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FOOTSTEPS ON THE BORANE TRAIL*

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Summary

The course of nearly four decades of research on the preparation and reactions of diborane and its derivatives is reviewed.

Introduction

With the growth of chemical research in recent years, there has been a growing tendency for chemical education to emphasize those topics of current interest. Relatively little attention is paid to the origins of each problem and concept and to the often tortuous path by which we have arrived at our present position in these areas. As a consequence, chemists thus trained appear to have a two-dimensional view of chemistry, they often lack the perspective of those trained in an earlier, less hurried time. My recent book, *Boranes in Organic Chemistry*, [1], was written in the hope that it might contribute to providing such perspective to its readers. The commemoration of the one hundredth volume of the *Journal of Organometallic Chemistry* appears to provide another opportunity to contribute to the amelioration of this problem.

Beginnings

The presentation to me in 1936 of the book by Alfred Stock, *Hydrides of Boron and Silicon* [2], as a graduation gift by my classmate (later my wife), Sarah Baylen, interested me in this exotic area. Accordingly, when I began graduate work at the University of Chicago in that year I decided to work with the late Professor H.I. Schlesinger on his program of research on the hydrides of boron. Such can be the momentous consequences of minor decisions, such as the selection of a particular title of a book to be presented as a gift!

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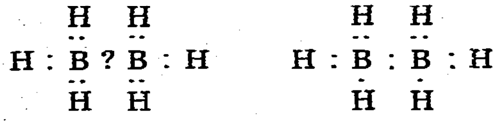
* Based in part upon the Roger Adams Award Address, *Boranes in Organic Chemistry*, presented to the Division of Organic Chemistry of the American Chemical Society in Ann Arbor, Michigan, June 15, 1971 (H.C. Brown, Advan. Organometal. Chem., 11 (1973) 1).

At that time, the structure of diborane was a subject of considerable study and speculation [2].

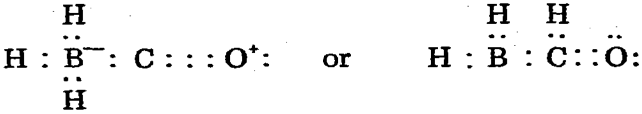


$$\mathrm{H} : \underset{\underset{\mathrm{H}}{\cdot\cdot}}{\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\mathrm{B}}} \; ? \; \underset{\underset{\mathrm{H}}{\cdot\cdot}}{\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\mathrm{B}}} : \mathrm{H} \qquad \mathrm{H} : \underset{\underset{\mathrm{H}}{\cdot}}{\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\mathrm{B}}} : \underset{\underset{\mathrm{H}}{\cdot}}{\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\mathrm{B}}} : \mathrm{H}$$

Professor H.I. Schlesinger was studying the reactions of diborane in the hope of obtaining information that would throw light on the problem of the structure. At the time I began, the synthesis of borane carbonyl had just been completed [3].

$(BH_3)_2 + CO \rightleftharpoons H_3B{:}CO$

There was discussion as to whether borane carbonyl was best represented as a simple addition compound, or whether the reaction involved migration of a hydride moiety from boron to carbon.



$$\mathrm{H} : \underset{\underset{\mathrm{H}}{\cdot\cdot}}{\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\mathrm{B}^{-}}} : \mathrm{C} : : : \mathrm{O}^{+} : \qquad \text{or} \qquad \mathrm{H} : \overset{\overset{\mathrm{H}}{\cdot\cdot}}{\mathrm{B}} : \overset{\overset{\mathrm{H}}{\cdot\cdot}}{\mathrm{C}} : : \overset{\cdot\cdot}{\mathrm{O}} :$$

It was suggested that I undertake a study of the reaction of diborane with aldehydes and ketones in the hope the results would contribute to a decision as to the structure of borane carbonyl.

