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ORGANOBORANES FOR SYNTHESIS. 2. OXIDATION OF ORGANOBORANES WITH ALKALINE HYDROGEN PEROXIDE AS A CONVENIENT ROUTE FOR THE *cis*-HYDRATION OF ALKENES *via* HYDROBORATION[1]

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Abstract - Aqueous hydrogen peroxide in the presence of dilute alkali effects the oxidation of organoboranes. The conditions necessary for a clean and quantitative transformation of organoboranes into the corresponding alcohols have been established. Thus, one mole of trialkylborane reacts with three moles of hydrogen peroxide in the presence of one mole of sodium hydroxide to provide three moles of the corresponding alcohol. The concentrations of these reagents or the reaction temperature can be varied widely without affecting the yield significantly. Oxidation proceeds well in water-miscible solvents, such as diglyme and THF. However, the reaction is slow and incomplete in diethyl ether. The addition of ethanol as a cosolvent circumvents this difficulty. Wide variations in the structure of organoboranes do not affect the reaction greatly. A variety of common organic functional groups, such as alkenes, alkynes, esters, ketones, nitriles, etc., are unaffected under the normal oxidation conditions. However, aldehydes are somewhat unstable under these conditions, although they do not interfere with the oxidation of organoboranes

The alkaline hydrogen peroxide oxidation has been utilized earlier for the conversion of aryl- and alkylboranes to the corresponding alcohols.[3,4] A complete dealkylation of tri-*n*-butylborane to *n*-butanol and boric acid was achieved by alkaline hydrogen peroxide.[4] The reaction was suggested as a convenient method for the determination of boron in organoboranes and was later developed as an analytical procedure.[5] The conditions employed were quite vigorous, involving heating a mixture of alkylborane, hydrogen peroxide and saturated sodium hydroxide under reflux. Our early applications of alkaline hydrogen peroxide oxidation in connection with the hydroboration reaction also utilized more vigorous conditions than were subsequently found necessary.[6,7]

The powerful synthetic tool of the hydroboration reaction, when coupled with oxidation, represents a convenient procedure for the *cis-anti*-Markovnikov hydration of carbon-carbon multiple bonds. Consequently, we undertook a detailed study of this reaction with special emphasis on establishing the conditions for the oxidation of organoboranes, particularly in the presence of functional groups.

RESULTS AND DISCUSSION

The present study was primarily intended to examine the effect of peroxide concentration, base concentration, temperature and solvents on the oxidation of trialkylboranes. The optimum oxidation conditions found in this way were applied to study the effect and stability of common organic functional groups. Finally, the organoboranes derived from alkenes of different structural types were oxidized under standard conditions in order to determine the effect of structure on the yield of alcohol.

The standard oxidation conditions selected for the present study were based on our previous experience from the oxidation of organoboranes. Thus, 50 mmol of 1-hexene in diglyme was treated with 15 mL of 1 *M* solution of sodium borohydride in diglyme (20% excess) and sufficient boron trifluoride etherate was added. The resulting tri-*n*-hexylborane was oxidized with 15 mmol of sodium hydroxide and 60 mmol of hydrogen peroxide (30-35%) at 25-35°C. The aqueous phase was saturated with anhydrous K_2CO_3 and the organic phase was analyzed by GC. The product was a 94% yield of alcohols (94% 1-hexanol, 6% 2-hexanol).

Effect of Peroxide Concentration. It is evident that one mole of hydrogen peroxide is required for the oxidation of each B–C bond (eq 1). The data in Table 1 indicate that either the use of excess hydrogen peroxide over the required amount or the concentration of hydrogen peroxide (30-35%, 15%, 7.5%) has no significant effect on the yield of alcohol. Some decomposition of hydrogen peroxide was observed when it was added simultaneously with the alkali. These results confirm that for the oxidation of one B–C bond, an equivalent amount of hydrogen peroxide is required. In practice, use of a 20% excess hydrogen peroxide is recommended, taking into account the loss due to decomposition.

$$R_3B + 3\ H_2O_2 \longrightarrow 3\ ROH + B(OH)_3 \qquad (1)$$

Table 1. Effect of Hydrogen Peroxide Concentration and Amount on the Oxidation of Tri-*n*-hexylborane[a]

H_2O_2, mmol	NaOH, mmol	*n*-HexOH,[b] %
60	15	94
60[c]	15	97
60[d]	15	92
30	15	50
43	45	80
57	45	97
72	45	97
90	45	97

[a] Tri-*n*-hexylborane (16.6 mmol) in diglyme and a 30-35% solution of H_2O_2 were used, unless mentioned otherwise. [b] Combined yield of 1-hexanol and 2-hexanol determined by GC. [c] A 15% H_2O_2 solution was used. [d] A 7.5% H_2O_2 solution was used.

