184°; therefore, it appears likely that the acid of m.p. 182–187° consisted of 2,2,4-triphenylbutanoic acid with less than 2 mole % impurity. A portion (2.00 g.) of the acid of m.p. 182–187° was recrystallized from benzene and then sublimed *in vacuo* to give 1.80 g. of acid, m.p. 186.1–187.1°. This acid gave no depression of m.p. when mixed with an authentic sample of 2,2,4-triphenylbutanoic acid.

The authentic sample of 2,2,4-triphenylbutanoic acid was prepared from 1,1,3-triphenylpropanol-1 which was made from 2-phenylethylmagnesium bromide and benzophenone after the method of Kharasch and Burt.[19] This alcohol was converted to its methyl ether and the ether was cleaved by Na–K alloy by the procedure of Ziegler and co-workers[6] ex-

cept that instead of shaking with the alloy, stirring for 6 hours on a high-speed stirrer[16] was employed. Carbonation of the reaction mixture gave after the usual isolation and purification procedure 2,2,4-triphenylbutanoic acid, m.p. 186.1–186.9° (recorded[6] m.p. 181°).

(19) M. S. Kharasch and J. G. Burt, *J. Org. Chem.*, **16**, 150 (1951).

Amine Boranes. VIII. The Hydroboration of Terminal Olefins, Dienes and Terminal Acetylenes with Trimethylamine *t*-Butylborane[1]

BY M. FREDERICK HAWTHORNE[2]

RECEIVED FEBRUARY 2, 1961

Trimethylamine *t*-butylborane reacted with terminal olefins to afford a convenient synthesis of *t*-butyldialkylboranes. Similarly, 1,4-pentadiene, 1,3-butadiene and 2-methyl-1,3-butadiene formed 1-*t*-butyl-1-boracycloalkanes when treated with trimethylamine *t*-butylborane. Divinyl ether and dimethyldivinylsilane afforded similar cyclic derivatives which contained an additional heteroatom. Terminal acetylenes and trimethylamine *t*-butylborane provide a route to *t*-butyl di-(1-alkenyl)-boranes of unknown stereochemistry.

The recent application of pyridine borane[3] and trimethylamine borane[4,5] to the hydroboration[6] of olefins suggested the possibility of similar reactions with the recently described trimethylamine alkylboranes.[7] As previously reported,[7] the latter materials were prepared by the lithium aluminum hydride reduction of alkylboronic anhydrides in the presence of trimethylamine.
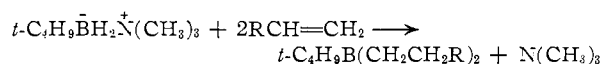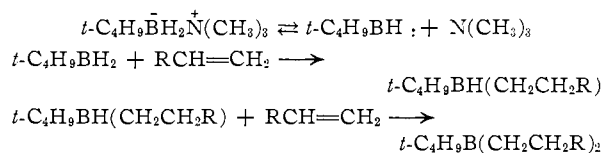
Hennion, McCusker and Rutowski[8] have convincingly demonstrated that the mixed trialkylborane, *t*-butyldiisobutylborane, is relatively stable toward disproportionation. This enhanced stability presumably arises from the large steric requirement of the *t*-butyl group in the transition state which leads to disproportionation.

Brown and Zweifel[9] have employed a sterically encumbered dialkylborane in their study of terminal acetylene hydroboration. This reagent was di-(3-methyl-2-butyl)-borane prepared from diborane and 2-methyl-2-butene. This same reagent was also employed to provide steric control of olefin hydroboration.[10] Thus the stabilization of mixed trialkylboranes and the moderation of the facile hydroboration reaction have been accomplished by the use of bulky alkyl substituents on boron. In view of these results and our own past experiences

with trialkylamine alkylboranes, it appeared to be possible to utilize a sterically moderated member of that series of reagents in selective hydroboration reactions. Such reactions could conceivably lead to the preparation of novel boranes. Trimethylamine *t*-butylborane was chosen as the hydroboration reagent and employed with such model substrates as terminal olefins, dienes and terminal acetylenes.