I soon discovered that simple aldehydes and ketones react rapidly with diborane at 0°. Hydrolysis then produces the corresponding alcohol.

$$2\ R_2C{=}O + \tfrac{1}{2}(BH_3)_2 \rightarrow [R_2CHO]_2BH \xrightarrow{H_2O} 2\ R_2CHOH + H_2 + B(OH)_3$$

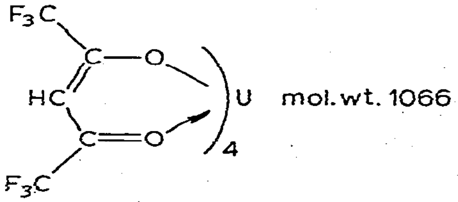
My thesis was completed in 1938 and the results were published in 1939: *Hydrides of Boron. XI. The Reaction of Diborane with Organic Compounds Containing a Carbonyl Group* [4].

Interest in this development among organic chemists was minimal. Diborane was a chemical rarity at the time, available only in milligram quantities through complex procedures. I wish I could say that we had the intelligence to recognize that this was an important synthetic procedure which would require only the development of a practical route to diborane to make it useful. However, we did not. We were later to do so as a result of research forced upon us by World War II.

Volatile compounds of uranium

This situation was altered late in 1941. Professor Schlesinger was asked by an agency of the Government to undertake a research program on the preparation of new volatile compounds of uranium. I had become his research assistant in 1939, so I became associated with this program.

Originally we undertook to prepare uranium(IV) acetonylacetonates and related derivatives. Indeed, the hexafluoroacetonylacetonate possessed promising characteristics.



However, when we happily reported this development the blow came. We were informed that there was a little requirement of which we had not been informed previously. It was necessary that the compound have a low molecular weight, preferably not higher than 238! Clearly this approach was not practical.

Just prior to this time, aluminum borohydride [5] and beryllium borohydride [6] had been prepared in our laboratories, $Be(BH_4)_2$ and $Al(BH_4)_3$. These are the most volatile compounds known of beryllium and aluminum. Accordingly, it was decided to undertake the preparation of uranium borohydride, $U(BH_4)_4$.

Accordingly, in the usual high vacuum apparatus I placed aluminum borohydride onto a sample of uranium tetrafluoride. I observed an immediate reaction, with formation of green crystals which could be moved about the vacuum apparatus. As it happened, on the very day I was performing the synthesis, we had a visit from Professor H.C. Urey, who was in charge of the overall study. He immediately asked us to increase our research effort and undertake to prepare uranium tetraborohydride on a relatively large scale, adequate for testing.

The alkali metal hydride synthesis of diborane [7]

At this time the only known routes to diborane was that introduced by Stock involving hydrolysis of magnesium boride [2], and that developed by Schlesinger and Burg involving the reaction of boron trichloride with hydrogen in the silent electric discharge [8]. These methods made diborane available in relatively small quantities, inadequate for our requirements in synthesizing uranium(IV) borohydride in the desired quantity. Consequently, we were forced to consider new approaches.

We soon discovered that lithium hydride would reduce boron trifluoride in ethyl ether solution to give diborane.

$$6\ LiH + 8\ BF_3{:}OEt_2 \xrightarrow{Et_2O} (BH_3)_2 + 6\ LiBF_4$$

Lithium hydride added diborane to form lithium borohydride.

$$LiH + \tfrac{1}{2}(BH_3)_2 \xrightarrow{Et_2O} LiBH_4$$

Lithium borohydride reacted with aluminum chloride to produce aluminum borohydride.

$AlCl_3 + LiBH_4 \xrightarrow{\Delta} Al(BH_4)_3\uparrow + 3\ LiCl$

Finally, uranium borohydride could be produced by the method we had originally used.

$UF_4 + 2\ Al(BH_4)_3 \rightarrow U(BH_4)_4 + 2\ AlF_2BH_4$

This was obviously a major improvement over the original procedure, which involved many more steps, some of them quite difficult. We happily reported this improved synthesis and undertook to use it to produce uranium(IV) borohydride for large scale testing.

We were then informed that lithium was in very short supply and could not be used on a commercial scale. On the other hand, the supply of sodium was ample. Consequently, we had to find a route through sodium hydride.

Unfortunately, the same reactions failed to proceed with sodium hydride.

