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ORGANOBORANES IN ORGANIC SYNTHESSES INCLUDING SUZUKI COUPLING REACTION

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In 1962 I had a lively interest in Wacker reaction [the oxidation of ethylene to acetaldehyde in the presence of palladium chloride and cupric chloride (*Angew. Chem.* **1959**, *71*, 176)] and began a literature survey. One Saturday afternoon during that time, I went a bookstore in Sapporo to look at new chemistry books and found a red and black two-tone colored book on the shelf that did not look like a chemistry book. The book was "Hydroboration" written by Professor Herbert C. Brown of Purdue University. It seemed to be an interesting book, so, I bought it. This book changed the course of my career, and my fascination with the chemistry of hydroboration reaction and organoboron compounds thus prepared by hydroboration began after reading the book.

I immediately wrote to Professor Brown requesting to work as a postdoctoral research fellow. At that time Professor Brown was at Heidelberg in Germany as a visiting professor. He kindly wrote me a letter of acceptance, and I began a study of the stereochemistry of hydroboration reaction at Purdue (1963-65). Through this work I came to understand hydroboration and the interesting characteristics of organoboranes.

My family (wife and two small girls) and I had a very good time there and made good friends. Of course I enjoyed chemistry. After a stay of about two years at Purdue, I returned to Japan with my family at the end of March 1965. On our return flight, I considered my next research project in Sapporo. Finally, I decided to open up a new field in synthetic methodology employing organoboron compounds.

The facile addition of a boron-hydrogen moiety to carbon-carbon multiple bonds of unsaturated organic derivatives gives organoboranes. This hydroboration has various characteristic properties. The reaction is very rapid, usually being completed within a few minutes at temperatures below 25 °C. In general, the hydroboration proceeds *via* a *cis* addition of the boron-hydrogen moiety to the carbon-carbon multiple bond from the less- hindered side, to place the boron atom predominantly at the less-substituted carbon atom. Organoboranes thus obtained have interesting features.

For about past 30 years, we had investigated organic syntheses using organoboranes and discovered that organoboranes are versatile intermediates. The ready availability of organoborans with a wide variety of structures by the hydroboration of alkenes and alkynes is one of most remarkable advantages,

compared with other organometallic compounds. In addition, organoboranes thus obtained have highly favorable characteristics for organic synthesis. For example, as shown in Figure 1, the organoborane (**B**) prepared from the olefine (**A**) at room temperature gives the alcohol (**D**) by alkaline hydrogen peroxide oxidation. The organoborane (**B**) is easily isomerized by heating at 150 °C to **C**, which is oxidized with hydrogen peroxide under alkaline conditions to produce the alcohol (**E**). Consequently, two different alcohols can be selectively obtained in good yields from an alkene.