Results and Discussion

The reversible thermal dissociation of trimethylamine-*t*-butylborane[1] would produce *t*-butylborane. If this process were carried out in the presence of an unsaturated substrate the free *t*-butylborane might be easily captured to produce a hydroboration product. Since *t*-butylborane contains two boron—hydrogen bonds, this process could be repeated once again with the release of trimethylamine.[11]

$$t\text{-}C_4H_9\bar{B}H_2\overset{+}{N}(CH_3)_3 \rightleftarrows t\text{-}C_4H_9BH\text{:} + N(CH_3)_3$$

$$t\text{-}C_4H_9BH_2 + RCH{=}CH_2 \longrightarrow$$
$$t\text{-}C_4H_9BH(CH_2CH_2R)$$

$$t\text{-}C_4H_9BH(CH_2CH_2R) + RCH{=}CH_2 \longrightarrow$$
$$t\text{-}C_4H_9B(CH_2CH_2R)_2$$

$$t\text{-}C_4H_9\bar{B}H_2\overset{+}{N}(CH_3)_3 + 2RCH{=}CH_2 \longrightarrow$$
$$t\text{-}C_4H_9B(CH_2CH_2R)_2 + N(CH_3)_3$$

***t*-Butyldialkylboranes from Terminal Olefins.**— In contrast to the reactions of pyridine borane[3] and trimethylamine borane[4,5] with olefins, trimethylamine *t*-butylborane reacted readily with such simple olefins as ethylene and propylene at temperatures as low as fifty degrees. The amine

(1) Previously presented in part as a Communication to the Editor, *J. Am. Chem. Soc.*, **82**, 748 (1960).

(2) Visiting Lecturer, Harvard University, Fall, 1960.

(3) M. F. Hawthorne, *J. Org. Chem.*, **23**, 1788 (1958).

(4) R. Köster, *Angew. Chem.*, **69**, 684 (1957).

(5) E. C. Ashby, *J. Am. Chem. Soc.*, **81**, 4791 (1959).

(6) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957).

(7) M. F. Hawthorne, *J. Am. Chem. Soc.*, **81**, 5836 (1959).

(8) G. F. Hennion, P. A. McCusker and A. J. Rutowski, *ibid.*, **80**, 617 (1958).

(9) H. C. Brown and G. Zweifel, *ibid.*, **81**, 1512 (1959).

(10) H. C. Brown and G. Zweifel, *ibid.*, **82**, 3222 (1960); **82**, 322? (1960).

(11) Since the higher molecular weight trialkylboranes have low vapor pressures and form weak complexes with trimethylamine, this result was anticipated.

TABLE I

Reactions of Trimethylamine t-Butylborane with Unsaturated Substrates

Substrate	Product	Yield, %	B.p. °C.	Mm.	Calcd. C	Calcd. H	Calcd. B	Found C	Found H	Found B
Ethylene	t-Butyl diethylborane	35	60	70	76.22	15.19	8.59	75.92	14.96	8.66
Propylene	t-Butyldi-(1-propyl)-borane	88	67	22	77.93	15.04	7.03	77.68	14.93	6.91
1-Butene	t-Butyldi-(1-butyl)-borane	90	74	6	79.12	14.94	5.94	78.92	14.79	6.19
Isobutene	t-Butyldi-(i-butyl)-borane	85	62	7.5	79.12	14.94	5.94	78.99	14.76	6.08
1,3-Butadiene	1-t-Butyl-1-borocyclopentane	60	55	55	77.46	13.82	8.72	77.20	13.77	8.89
2-Methyl-1,3-butadiene	1-t-butyl-3-methyl-1-borocyclopentane	55	67	54	78.29	13.87	7.84	78.08	13.85	7.64
1,4-Pentadiene	1-t-Butyl-1-borocyclohexane	38	44	12	78.29	13.87	7.84	77.98	13.88	8.01
Divinyl ether	1-t-Butyl-1-boro-4-oxacyclohexane	70	90	56[a]	[b]	[b]	7.73	[b]	[b]	7.72
Dimethyldivinylsilane	1-t-Butyl-1-boro-4,4-dimethyl-4-silacyclohexane	58	44	2	65.93	12.73	5.94	66.16	12.83	6.11
1-Butyne	t-Butyldi-(1-butenyl)-borane	65	40	0.3	80.92	13.02	6.06	80.66	13.06	6.06
1-Pentyne	t-Butyldi-(1-pentenyl)-borane	41	65	.4	81.55	13.20	5.25	81.32	13.14	5.38
1-Hexyne	t-Butyldi-(1-hexenyl)-borane	70	72	.1	82.04	13.34	4.62	82.08	13.34	4.73