$6\ NaH + 8\ BF_3{:}OEt_2 \xrightarrow{Et_2O} \text{No reaction}$

$NaH + \frac{1}{2}(BH_3)_2 \xrightarrow{Et_2O} \text{No reaction}$

These reactions proceed nicely in diglyme or tetrahydrofuran [9], but these solvents were not available at that time.

A new compound, sodium trimethoxyborohydride, solved the problem.

$NaH + B(OCH_3)_3 \rightarrow NaBH(OCH_3)_3$

This compound was very active and achieved the desired reactions without any solvent.

$6\ NaBH(OCH_3)_3 + 8\ BF_3{:}OEt_2 \rightarrow (BH_3)_2 + 6\ B(OCH_3)_3 + 6\ NaBF_4 + 8\ Et_2O$

$NaBH(OCH_3)_3 + \frac{1}{2}(BH_3)_2 \rightarrow NaBH_4 + B(OCH_3)_3$

$AlCl_3 + 3\ NaBH_4 \rightarrow Al(BH_4)_3\uparrow + 3\ NaCl$

At this time it was reported to us that the problems encountered in the use of uranium hexafluoride had been overcome, so there was no longer any need for other volatile compounds of uranium.

Alkali metal borohydrides [7]

At this point (1943) we were visited by representatives of the Signal Corps. They had learned through our reports that we had a new chemical that might be used for the field generation of hydrogen. They felt that their present method, based on the reaction of alkali with ferrosilicon, was cumbersome and they were seeking a more convenient hydrogen source.

We pointed out that sodium borohydride on a weight basis should be far more efficient than sodium hydroxide and ferrosilicon. Although we had never used it for hydrogen generation, we had no doubt that it would be similar to diborane in reacting readily with water to liberate hydrogen. They asked for a demonstration.

I placed a weighed quantity of sodium borohydride in a flask and attached it to a dropping funnel which contained water. The outlet from the flask was connected to a gas meter. The entire assembly was placed behind an explosion screen, since I did not know how violent the reaction might be.

With Professor Schlesinger and all of the representatives watching me from a safe distance, I cautiously reached behind a screen and turned the stopcock to allow water to flow into the borohydride.

The borohydride dissolved and the solution sat there merely looking at me!

This was one of the great shocks of my life and was the way we discovered that sodium borohydride possesses a remarkable stability (for a simple boron—hydrogen compound) in water.

Fortunately, the Signal Corps was persuaded to support research to find improved methods of preparing sodium borohydride and catalysts to facilitate its solvolysis. We soon discovered that sodium borohydride could readily be prepared by treating sodium hydride with methyl borate at 250°.

$$4\ NaH + B(OCH_3)_3 \xrightarrow{250^\circ} NaBH_4 + 3\ NaOCH_3$$

Then we discovered that the addition of 2% of a cobalt salt to pellets of sodium borohydride caused rapid hydrolysis with liberation of hydrogen.

We needed a solvent to separate sodium borohydride from sodium methoxide, concurrently produced in the synthesis. This led to a search for solvents for sodium borohydride. Among the solvents tested was acetone. A vigorous reaction ensued upon addition of the sodium borohydride, the active "hydride" disappeared, and analysis revealed the presence of four moles of isopropyl alcohol per mole of sodium borohydride introduced.

$$NaBH_4 + 4\ (CH_3)_2CO \rightarrow NaB[OCH(CH_3)_2]_4 \xrightarrow{H_2O} 4\ (CH_3)_2CHOH + NaB(OH)_4$$

In this way we discovered that sodium borohydride was a valuable reagent for the hydrogenation of organic molecules!

Sodium borohydride has been manufactured commercially by this process for many years. It is of interest that a chemical discovered in the course of war research has found its chief application in the manufacture of pharmaceuticals.

