminum hydride under reduced pressure. 1-Butene, *cis*-2-butene and isobutene (Phillips Petroleum Co.), 1-hexyne (Chem Samples) and norbornene (Aldrich) were used directly as obtained. Sodium borohydride and boron trifluoride etherate for the generation of diborane were used directly as obtained from Metal Hydrides Inc. and Matheson, Coleman & Bell respectively. Tri-*n*-butyl- and triisobutylborane were used directly as obtained from Callery Chemical Co. Aqueous hydrogen peroxide solutions (Mallinckrodt), 30% and 3%, and manganese dioxide, technical grade, were used directly.

Analysis. The automatic gas generator was obtained from Delmar Scientific Laboratories. A Varian T-60 was used for NMR analysis. Infrared spectra were recorded on a Perkin-Elmer 137 sodium chloride spectrophotometer. Alcohols were analyzed on a Hewlett-Packard 5750 gas chromatograph using a 6 ft x 1/4 in 10% Carbowax 20M column. Undecane was used as an internal standard for GC. *exo*- and *endo*-Norbornyl alcohols were separated on a 150 ft x 0.01 in Ucon polar capillary column on a Perkin-Elmer 226 gas chromatograph. The column was run at 65°C for 20 min, then programmed at 5°/min to 100° and run isothermally until the alcohols were eluted. The *exo* alcohol had a retention time

of about 45 min and the *endo* alcohol about 47 min.

Standardization of Hydrogen Peroxide. Hydrogen peroxide, 3%, was standardized by injecting an aliquot (15 mL) into a 500-mL flask containing 2 g of manganese dioxide, 2 mL of 3 *N* sodium hydroxide and 10 mL of water maintained at 0°C. The oxygen generated, about 220 mL, was measured using a gas buret, the volume was reduced to standard temperature and pressure and the mmol of oxygen per mL of solution calculated. The 30% solution of hydrogen peroxide was standardized by injecting 2 mL into the generator and measuring the volume of oxygen.

Oxidation of Representative Organoboranes. A representative procedure is that utilized for the conversion of 2,4,4-trimethyl-1-pentene into 2,4,4-trimethyl-1-pentanol. A dry 200-mL flask equipped with a septum inlet and a stirring bar with Teflon collar was flushed with nitrogen. The flask was charged with 50 mL of dry tetrahydrofuran and 16.9 g of 2,4,4-trimethyl-1-pentene (150 mmol) and cooled to 0°C. Hydroboration was carried out by the dropwise addition of 18 mL of a 2.68 *M* solution of borane in tetrahydrofuran (150 mmol of hydride) at 0°C, followed by stirring at room temperature for 1 h. The solution was cooled to 0°C and the flask was attached to an automatic oxygenator previously flushed with oxygen (slowly inject 15 mL of 30% hydrogen peroxide into the generator with an empty 100-mL flask in place of the reaction flask). The system was further flushed by injecting 2 mL of 30% hydrogen peroxide once the flask was in place. The stirrer was started and oxygen absorption (with the reaction flask immersed in an ice bath) was followed by reading the buret filled with freshly standardized 30% hydrogen peroxide. After the theoretical absorption of oxygen, the flask was removed and 18 mL of 3 *N* sodium hydroxide added dropwise at 0°C (exothermic reaction). The solution was stirred for 5 min, the aqueous layer was saturated (K_2CO_3), separated and washed with diethyl ether and the combined extracts were dried (K_2CO_3). Distillation gave 17.3 g (88% yield) of 2,4,4-trimethyl-1-pentanol, bp 169-170°, $n^{20}D$ 1.4263. In a similar manner, cyclohexanol was isolated in an 80% yield. Reactions for GC analysis were run using 10 mmol of organoborane in 20 mL of tetrahydrofuran at 0°C. Nitrogen was removed from above the primary alkylborane solutions by carefully injecting 1.5-2.0 mL of 30% hydrogen peroxide into the generator. For the more reactive secondary alkylboranes, 100 mL of gas was removed by syringe from above the tetrahydrofuran solution while adding 100 mL of oxygen by syringe into the generator.

Determination of Stoichiometry. Tris(2,4,4-trimethyl-1-pentyl)borane (10 mmol) was prepared in 20 mL of tetrahydrofuran. Undecane (10 mmol) was added as an internal standard. The organoborane was cooled to 0°C and oxidized as above. The oxidation became slow in the latter stages. Aliquots (1.0 mL) were removed periodically and added to 0.7 mL of 3 *N* sodium hydroxide under nitrogen. The solution was then dried (K_2CO_3) and analyzed by GC for alcohol. The results are given in Table 1.

Determination of Stereochemistry. Tri-*exo*-norbornylborane (10 mmol) was prepared in 20 mL of tetrahydrofuran. The solution was cooled to 0°C and oxidized as above for secondary boranes. After absorption of 15 mmol of oxygen, 3.3 mL of 3 *N* sodium hydroxide was added. The aqueous phase was saturated (K_2CO_3) and removed. The GC analysis of tetrahydrofuran solution revealed the presence of 86% *exo*- and 14% *endo*-norbornyl alcohol. Likewise, the organoborane from 1-methylcyclopentene, upon oxidation and workup as above, gave 81% *trans*- and 19% *cis*-2-methylcyclopentanol.

Oxidation of a Dilute Solution of Tris(2-methylcyclopentyl)borane. A dry 100-mL flask with standard equipment was flushed with nitrogen, charged with 2.0 mmol of 1-methylcyclopentene and 2 mL of tetrahydrofuran, followed by 0.56 mol of borane. After 24 h, the solution was diluted to 25 mL with tetrahydrofuran and cooled to 0°C. The flask was placed on an automatic oxidizer filled with oxygen and the remaining nitrogen removed by injecting 4 mL of 30% hydrogen peroxide into the generator. Stirring was then started and the theoretical amount of oxygen was absorbed in about 10 min. The excess hydride was destroyed after 0.5 h with wet tetrahydrofuran. The solution was dried (K_2CO_3) and concentrated to about 5 mL. Analysis by GC revealed 36.6% *cis*- and 63.4% *trans*-2-methylcyclopentanol.