[a] M.p. 65–68°. [b] C and H analyses unavailable.

complexes of unsubstituted borane required much higher temperatures and longer reaction times for complete utilization in the hydroboration reaction. This greater reactivity of the t-butylborane derivative might be attributed to the greater rate of dissociation of its trimethylamine complex.[12]

The products of these reactions with simple olefins were trimethylamine and the corresponding t-butyldialkylboranes. These reactions were routinely carried out without solvent and the trialkylborane product was easily purified by fractional distillation at reduced pressures. Table I presents analytical and preparative data for the products obtained from ethylene, propylene, 1-butene and 2-methylpropene. The infrared spectra of the products contained no evidence of a B–H group but only bands commonly attributed to alkyl group absorptions. The H[1] nuclear magnetic resonance spectra were not easily interpreted since the alkyl groups gave resonance lines which often closely coincided with the relatively strong t-butyl group resonance. However, the spectrum obtained with t-butyldiisobutylborane was superimposible upon the spectrum obtained by Davies, Hare and White[13] except that the small and ambiguous resonance reported by these authors did not appear.[14] Due to the fact that the isobutyl group in t-butyldiisobutylborane and similar species[13] presents a resonance line at higher field than that which arises from the t-butyl group, the products obtained in this study were seen to be free of isobutyl group contamination. Such contamination could arise from the thermal isomerization of the t-butyl group. The highest field resonance line observed with all products, other than t-butyldiisobutylborane, was of very high intensity and centered near 5.87 p.p.m. higher field than benzene. This resonance line is assigned to the t-butyl group since it is essentially congruent with
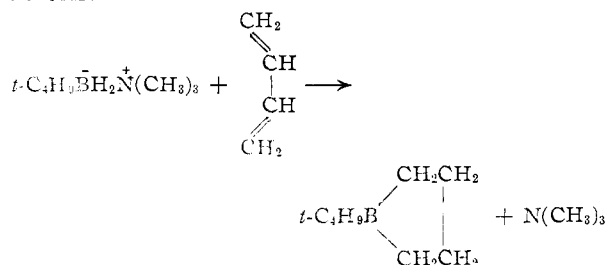
(12) Such an acceleration is not unexpected if the trimethylamine t-butylborane molecule is subject to "B-strain" not present in the trimethylamine borane species. This "B-strain" would be lost upon dissociation. See H. C. Brown and R. B. Johannesen, J. Am. Chem. Soc., 75, 16 (1953), for a summary of steric strains.

(13) A. G. Davies, D. G. Hare and R. F. M. White, J. Chem. Soc., 1040 (1960).

(14) In a private communication Dr. Davies (who examined our spectrum) suggested that this small line may be due to an oxidation product and not restricted rotation as previously proposed.[13]

that observed by Davies, Hare and White.[13] These data show that simple terminal olefins are hydroborated in the terminal position without rearrangement of the attached t-butyl group.

1-t-Butyl-1-boracycloalkanes and 1-t-Butyl-1-boracyclohexanes with an Additional Intracyclic Heteroatom.—The successful hydroboration of terminal olefins described above clearly illustrated the bifunctional character of t-butylborane. Thus, the reaction of t-butylborane with dienes was a logical extension of this reaction which was expected to yield cyclic products. Cyclic boranes of this type have been previously described by Köster.[15]

$$t\text{-}C_4H_9\bar{B}H_2\overset{+}{N}(CH_3)_3 + \begin{matrix} CH_2 \\ \diagdown\diagdown \\ CH \\ | \\ CH \\ \diagup\diagup \\ CH_2 \end{matrix} \longrightarrow$$

$$t\text{-}C_4H_9B\begin{matrix} CH_2CH_2 \\ \diagup \quad | \\ \quad \quad | \\ \diagdown \quad | \\ CH_2CH_2 \end{matrix} + N(CH_3)_3$$

Butadiene, isoprene and 1,4-pentadiene were found to react rapidly with trimethylamine t-butylborane to produce easily purified and air sensitive products. These products were assigned the structures 1-t-butyl-1-boracyclopentane, 1-t-butyl-1-bora-3-methylcyclopentane and 1-t-butyl-1-boracyclohexane, respectively. The preparative reactions were conducted at atmospheric pressure and at 65° without solvent. Table I presents the pertinent preparative and characterization data.