Selective reductions [10, 11]

Lithium aluminum hydride is an exceptionally powerful reducing agent, whereas sodium borohydride is a mild one. We undertook to develop a family of reducing agents with capabilities between these extremes [12, 13].

$$\underrightarrow{NaBH_4 < LiBH_4 < Mg(BH_4)_2 < Al(BH_4)_3}$$

increasing reducing power

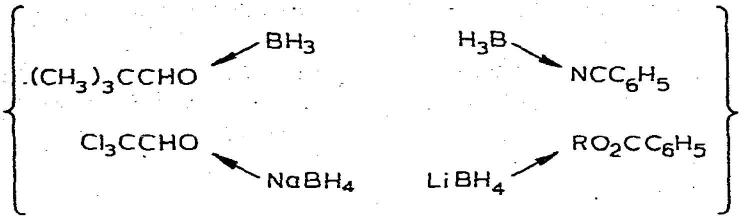
$$\underleftarrow{LiAlH(OtBu)_3 < LiAlH(OMe)_3 < LiAlH_4}$$

decreasing reducing power

Then we established that borane and its derivatives are "acidic" reducing agents [14-17], in contrast to the "basic" reducing agents, the complex hydrides.

"Basic": MBH_4, $MBH(OR)_3$, $MBHR_3$, $MAlH_4$, $MAlH(OR)_3$, $MAlHR_3$.
"Acidic": BH_3, $BHCl_2$, BHR_2, AlH_3, $AlHCl_2$, $AlHR_2$.

We can now do many selective reductions of one group in the presence of a second, or vice versa [11].

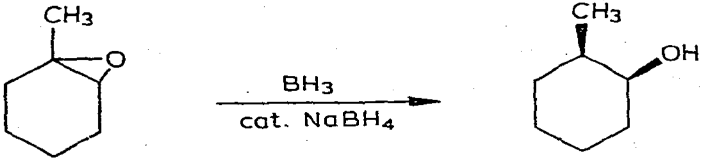


Many interesting reductions are now possible, as indicated in the following reactions [12].

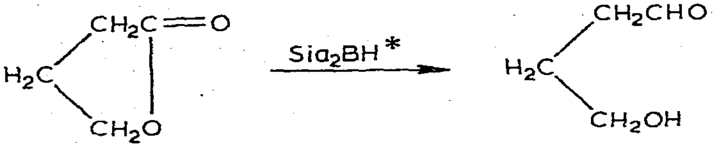
$$RCOCl \xrightarrow{LiAlH(O\text{-}t\text{-}Bu)_3} RCHO$$

$$RCN \xrightarrow{LiAlH(OC_2H_5)_3} RCHO$$

$$RCON(CH_3)_2 \xrightarrow{LiAlH(OC_2H_5)_3} RCHO$$



cis only



The chief difficulty is that of educating chemists to do quantitative work with hydrides and to use the reagent most applicable for the desired transformation.

Discovery of hydroboration [18]

Perhaps the most valuable result of this study of new reducing agents was the discovery of hydroboration in 1956 [19]. The discovery was the result of a minor experimental discrepancy. In view of the special objectives of this review, it appears appropriate to present the background of the discovery in detail [18].

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* Sia_2BH ≡ Bis(3-methyl-2-butyl)borane.

At the time Dr. B.C. Subba Rao was exploring the enhanced reducing action of sodium borohydride under the influence of aluminum chloride [12]. He was following the reaction by adding a standard solution of the reagent to weighed samples of representative organic compounds. After standard intervals of time, aqueous hydrochloric acid was added to transform the residual "hydride" into hydrogen, which was collected and measured. The decrease in the amount of hydrogen obtained from that realized in blank determinations gave us the moles of hydride utilized per mole of compound.

In this manner he established that representative aldehydes and ketones utilized one "hydride" per mole. Obviously reduction was occurring to the alcohol stage. Nitriles utilized 2 moles of "hydride", corresponding to reduction to the amine. Esters, such as ethyl acetate and ethyl stearate, revealed the uptake of 2 moles of hydride. Evidently, reduction to the alcohol was occurring here also. One of the compounds Dr. Subba Rao examined was ethyl oleate. It showed a "hydride" uptake of 2.4.

Dr. Subba Rao is a most productive laboratory worker. He came to me with the data for many, many compounds. The discrepancy was noted and discussed. Dr. Subba Rao suggested that the ethyl oleate might not have been pure, the difficulties of getting pure samples of oleic acid are well known.