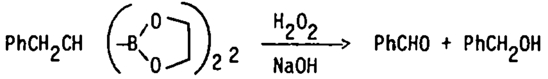
Table 2. Effect of Base on the Oxidation of Tri-*n*-hexylborane With Hydrogen Peroxide[a]

Base	Mmol	Temp., °C	Yield,[b] %
none		25-35	56
none		70-80	67
NaOH	15	25-35	94
	30	25-35	92
	45	25-35	97
Na_2CO_3	30	25-35	85
Na_3PO_4	30	25-35	74
$Na_2B_4O_7$	30	25-35	70
NaOAc	30	25-35	62
	30	70-80	87

[a] Tri-*n*-hexylborane (16.6 mmol) and 60 mmol of 30-35% H_2O_2 were used. [b] Combined yield of 1-hexanol and 2-hexanol determined by GC.

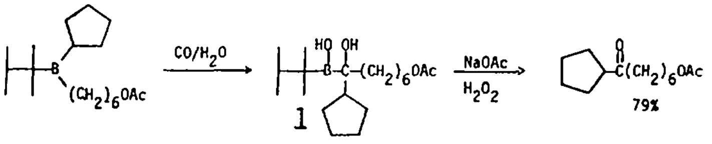
Effect of Base. The oxidation of tri-*n*-hexylborane is essentially quantitative in the presence of the stoichiometric amount of sodium hydroxide. An excess of base does not affect the yield of hexanol. On the other hand, oxidation in the absence of base results in significantly lower yields of hexanol. Similarly, in the presence of weaker bases, the yields were noticeably lower Table 2). It is noteworthy that the basicity, rather than nucleophilicity, of the reagent is important for complete oxidation. The base acts as a catalyst to generate the hydroperoxide anion. Although the amount of base is not critical, one mole of sodium hydroxide per mole of borane is used in practice.

The reaction of organoboranes with neutral hydrogen peroxide leads to considerable amounts of radical coupling.[8] Such coupling has been observed in small amounts, even under alkaline conditions. In the oxidation of phenylethane-1,2- and -2,2-diboronic esters with alkaline hydrogen peroxide, unexpected products have been noted (eq 2).[9] The oxidation of alkylboronic acids has also been carried out under mild conditions.[10]



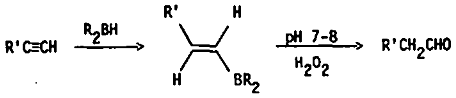
(2)

A wide range of bases catalyze the oxidation of organoboranes with hydrogen peroxide. Consequently, it is possible to apply this method in a variety of synthetic operations. For example, the borane intermediate (1), obtained from the carbonylation of thexyldialkylborane, has been oxidized to ketone without affecting the acetate functionality (eq 3).[11] Likewise, sodium acetate was used in the oxidation of cyclopropylboron derivatives to cyclopropanol.[12] In the presence of trimethylamine (to inhibit hydrolysis), tricrotylborane has been oxidized without rearrangement.[13]



(3)

In view of the instability of aldehydes to strong, bases, hydrogen peroxide at controlled pH has been employed where the product is an aldehyde (eqs 4 and 5).[14,15]



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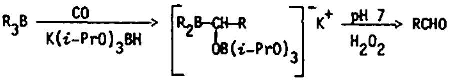
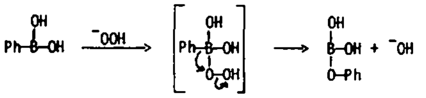


(5)