Oxidation at Various Oxygen Concentrations. The automatic oxidizer was flushed with nitrogen with the reaction flask on the system. The reaction flask was then charged with 20 mL of dry tetrahydrofuran and cooled to 0°C. Tri-*n*-butylborane (10 mmol) was held in a syringe with its tip below the tetrahydrofuran solution. A bubbler was attached to a water aspirator and a manometer by a 3-way stopcock.[10] The nitrogen was removed until the desired partial pressure was obtained. The stopcock was then closed and the system brought back to atmospheric pressure by carefully injecting 30% hydrogen peroxide into the generator. The organoborane was then injected into the tetrahydrofuran and the stirrer started. The reaction was followed by reading the buret filled with standardized 3% hydrogen peroxide. The results are shown graphically in Figure 1.

Preparation of Di-*n*-octylthexylborane. A dry 100-mL flask equipped with a septum inlet and magnetic stirring bar was flushed with nitrogen. The flask was cooled to 0°C and charged with 15 mL of dry tetrahydrofuran and 10 mmol of borane in 3.6 mL of tetrahydrofuran. Thexylborane was prepared by the dropwise addition (0.84 g) of 2,3-dimethyl-2-butene (10 mmol), followed by stirring at 0°C for 3 h. 1-Octene (2.46 g, 22 mmol) was added dropwise at 0°C, then stirred at room temperature for 1 h. Oxidation was achieved by cooling the solution to 0°C and placing the flask on an automatic oxidizer which had been previously filled with oxygen. The remaining nitrogen was removed by injecting 1.5 mL of 30% hydrogen peroxide into the generator. Stirring initiated a rapid absorption of oxygen, which was followed by reading the buret filled with 3% aqueous hydrogen peroxide. After 6 min, 1.5 mol of oxygen was absorbed. Sodium hydroxide (3.3 mL of a 3 *N* solution) was added dropwise and the solution saturated with K_2CO_3. Analysis by GC revealed 94.4% of 1-octanol and 94.1% of thexyl alcohol (2,3-dimethyl-2-butanol).

Preparation and Selective Oxidation of Dicyclohexyl-*n*-octylborane. The usual 100-mL reaction flask was flushed with nitrogen and charged with 10 mmol of borane in a total of 20 mL of tetrahydrofuran. Cyclohexene (1.64 g, 20 mmol) was added dropwise at 0°C and stirred for 4 h. Then, 1.12 g (10 mmol) of 1-octene was added and the solution stirred for 3 h at 20°C. Undecane (10 mmol) was added as an internal standard. The organoborane was oxidized as above. After 0.5 mol of oxygen was absorbed, 1 mL of the aliquot was removed and added to 1 mL of 1.65 *M* lithium aluminum hydride in tetrahydrofuran. The solution was hydrolyzed with dilute hydrochloric acid and saturated with potassium carbonate. The alcohols were analyzed by GC as the trimethylsilyl ethers, preapred by adding 2-3 drops of solution to 0.8 mL of Tri-Sil. There was found 9.0 mmol of cyclohexanol and 1.55 mmol of octanol. This gives a ratio of 2.9:1. A second reaction gave a relative reactivity of 3.2.

Preparation and Selective Oxidation of Cyclohexyldisiamylborane. To 10 mmol of borane in 20 mL of tetrahydrofuran was added 1.40 g (20 mmol) of 2-methyl-2-butene at 0°C. The solution was stirred at 0°C for 4 h, then 0.84 g of cyclohexene (10 mmol) was added and the solution was stirred for an additional 48 h at 20°C. The organoborane was oxidized and worked up as above. Analysis gave 3.4 mmol of 3-methyl-2-butanol and 5.0 mmol of cyclohexanol. This gives a ratio of 0.34 for siamyl/cyclohexyl.

Preparation and Oxidation of *B*-Cyclohexyl-9-BBN. 9-BBN was prepared according to the procedure of Knights and Brown.[9] Ten millimoles of cyclohexene was added to 16.5 mL of a 0.61 *M* solution of 9-BBN in tetrahydrofuran. After stirring at room temperature for 18 h, the organoborane was oxidized as above. Analysis gave 8.1 mmol of cyclohexanol, plus many other peaks.

Preparation and Oxidation of Divinylthexylborane. Thexylborane was prepared as described. Twenty millimoles of 1-hexyne was added at 0°C and stirred for 1.5 h. Ten millimoles of oxygen was absorbed in 15 min upon oxidation. The reaction was worked up as previously described. Analysis gave 9.5 mmol of thexyl alcohol. No 1-hexanol was detected by GC.

Preparation and Oxidation of Cyclohexylvinylborane. Dicyclohexylborane was prepared as above. 10 mmol of 1-hexyne was added at 0°C and the solution stirred at room temperature overnight. The solution was oxidized at 0°C. Titration gave 16.6 mmol of peroxide. Analysis after lithium aluminum hydride reduction gave 19.1 mmol of cyclohexanol and a trace of 1-hexanol. The solution was then oxidized at -78°C. After 3 min, 1 mol of oxygen was absorbed. After 60 min, 1.5 mol was absorbed. The remaining 0.5 mol of oxygen was absorbed upon warming to 0°C. Titration revealed 17 mmol of peroxide. Lithium aluminum hydride reduction gave 19.0 mmol of cyclohexanol and a trace of 1-hexanol.

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