We discussed the possibility of dropping the experiment. After all, this was merely one odd result in several hundred experiments. Fortunately, the research director is in an enviable position to insist on high standards, he does not have to do the experimental work. It was recommended that Dr. Subba Rao repeat the experiment with a purified sample.

This yielded the same result! The original sample of ethyl oleate had been pure. It required only a little more effort to establish that we were achieving the simultaneous reduction and hydroboration of ethyl oleate.

How is it possible that a reaction of such generality was not uncovered and utilized long ago?

As I look back from my present knowledge, it appears to me that we should have recognized the reaction much earlier. In 1936 I was beginning my doctorate research in the area of diborane chemistry. I was cautioned not to use stopcocks in any area of the vacuum line exposed to diborane vapor. Stopcock grease became very gummy when exposed to the vapor. At that time the stopcock greases had a rubber base. Later, when the Apiezon greases, prepared from a petroleum base, became available, the difficulty disappeared. I recall thinking about the phenomenon, but did not put two and two together and recognize that diborane must be cross-linking the unsaturated centers in the rubber-based grease.

Again, some time later, we utilized trimethylborane as a means of obtaining thermodynamic data for the dissociation of addition compounds [20]. We encountered no difficulty in purifying and storing trimethylborane. However, later when I attempted to utilize triethylborane for similar studies, I encountered major difficulties. A sample of triethylborane would be purified thoroughly. It would be placed in storage while other reactants were purified. But when the time came to use it, the material was impure. It appeared to evolve small quantities of ethylene. Today, I should interpret the reaction as involving a reversible dissociation of the triethylborane into diethylborane and ethylene.

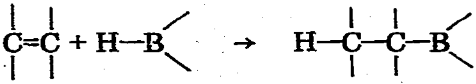
$$(C_2H_5)_3B \overset{\Delta}{\rightleftharpoons} (C_2H_5)_2BH + C_2H_4$$

Finally, triethylborane was used only in qualitative estimates of the base strengths of amines [21].

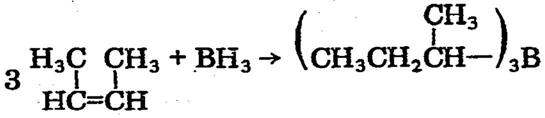
When one is young, he is impatient with these little discrepancies and tends to hurry past them to the main objective. As one gains experience, he appreciates better the importance of these discrepancies, but professional obligations render it more and more difficult to maintain direct contact with experimental observations, where there is an opportunity to recognize these nuggets.

Hydroboration [18, 22, 23]

Research soon revealed that diborane in ether solvents reacts readily with olefins [24], acetylenes [25], dienes [26], etc.

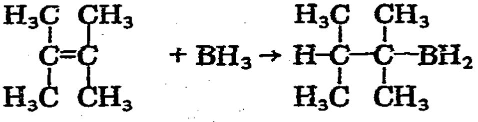


The reaction is quantitative and practically instantaneous [18].



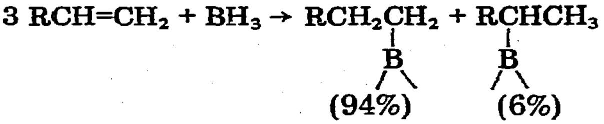
$$3\ \mathrm{H_3C\text{-}CH{=}CH\text{-}CH_3} + BH_3 \rightarrow \left(CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}H\text{—}\right)_3B$$

Practically all unsaturated compounds, even highly hindered olefins, react [27].



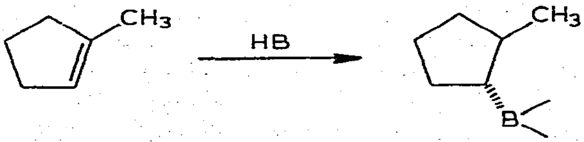
$$(H_3C)_2C{=}C(CH_3)_2 + BH_3 \rightarrow H\text{—}C(CH_3)_2\text{—}C(CH_3)_2\text{—}BH_2$$

The addition is predominantly anti-Markovnikov [28].