The H[1] nuclear magnetic resonance spectra of these substances exhibited the resonance line attributed to the t-butyl group (vide ultra) plus undefined resonances at slightly lower field. In addition, the spectrum obtained with the 1,4-pentadiene product contained a small shoulder on the high field side of the strong t-butyl group resonance line. This shoulder is attributed to the 4-methylene group of 1-t-butyl-1-boracyclohexane product rather than

(15) R. Köster, Angew. Chem., 520, 521 (1959) briefly reports the preparation of 1-alkyl-1-boracyclopentanes and the analogous cyclohexane derivatives.

to contamination of the analytical sample by the B-isobutylisomer.

Infrared spectra of each of these products was devoid of absorptions characteristic of boron–hydrogen bonds or carbon–carbon double bonds. Furthermore, the boiling points of purified products were sufficiently low to rule out the unlikely possibility of dimer formation.

Divinyl ether and trimethylamine t-butylborane were allowed to react without solvent at atmospheric pressure and at 70°. As the reaction proceeded a volatile crystalline solid was seen to form. This material proved to be the principal reaction product. Purification was carried out by distillation or by recrystallization from pentane at low temperatures. The purified product (m.p. 65–68°) was exceedingly reactive toward traces of oxygen but glove-box techniques allowed a determination of its molecular weight and H^1 nuclear magnetic resonance spectrum. Attempts to obtain its C and H analyses were fruitless with the techniques available. A boron analysis was obtained by the analysis of aliquots of a solution of known concentration prepared in acetonitrile in the glove-box. These analytical results are shown in Table I. The molecular weight was obtained in benzene solution by the cryoscopic method (found 142 and 144, theory 140). The H^1 nuclear magnetic resonance spectrum obtained was in excellent agreement with the assigned structure.
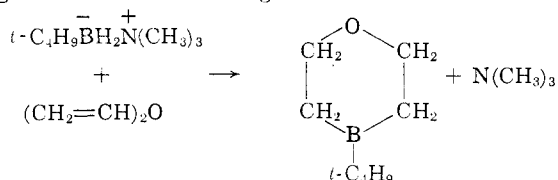
Two triplets of equal area were observed at +2.68 and +4.96 p.p.m. relative to a benzene internal standard. These triplets may be assigned to the two methylene groups bonded to oxygen (low field triplet) and the two methylene groups bonded to boron (high field triplet). The t-butyl group was observed as a single sharp peak at +5.56 p.p.m. An estimate of resonance peak areas (4:4:9) agreed with this assignment.

Dimethyldivinylsilane and trimethylamine t-butylborane reacted in a similar fashion to afford an easily purified liquid product. Analyses proved this product to be 1 : 1 adduct.
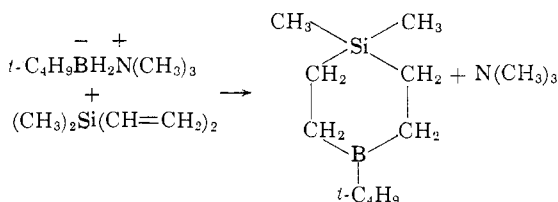
The H^1 nuclear magnetic resonance spectrum was characterized by the t-butyl group resonance at +5.75 p.p.m., a poorly defined triplet centered at +5.38 p.p.m. and an additional pair of sharp peaks with shoulders centered near +6.70 p.p.m. relative to benzene. The low field triplet may be assigned to the two methylene groups which are bonded to boron. The remaining absorptions

which appear at high field may be assigned to the two methyl groups and the two methylene groups which are bonded to silicon and give nearly identical resonances. The infrared spectrum of this compound was compatible with the assigned structure in that no B–H or carbon–carbon double bond absorptions were seen.

t-Butyldi-(1-alkenyl)-boranes from Terminal Acetylenes.—The reactions of trimethylamine t-butylborane with the terminal acetylenes 1-butyne, 1-pentyne and 1-hexyne were examined. In each case the reaction was strongly exothermic and required the use of tetrahydrofuran as a temperature moderating solvent. The selected reaction temperature was 60° and the reaction products were separated and purified by fractional distillation at reduced pressures. Table I records the preparative and characterization data obtained in these reactions.