Mechanism of Oxidation. Kinetic investigations by Kuivila and coworkers[16] revealed that the oxidation of phenylboronic acid is independent of pH and is base-catalyzed. These results are compatible with the following mechanism in which the preoxide anion coordinates with the electron-deficient boron. The intramolecular migration of the phenyl group from the electron-rich boron atom to the electron-deficient oxygen, accompanied by the displacement of hydroxide ion, affords the borate ester (eq 6). A similar mechanism is proposed for the oxidation of the borinic acids.[17]

The reaction of alkylboronic acids with hydrogen peroxide has been shown to proceed via an S_E2 mechanism and the relative migratory aptitudes are in the order: bridgehead > tertiary > secondary > primary > vinyl ∿ phenyl > methyl.[10b]



(6)

The oxidation of trialkylborane proceeds accordingly in three successive stages. In aqueous solution, the resulting trialkylborate is hydrolyzed to alcohol and boric acid, the latter being converted to sodium borate in the presence of sodium hydroxide (eq 7). The mechanism shown in eq 6 is consistent with the observed retention of configuration in the hydration of alkenes via hydroboration-oxidation.[18]

$$R_3B + 3\ H_2O_2 + NaOH \longrightarrow 3\ ROH + NaB(OH)_4 \qquad (7)$$

Effect of Temperature. In earlier applications of hydrogen peroxide oxidation, drastic conditions were employed. A detailed study revealed that organoboranes are oxidized at temperatures ranging from 0-80°C essentially quantitatively (Table 3).

Effect of Solvent. The hydroboration reaction is generally carried out in diglyme or THF. When organoboranes were oxidized in these solvents, no difficulties were encountered. However, significantly lower yields were realized when the oxidation was carried out in diethyl ether, presumably because of the immiscibility of this solvent with water. Since diethyl ether is a common solvent, it offers several advantages, especially when the ether-soluble reagents, such as lithium borohydride or lithium aluminum hydride, are used as the hydride sources. In order to circumvent this difficulty, the effect of higher temperature, vigorous stirring and of cosolvent on the oxidation of tri-*n*-hexylborane in ether was investigated.

Table 3. Effect of Temperature on the Oxidation of Tri-*n*-hexylborane[a]

Temp., °C	Yield, %
0-5	97
25-35	96
50-55	94
75-80	89

[a]The oxidation was carried out with 16.6 mmol of borane, 60 mmol of 30-35% H_2O_2 and 45 mmol of sodium hydroxide.

The hydroboration of 1-hexene was carried out in diethyl ether using lithium borohydride and boron trifluoride etherate. As seen from the data in Table 4, vigorous stirring or heating the reaction mixture under reflux provides hexanol in nearly quantitative yield. An alternative procedure has been reported in which ether is replaced by ethanol following the completion of hydroboration.[19]

Table 4. Effect of Solvent on the Oxidation of Tri-*n*-hexylborane[a]

Solvent	Temp., °C	Yield, %
diglyme	25-35	94
tetrahydrofuran	25-35	93
diethyl ether	25-35	61
diethyl ether[b]	25-35	90
diethyl ether	reflux	92
diethyl ether + ethanol	25-35	98

[a]Hydroboration with $LiBH_4$ and $BF_3{\cdot}OEt_2$. Oxidation of 16.6 mmol of tri-*n*-hexylborane with 60 mmol of H_2O_2 and 15 mmol of NaOH. [b]Vigorous stirring.

Table 5. Effect of the Structure of Alkenes on Oxidation[a]

Alkene	ROH Yield, %
1-hexene	94
2,4,4-trimethyl-1-pentene	95
cyclohexene	97
2-methyl-2-butene[b]	98
2,4,4-trimethyl-2-pentene[c]	78
1,2-dimethylcyclohexene[c]	82
styrene	99

[a]50 mmol of alkene was hydroborated and oxidized: 60 mmol of H_2O_2 (30%), 15 mmol of NaOH. [b]Hydroboration to the dialkylborane stage. [c]Hydroboration to the monoalkylborane stage.

However, we found that a high yield of hexanol can be obtained with less experimental work by simply adding ethanol as a cosolvent.

Effect of the Structure of Alkenes on Oxidation. The present study reveals that under the standard oxidation conditions, the secondary and tertiary alkyl groups on boron are oxidized with the same ease as primary alkyl groups. In all cases, alcohols were obtained in 80-99% yield (Table 4).