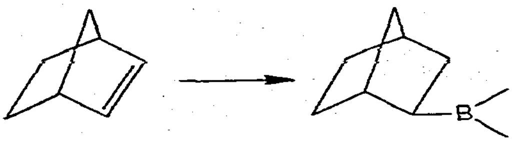


$$3\ RCH{=}CH_2 + BH_3 \rightarrow \underset{(94\%)}{RCH_2CH_2B\langle} + \underset{(6\%)}{RCH(B\langle)CH_3}$$

The addition is *cis* [29].

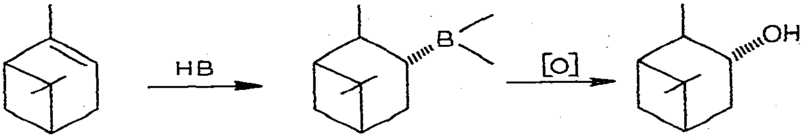


The addition takes place preferentially from the less hindered side of the double bond [29].



(99.5 %, *exo*)

No rearrangements of the carbon skeleton have been observed [30].



Many fractional groups can tolerate hydroboration [31, 32, 33].

$CH_2{=}CHCH_2CO_2R \xrightarrow{HB} {>}B{-}CH_2CH_2CH_2CO_2Et$

$CH_2{=}CHCH_2CN \rightarrow {>}B{-}CH_2CH_2CH_2CN$

$CH_2{=}CHCH_2Cl \rightarrow {>}B{-}CH_2CH_2CH_2Cl$

Thus, for the first time the organic chemist has readily available organometallics ~~containing functional groups. This promises to have a revolutionary influence~~ upon synthetic procedures in organic chemistry.

The versatile organoboranes [23, 34, 35]

The ready availability of organoboranes next prompted a detailed exploration of their reactions, with emphasis on reactions of utility in synthesis. This exploration proved to be remarkably fruitful. It is clear that the organoboranes are the most versatile organometallics available to the chemist.

Even though our program in this area is relatively young, with serious research being initiated only five years ago, the results can no longer be adequately treated in a brief review. Consequently, I can only attempt to indicate the scope of the developments by listing the topics discussed in a recent review [35].

A. Partially alkylated boranes [18, 23, 36]: RBH_2, R_2BH

B. Isomerization [18]: $R{-}B{<} \xrightarrow{\Delta} R'{-}B{<}$

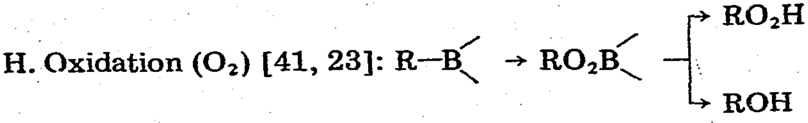
C. Displacement [18]: $RCH_2CH_2B{<} + R'CH{=}CH_2 \overset{\Delta}{\rightleftharpoons} RCH{=}CH_2 + R'CH_2CH_2B{<}$

D. Contrathermodynamic isomerization [18]: 

E. Cyclization [37]: $\overset{\frown}{CH_3HB}{-} \xrightarrow{\Delta} \overset{\frown}{CH_2{-}B}{-}$

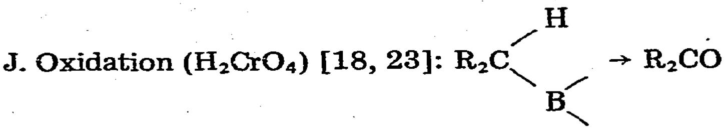
F. Protonolysis [38]: $R{-}B{<} \rightarrow R{-}H$

G. Halogenolysis [39, 40]: $R{-}B{<} \rightarrow RX$



H. Oxidation (O_2) [41, 23]: $\mathrm{R{-}B}\langle \rightarrow \mathrm{RO_2B}\langle \rightarrow \mathrm{RO_2H}$ / ROH

I. Oxidation (H_2O_2) [18, 23]: $\mathrm{R{-}B}\langle \rightarrow \mathrm{ROH}$



J. Oxidation (H_2CrO_4) [18, 23]: $\mathrm{R_2C(H)(B\langle)} \rightarrow \mathrm{R_2CO}$

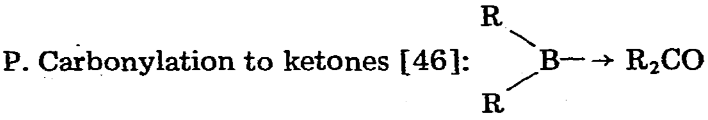
K. Amination [42]: $\mathrm{R{-}B}\langle \rightarrow \mathrm{RNH_2}$