$$t\text{-}C_4H_9\overset{-}{B}H_2\overset{+}{N}(CH_3)_3 + 2RCH\!\!\equiv\!\!CH \longrightarrow$$
$$t\text{-}C_4H_9B(CH\!\!=\!\!CHR)_2 + N(CH_3)_2$$
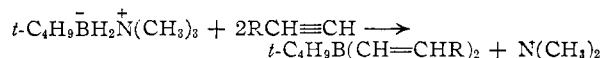
Aside from the analytical data presented in Table I the infrared absorption spectrum and the H^1 nuclear magnetic resonance spectrum of each of the products supported their assigned structures. In the infrared, each product displayed strong carbon–carbon double bond absorption at 6.20 μ and strong absorption at 10.0 μ. The H^1 nuclear magnetic resonance spectra contained the strong resonance line of the t-butyl group at 5.92 p.p.m. higher field than benzene and an unresolved peak at 0.50 p.p.m. higher field than benzene. The latter peak is attributed to the two hydrogen atoms attached to unsaturated carbon atoms. Other resonance lines were observed which were not clearly resolved but were nonetheless compatible with alkyl group resonances.

Additional evidence for the assigned structures was the oxidation of the product from 1-butyne with dilute hydrogen peroxide to produce n-butyraldehyde. Similar oxidation reactions were previously demonstrated by Brown and Zweifel in their study of terminal acetylene hydroboration.[9]

Although the products derived from terminal acetylenes in this study are undoubtedly t-butyl-di-alkenyl boranes, their steric arrangement about the carbon–carbon double bond is presently unknown.

Examination of the B^{11} nuclear magnetic resonance spectrum of the t-butyldi-(1-butenyl)-borane obtained in this study revealed a single resonance line centered at 40 p.p.m. lower field than trimethyl borate. The position of this peak is considerably displaced toward trimethyl borate in comparison with the B^{11} resonances obtained with simple trialkylboranes.[16] The latter materials exhibit B^{11} resonances near 60 p.p.m. lower field than trimethyl borate. This result suggests that either hybridization changes are important or that the boron atom receives some electron release from the 1-alkenyl group in the ground state.

Experimental

Trimethylamine t-butylborane was prepared as previously described.[7] All other reagents were of the highest purity commercially available.

(16) W. D. Phillips, H. C. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).

General Procedure for the Hydroboration of Gaseous Olefins and Dienes.—One-tenth mole (13.0 g.) of crude trimethylamine *t*-butylborane was placed in a 50-ml. three-necked flask equipped with a gas inlet tube, reflux condenser, thermometer and magnetic stirrer. The system was flushed with the desired olefin or diene and the temperature of the reaction vessel slowly raised to 60° with stirring. At this point the pressure began to fall in the reaction vessel and a slow stream of olefin or diene was passed through the reaction mixture. Trimethylamine was observed at the gas bubbler which served as an outlet of the reflux condenser. After approximately 2 hours, trimethylamine ceased to be evolved and the reaction system was purged with nitrogen and cooled. The liquid products were transferred to a spinning-band distillation column and separated by distillation at reduced pressures. Air was excluded at all times. Table I presents the boiling points, yields and analyses of the products obtained.

General Procedure for the Hydroboration of Liquid Dienes.—The procedure employed here was identical to that described above with two exceptions. A Dry Ice cooled condenser was employed and the theoretical quantity of diene was added from a small dropping funnel in a slow stream of nitrogen. The cessation of trimethylamine evolution signaled the completion of the reaction.

The Preparation of 1-*t*-Butyl-1-bora-4-oxacyclohexane.—In a 100-ml. three-necked round-bottom flask was placed 22.5 g. (0.173 mole) of crude trimethylamine *t*-butylborane. The system was equipped with a Dry Ice cooled reflux condenser, a magnetic stirrer and a small pressure-equalized dropping funnel which carried a nitrogen inlet. The Dry Ice cooled condenser was attached to a gas bubbler which served as a seal to the atmosphere. Divinyl ether (12 g., 0.173 mole) was added to the dropping funnel, the system flushed with dry nitrogen and heating commenced. When the reaction mixture reached 60°, divinyl ether as added dropwise over a period of 3 hours. During the addition white crystals formed on the reflux condenser and the upper portions of the reaction flask. The reaction mixture was cooled to room temperature in a stream of nitrogen and 50 ml. of pentane was added through the reflux condenser. By cooling the resulting pentane solution to −80°, a large amount of crystalline product was collected by filtration in an air-free glove-box (m.p. 65–68°). The extreme reactivity of the product with air did not suggest this method of isolation for preparative use. As an alternative isolation

method, the pentane solution of product was distilled with a spinning-band distillation column and the product collected at 90° (56 mm.). The yield amounted to 17.0 g. or 70% of theory. Analysis for carbon and hydrogen was impossible due to the extreme air sensitivity of the product. However, two solutions of known concentration in benzene were prepared in the glove-box. These solutions were employed in a cryoscopic determination of the molecular weight (found 142 and 144, theory 140). Aliquots of these same benzene solutions were then analyzed.