Functional Group Tolerance in the Hydrogen Peroxide Oxidation. In the preceding sections it was shown that the oxidation of organoboranes can be carried out under mild conditions. In a number of cases the hydroboration of alkenes and alkynes has been carried out in the presence of certain functional groups, such as esters, nitriles, alkyl halides, etc.[20] If such functional groups can be tolerated under the conditions of oxidation, the synthetic applications of hydroboration-oxidation would be greatly enhanced. Consequently, it appeared interesting to examine the stability of such functional groups under the oxidation conditions.

In the present study, the effect of common functional groups in the oxidation of tri-*n*-hexylborane was examined. The hydroboration of 50 mmol of 1-hexene was carried out in diglyme, as already described. The excess of hydride was decomposed by adding water and 50 mmol of the chosen compound containing the desired fucntional group. The organoborane, in the presence of added compound, was oxidized by adding 60 mmol of hydrogen peroxide (30%) and 15 mmol of sodium hydroxide. The aqueous layer was saturated with anhydrous potassium carbonate and the organic layer was analyzed by GC for hexanols and the remaining added compound. In some cases, the reaction mixture was extracted with ether. The results are summarized in Table 6.

These results indicate that alkenes, alkynes, esters, ketones, halides and nitriles are stable under the standard oxidation conditions and do not interfere with the oxidation of organoboranes. Thioethers and aldehydes are not affected significantly by alkaline hydrogen peroxide. Recently, a method for the selective oxidation of organoboranes in the presence of thioethers has been developed.[21]

The satisfactory stability of aldehydes under these conditions permits the oxidation of terminal vinylboranes to the corresponding aldehydes (eq 4).[14] Thus, the vinylborane derived from 1-octyne and *bis*(3-methyl-2-butyl)borane (disiamylborane) was oxidized at 0°C with a 15% solution of hydrogen peroxide, maintaining the pH of the reaction mixture between 7 and 8 by the controlled addition of 3 *N* sodium hydroxide. *n*-Octanal was obtained in 70% yield.[14]

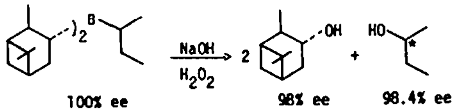
Table 6. Functional Group Tolerance in the Oxidation of Tri-*n*-hexylborane[a]

Added Compound	Compound Recovered, %	1- + 2-HexOH, %
1-hexene	96	95
1-hexyne	92	100
3-hexyne	98	95
1,3-cyclohexadiene	96	95
2-butanone	94	99
isobutryaldehyde[b]	80	93
isobutyaldehyde[c]	83	99
ethyl acetate	92	95
n-butyl bromide	93	99
acetonitrile	97	99
phenyl-*n*-propyl sulfide[d]	95	92
1,4-oxathiane[d,e]		98

[a] Tri-*n*-hexylborane (16.6 mmol) and the compound (50 mmol) were treated with sodium hydroxide (15 mmol) and hydrogen peroxide (60 mmol). [b] Extracted with ether prior to analysis. [c] Ether extraction immediately after peroxide oxidation. [d] Experiment carried out in THF. [e] See ref. 21. Experiment carried out with tri-*n*-octylborane; 45 mmol of NaOH was added to suppress the oxidation of 1,4-oxathiane; only 50 mmol of H_2O_2 was used.

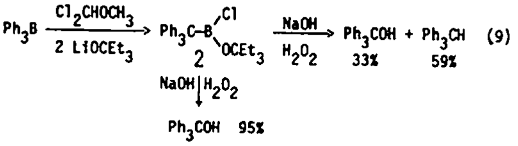
Oxidation of organoboranes containing some other functional groups appears to offer no difficulties. Thus, vinyltrimethylsilane was converted to the corresponding alcohol.[22] Both *p*-chlorostyrene and *p*-methoxystyrene were converted to the corresponding alcohols in good yields.[23] More recently, a number of functionally substituted alkenes have been transformed into the corresponding alcohols via hydroboration-oxidation.[20]

When the oxidation involves the replacement of boron from a chiral center, no racemization is observed (eq 8).[24]



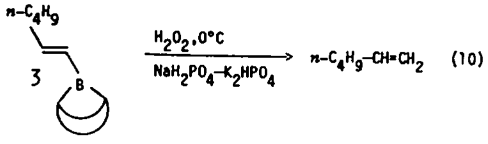
(8)