L. Metalation [43]: $\mathrm{R{-}B}\langle \rightarrow \mathrm{RM}$

M. Coupling [44]: $2\ \mathrm{R{-}B}\langle \rightarrow \mathrm{R{-}R}$

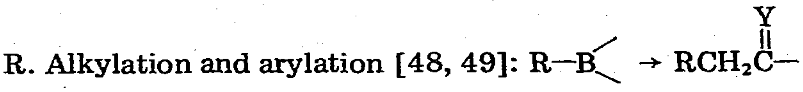
N. Cyclopropane synthesis [45]: $\rangle\mathrm{BCH_2CH_2CH_2X} \rightarrow$ △

O. Carbonylation to aldehydes [46, 47]: $\mathrm{R{-}B}\langle \rightarrow \mathrm{RCHO}$



P. Carbonylation to ketones [46]: $\mathrm{R_2B{-}} \rightarrow \mathrm{R_2CO}$

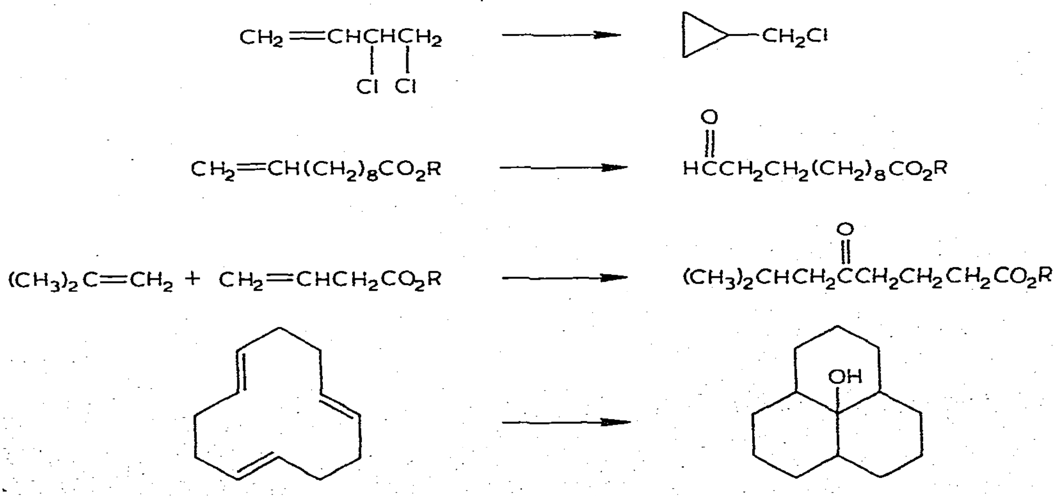
Q. Carbonylation to tertiary alcohols [46]: $R_3B \rightarrow R_3COH$



R. Alkylation and arylation [48, 49]: $\mathrm{R{-}B}\langle \rightarrow \mathrm{RCH_2C({=}Y){-}}$

S. Conjugate additions [50]: $\mathrm{R{-}B}\langle \rightarrow \mathrm{RCH_2CH_2CHO}$

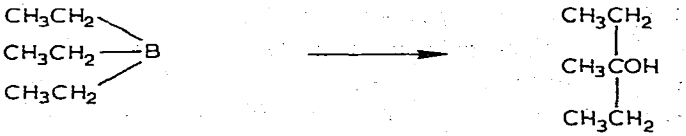
The following transformations indicate some of the new possibilities for synthetic work [45, 46, 51-53].