Anal. Calcd., B: 7.73. Found: B, 7.72.

General Procedure for the Hydroboration of Terminal Acetylenes.—One-tenth mole (13.0 g.) of crude trimethylamine *t*-butylborane was dissolved in 75 ml. of purified tetrahydrofuran and employed in accordance with the general procedures described above. The reaction temperature was 60° in all cases and the products were isolated by distillation as described above.

Oxidation of *t*-Butyldi-(1-butenyl)-borane to *n*-Butyraldehyde.—Three grams of purified *t*-butyldi-(1-butenyl)-borane dissolved in 20 ml. of pure diethyl ether was added dropwise with cooling and stirring to a solution of 15 ml. of water, 5 ml. of 30% hydrogen peroxide and 2 ml. of 10% sodium hydroxide. Following the addition the mixture was stirred at 0° for 15 minutes, the ether layer separated and washed with saturated aqueous ferrous ammonium sulfate which contained 5% sulfuric acid. The ether layer was then treated with an equal volume of saturated alcoholic 2,4-dinitrophenylhydrazine hydrochloride and allowed to stand at room temperature overnight. Removal of solvent followed by chromatography on alumina with benzene solvent afforded 0.90 g. of *n*-butyraldehyde 2,4-dinitrophenylhydrazone (m.p. 121–122°) which was identical to an authentic sample in the infrared.

Nuclear Magnetic Resonance Measurements.—All nuclear magnetic resonance measurements were carried out on neat samples with benzene or trimethyl borate as an internal reference sealed in a capillary insert.

Hydroboration. IX. The Hydroboration of Cyclic and Bicyclic Olefins—Stereochemistry of the Hydroboration Reaction

BY HERBERT C. BROWN AND GEORGE ZWEIFEL[1]

The hydroboration of 1-methylcyclopentene, 1-methylcyclohexene and 1-phenylcyclohexene, followed by oxidation with alkaline hydrogen peroxide, yields the pure (>99%) *trans*-2-methylcyclopentanol, *trans*-2-methylcyclohexanol and *trans*-2-phenylcyclohexanol, corresponding to a pure *cis* hydration of the double bond. (However, 1-methylcycloöctene yielded several isomeric alcohols, presumably arising from a facile rearrangement of the organoborane formed initially.) That the stereochemistry of the reaction is not controlled by the stability of the product is revealed by the products obtained from 1,2-dimethylcyclopentene and 1,2-dimethylcyclohexene. In each case 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. Norbornene yields *exo*-norborneol. These results lead to the generalization that hydroboration proceeds through a *cis-anti*-Markownikoff addition of the boron–hydrogen bond to the carbon–carbon double bond, the reaction proceeding preferentially from the less hindered direction. In support of this generalization are the observations that hydroboration–oxidation converts α-pinene into isopinocampheol, β-pinene into *cis*-myrtanol, and camphene into *endo*-camphanol. 1-Methylcyclopentene and 1-methylcyclohexene are cleanly converted into 3-methylcyclopentene and 3-methylcyclohexene by (1) hydroboration, (2) oxidation, (3) tosylation and (4) elimination, providing a route of wide generality for the synthesis of 3-alkyl-cycloalkenes. In the hydroboration of 3-methylcyclopentene, 3-methylcyclohexene and 3,3-dimethylcyclohexene, diborane exhibits little selectivity between the two carbon atoms of the double bond, with only a modest selectivity exhibited by bis-3-methyl-2-butylborane. Hydroboration provides a valuable procedure for the synthesis of stereochemically defined alcohols.

The hydroboration of unsymmetrically substituted acyclic olefins, followed by oxidation with alkaline hydrogen peroxide, provides a convenient

synthetic route for the anti-Markownikoff hydration of double bonds.[2] It appeared that a study of

(2) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **78**, 2582 (1956); H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957); H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **81**, 6423, 6428 (1959); H. C. Brown and G. Zweifel, *ibid.*, **82**, 4708 (1960).