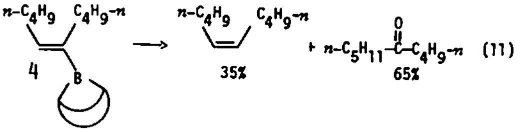
Although the alkaline hydrogen peroxide oxidation appears to be quite general for the conversion of alkylboron derivatives into the corresponding alcohols, undesirable side-products were obtained in some cases. The intermediate (2) obtained by the reaction of triphenylborane with α,α-dichloromethyl methyl ether in the presence of base gave predominantly the protonolysis product upon standard oxidation. Use of sodium acetate, however, afforded the desired carbinol (eq 9).[25] While the vinylboranes have been successfully oxidized to aldehydes (eq 4) and ketones using hydrogen peroxide in slightly basic media (pH 8), *B*-alkenyl-9-borabicyclo[3.3.1]nonanes (3, 4) failed to afford the expected carbonyl compounds cleanly under these conditions (eqs 10, 11).[26] Further study revealed that the *B*-alkenyl-9-BBN derivatives obtained from terminal alkynes react rapidly (< 5 min) with water, aqueous sodium hydroxide, methanol, and even with *t*-BuOH, with the quantitative formation of the corresponding terminal alkenes. Such facile protonolysis may be due to the more open steric environment of these boranes.



$$Ph_3B \xrightarrow[2\ LiOCEt_3]{Cl_2CHOCH_3} \underset{2}{Ph_3C{-}B(Cl)(OCEt_3)} \xrightarrow[H_2O_2]{NaOH} \underset{33\%}{Ph_3COH} + \underset{59\%}{Ph_3CH} \tag{9}$$

$$\underset{2}{Ph_3C{-}B(Cl)(OCEt_3)} \xrightarrow{NaOH|H_2O_2} \underset{95\%}{Ph_3COH}$$





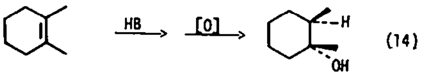
In one case, the highly hindered alkylboron derivative (5) resists oxidation even under drastic conditions (eq 12).[25] With sodium acetate, no

$$(s\text{-}C_4H_9)_3B \xrightarrow[2\ LiOCEt_3]{CHCl_2F} \underset{5}{(s\text{-}C_4H_9)_3C{-}B(F)(OECt_3)} \xrightarrow[excess]{NaOH,H_2O_2} \underset{21\%}{(s\text{-}C_4H_9)_3COH} + (s\text{-}C_4H_9)_3B(OH)(OCEt_3) \tag{12}$$

carbinol was obtained. Apparently the highly hindered boronic acid half-ester (6) resisted oxidation. This difficulty was circumvented by the treatment of 5 with an acid prior to oxidation (eq 13).[25]

$$5 \xrightarrow{CH_3SO_3H} (s\text{-}C_4H_9)_3C{-}B(OH)_2 \xrightarrow[H_2O_2]{NaOH} \underset{99\%}{(s\text{-}C_4H_9)_3COH} \tag{13}$$

Stereochemistry of Oxidation. A detailed investigation of the hydroboration of [*E*]- and [*Z*]-1-hexene-1,2-d_2 and the deuterioboration of [*E*]- and [*Z*]-1-hexene-1-*d* provides the direct evidence that the hydroboration reaction involves the cis addition of the boron-hydrogen moiety to the alkene unit.[27] Moreover, hydroboration-oxidation studies with acyclic,[28] cyclic,[18b] and bicyclic[18a] alkenes lead to the generalization that the alcohol obtained corresponds to a pure cis addition of the elements of water to the double bond, even though this results in the thermodynamically less stable isomer (eq 14).[18b] Consequently, hydroboration provides a valuable procedure for the synthesis of stereochemically defined alcohols.