$\mathrm{CH_2{=}CHCH(Cl)CH_2Cl} \longrightarrow$ cyclopropyl$\mathrm{{-}CH_2Cl}$

$\mathrm{CH_2{=}CH(CH_2)_8CO_2R} \longrightarrow \mathrm{HC({=}O)CH_2CH_2(CH_2)_8CO_2R}$

$\mathrm{(CH_3)_2C{=}CH_2 + CH_2{=}CHCH_2CO_2R} \longrightarrow \mathrm{(CH_3)_2CHCH_2C({=}O)CH_2CH_2CH_2CO_2R}$



Only a few years have passed since we initiated our systematic survey of the reactions of organoboranes. Optimistic as I was at the time this exploration was initiated, I must admit my own surprise at the immense amount of promising new chemistry that our studies have uncovered.

We have been fully occupied by our explorations. There has been no attempt as yet, in our laboratories or in others', to apply the chemistry to the synthesis of natural products or pharmaceuticals; there has been no attempt to utilize the chemistry for industrial requirements, nor has there yet been any systematic effort to develop the physical organic aspects of this area. The structural chemistry of organoboranes is in its infancy. Another major task before us is that of educating students in the experimental methods and techniques of this area of chemistry so that they will not hesitate to apply these fascinating new methods [23]. Fortunately, this task will be facilitated by the recent entry of the Aldrich Chemical Company into the supply of borane chemicals and reagents. Clearly we have uncovered a new continent, only partially explored. It will require a major effort on the part of many chemists to continue the exploration and to apply the chemistry for the benefit of mankind.

Conclusion

In this review I have traced the experiences of my research associates and myself as we explored the role of boranes in chemistry. Initially diborane was a very rare substance, made in milligram quantities in only a few laboratories throughout the world and explored purely for its scientific interest.

War research forced us to explore new synthetic routes and we discovered the alkali metal hydride route to diborane. This solved the synthetic problem. At the same time we discovered sodium borohydride and developed simple synthetic methods for its preparation and manufacture.

The search for solvents led to the discovery that sodium borohydride is an excellent reducing agent for aldehydes and ketones. The search for catalysts to enhance the reducing power of sodium borohydride led to an anomalous result in the reduction of ethyl oleate. Investigation of this anomalous result led to the discovery of hydroboration.

Hydroboration made the organoboranes readily available for the first time. This led to a systematic exploration of the chemistry of the organoboranes and established the fact that they constitute the most versatile organometallic available presently. A major new area awaits exploration and application.

On the theoretical side, study of the dissociation of addition compounds of amines with trimethylborane, boron trifluoride, and borane provided a new quantitative approach to steric strains. These studies quickly removed doubts as to the importance of steric effects in chemical behavior.

These studies led to the study of related carbon compounds and to the establishment of steric effects as an important factor in their behavior.

One phase of these studies involved steric assistance to ionization in highly branched tertiary halides and related derivatives. This concept was tested and fully supported by a number of studies.

An alternative explanation for the enhanced rates made its appearance. It was proposed that σ-participation in certain nonclassical ions provided a more satisfactory interpretation. This stimulated a detailed study of the norbornyl system, considered to provide the best available case for such nonclassical carbonium ion intermediates. The results failed to confirm the presence of significant σ-participation and supported the conclusion that the phenomena must be largely, if not entirely, steric in origin.

These theoretical studies were not discussed in this review, but are presented in detail elsewhere [1].

Consequently, these studies of boranes have led us into many areas, both theoretical and practical. There is no evidence that it is any more difficult now than it was 40 years ago to uncover interesting new areas of study. Indeed, our experience indicates the reverse to be true. I can only advise those beginning a research career that it has been my experience that optimism is an essential ingredient of fruitful exploratory research.

In the introduction I pointed out that I believe we have been doing our students a disservice in divorcing them so severely from knowledge of the past. I hope that this review will contribute to an amelioration of this situation.

Finally, I wish to acknowledge the major contributions of a remarkable group of students and research associates who have contributed to this program. In a review of this kind, covering nearly forty years of research, it was possible to mention only some of the high spots and to make reference to only a fraction of their publications. For a fuller treatment, see "*Boranes in Organic Chemistry*" [1].

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