CONCLUSIONS

The hydroboration reaction, with subsequent oxidation by alkaline hydrogen peroxide, provides a convenient method for the *cis-anti*-Markovnikov hydration of alkenes from the less hindered side. The oxidation occurs with the total retention of configuration, placing the hydroxyl group at the precise position occupied by the boron atom in the initial organoborane. The reaction proceeds under mild conditions, with no rearrangements of the carbon skeleton. Chiral alkyl groups are free from racemization and a number of common organic functional groups are unaffected under the reaction conditions. The precise regio- and stereochemistry of the hydroboration-oxidation sequence, coupled with satisfactory functional group tolerance, makes this operation highly popular in organic synthesis. Consequently, this is the most widely applied reaction in organoborane chemistry.[29,30]

EXPERIMENTAL SECTION

Materials. Diglyme, tetrahydrofuran, ether and boron trifluoride etherate were purified as described elsewhere.[31] The alkenes and alkynes were 95-99% pure (Phillips Petroleum and Farchan Research Laboratories). Other reagents were common laboratory chemicals, purified by conventional methods. The purities were ascertained by measuring refractive indices, by GC analysis, and by recording the NMR spectra.

Analyses. The GC analyses were carried out on a F&M-500 gas chromatograph 6 ft x 1/4 in columns packed with glycerol-acrylonitrile or Carbowax 20M deposited on Firebrick. Suitable internal standards were added for the quantitative GC analyses.

Methods. The techniques used in handling air-sensitive materials are described elsewhere.[31] All hydroboration and oxidation reactions were carried out under the atmosphere of dry nitrogen.

Standard Hydroboration-Oxidation (in Diglyme) Procedure. A dry 100-mL three-necked flask equipped with a thermometer well, reflux condenser, pressure-equalizing funnel and a magnetic stirring bar was charged with 20 mL of a 2.5 *M* solution of 1-hexene (50 mmol) in diglyme and 15 mL of a 1 *M* solution of sodium borohydride in diglyme (15 mmol, 20% excess). Diborane was generated by adding 2.53 mL of $BF_3{\cdot}OEt_2$ (20 mmol, 20% excess) in 4 mL of diglyme to the well-stirred reaction mixture over a period of 5-10 min, maintaining the flask at 25-35°C. The flask was kept at this temperature for an additional hour. The excess of hydride was decomposed by adding 2 mL of water and the organoborane was oxidized by adding 5 mL of 3 *N* NaOH (15 mmol), followed by 6 mL of 30% H_2O_2[32] at such a rate that a reaction temperature of 25-35°C was maintained when the flask was immersed in an ice bath. A total of 0.5 h was required. The flask was cooled to 0-5°C and NaOH pellets (5 g) were added with vigorous stirring. When the two phases separated, cyclohexanol (50 mmol) was added as an internal standard. A few mL's of the organic phase were withdrawn, dried over anhydrous $MgSO_4$ and analyzed by GC using a glycerol-acrylonitrile column. The results of these experiments are summarized in Tables 1-6. For the study of stability of certain functional groups, the chosen compound was added prior to the addition of $NaOH/H_2O_2$.

Oxidation of Tri-*n*-hexylborane in the Presence of Phenyl *n*-Propyl Sulfide (in THF). In a 100-mL reaction flask equipped as described above was placed 0.92 g of 1-hexene (11 mmol). To this flask was added 15 mL of 0.3 *M* solution of $BH_3 \cdot THF$ slowly at 0-5°C and the reaction mixture was maintained at this temperature for 1 h. Residual hydride was decomposed by adding 1 mL of water. To this mixture were added 1.52 g of phenyl propyl sulfide (10 mmol) and 0.92 g of 2-bromo-*p*-xylene (5 mmol, an internal standard for GC analysis). Oxidation was carried out by adding 1.5 mL of 3 *N* NaOH (4.5 mmol) and 1.65 mL of 22% H_2O_2 (11 mmol), maintaining the temperature at 0-5°C. The mixture was allowed to warm to room temperature, the aqueous phase was saturated with solid K_2CO_3, the organic layer was separated and the aqueous layer was extracted with ether (2 x 5 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and analyzed by GC on a Carbowax 20M column. The analysis revealed 9.54 mmol (95.4% recovery) of phenyl propyl sulfide, 9.43 mmol of 1-hexanol, and 0.66 mmol of 2-hexanol (a total yield of 92% for hexanols).

REFERENCES AND NOTES

1. For part 1 in this series, see: H. C. Brown and K. J. Murray, preceding paper in this issue.
2. Postdoctoral research associates on grants from a) the National Science Foundation and Ethyl Corporation (1959-1960). b) Ethyl Corporation (1958-1959). c) Upjohn Company, Park Davis & Company, and Merck & Company (1955-1957).
3. A. D. Ainley and F. Challenger, *J. Chem. Soc.*, 2171 (1930).
4. a) H. R. Snyder, J. A. Kuck and J. R. Johnson, *J. Am. Chem. Soc.*, 60, 105 (1938). b) J. R. Johnson and M. G. Van Campen, *J. Am. Chem. Soc.*, 60, 121 (1938).
5. R. Belcher, D. Gibbons and A. Sykes, *Mikrochim. Acta*, 40, 76 (1952).
6. H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, 78, 5694 (1956).
7. H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, 82, 4708 (1960).
8. a) H. C. Brown and D. J. Burton, unpublished results. b) D. B. Bigley and D. W. Payling, *J. Chem. Soc. B*, 1811 (1970).
9. D. J. Pasto, S. K. Arora and J. Chow, *Tetrahedron*, 25, 1571 (1969).
10. a) B. M. Mikhailov, P. M. Aronovich and V. G. Kiselev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 146 (1968). b) H. Minato, J. C. Ware and T. G. Traylor, *J. Am. Chem. Soc.*, 85, 3024 (1963).
11. E. Negishi and H. C. Brown, *Synthesis*, 196 (1972).
12. H. C. Brown and S. P. Rhodes, *J. Am. Chem. Soc.*, 91, 4306 (1969).
13. B. M. Mikhailov and V. F. Pozdnev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1477 (1967).
14. H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, 83, 3834 (1961).
15. H. C. Brown, J. L. Hubbard and K. Smith, *Synthesis*, 701 (1979).
16. H. G. Kuivila and A. G. Armour, *J. Am. Chem. Soc.*, 79, 5659 (1957).
17. W. T. Wechter, *Chem. & Ind. (London)*, 294 (1959).
18. a) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, 81, 247 (1959). b) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, 83, 2544 (1961). c) E. L. Allred, J. Sonnenberg and S. Winstein, *J. Org. Chem.*, 25, 26 (1960).
19. F. Sondheimer and S. Wolfe, *Can. J. Chem.*, 37, 1870 (1959).
20. H. C. Brown and J. C. Chen, *J. Org. Chem.*, 46, 3978 (1981) and references cited therein.
21. H. C. Brown and A. K. Mandal, *J. Org. Chem.*, 45, 916 (1980).
22. D. Seyferth, *J. Inorg. Nucl. Chem.*, 7, 152 (1958).
23. H. C. Brown and R. L. Sharp, *J. Am. Chem. Soc.*, 88, 5851 (1966).
24. a) H. C. Brown and N. M. Yoon, *Israel J. Chem.*, 15, 12 (1977). b) For more examples, see: H. C. Brown, P. K. Jadhav and A. K. Mandal, *Tetrahedron*, 37, 3547 (1981).
25. B. A. Carlson, Ph.D. Thesis, Purdue University, 1973.
26. C. G. Scouten, Ph.D. Thesis, Purdue University, 1975.
27. G. W. Kabalka, R. J. Newton and J. Jacobus, *J. Org. Chem.*, 43, 1567 (1978).
28. a) G. W. Kabalka and N. S. Bowman, *J. Org. Chem.*, 38, 1607 (1973). b) D. E. Bergbreiter and D. P. Rainville, *J. Org. Chem.*, 41, 3031 (1976).
29. H. C. Brown, G. W. Kramer, A. B. Levy and M. M. Midland, "Organic Syntheses via Boranes," Wiley-Interscience, New York, 1975.
30. a) G. M. L. Cragg, "Organoboranes in Organic Synthesis," Marcel Dekker, New York, 1973. b) A. Pelter and K. Smith in "Comprehensive Organic Chemistry," D. Barton and W. D. Ollis, Eds., Pergamon Press, Oxford, 1979, Vol. 3, Chapter 14.
31. Chapter 9 of reference 28.
32. The concentration of hydrogen peroxide was determined by density measurements and by the measurement of oxygen evolved on catalytic decomposition with solver. For details, see: W. C. Schumb, C. N. Satterfield and R. L. Wentworth, "Hydrogen Peroxide," Reinhold, New York, 1975, pp. 560, 563.