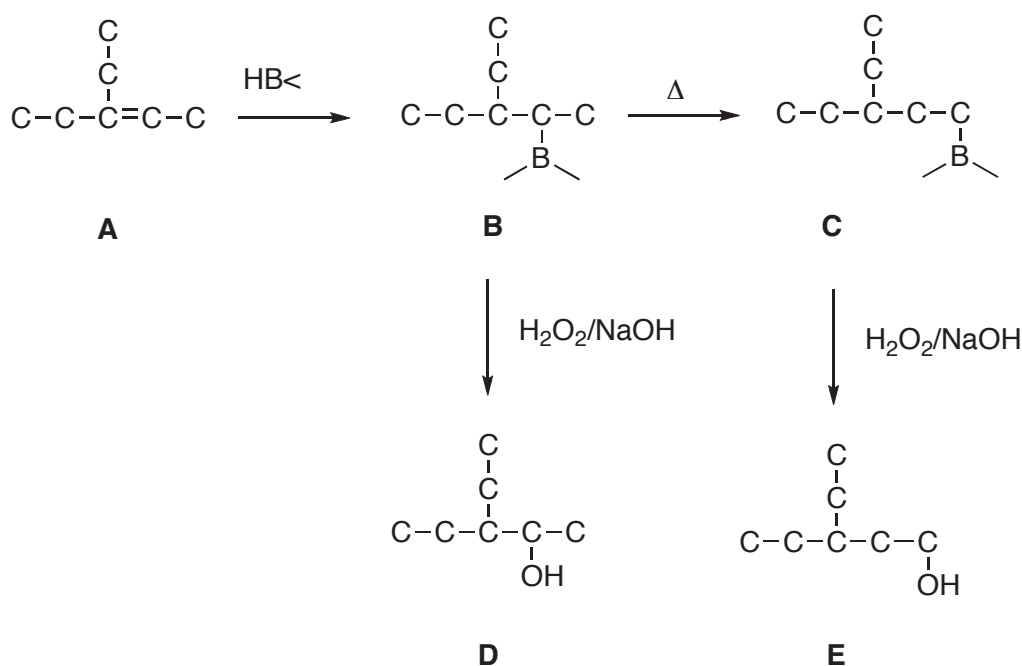


Figure 1

In spite of having such a merit for synthetic applications, organoboranes are chemically inert. For instance, trialkylboranes are markedly stable toward water, alcohols and phenols. Organoboranes do not undergo Grignard-type reactions with carbonyl compounds, and are not effective as catalysts in the chain-growth reaction of olefins, which is well-known in the case of alkylaluminum compounds. The reason why organoboranes have properties so different from those of other organometallics could be elucidated by the following three characteristics of organoboranes: (a) A small difference in the electronegativity between boron and carbon. (b) The second point is the vacant electron structure of the boron atom. Organoboranes are, therefore, readily attacked on the boron atom by bases and nucleophiles. This property provides a basis for a number of unique and selective synthetic reactions of organoboranes, as described later, (c) The third point is that the C-B bond length is almost the same length as that of C-C bond. Under considering such characteristics, we performed the investigation. Synthetic reactions discovered by our research group in Hokkaido University are briefly reviewed here.

1. Synthesis *via* the Oxygen-Induced Reaction of Organoboranes¹⁾

On the basis of the characteristics of organoboranes described previously, we planned first to explore the reaction of trialkylboranes with methyl vinyl ketone, in expectation that the carbonyl oxygen will coordinate to the boron atom to form an ate-complex **1**, in which π -electrons move with the migration of R on B to the vinyl carbon to give enolborinate **2**, which is then hydrolyzed with water to the corresponding saturated ketone (Figure 2). Actually, it was found that the reaction proceeds smoothly to provide ketones in almost quantitative yields.

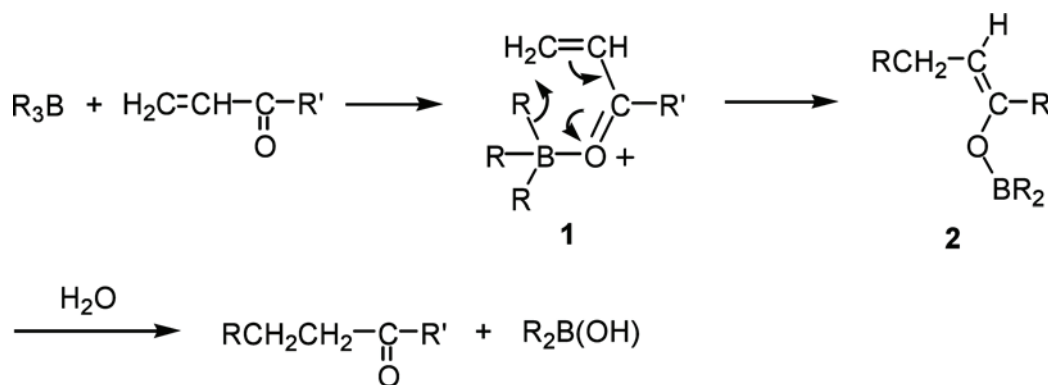
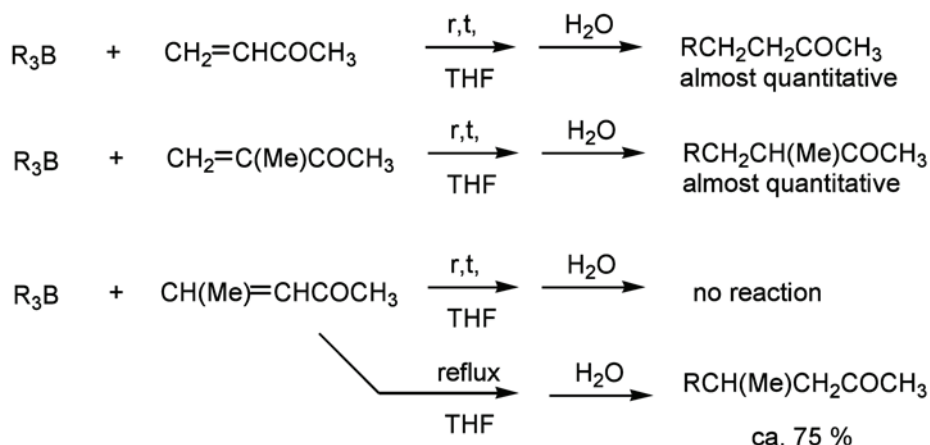


Figure 2

Then we carried out the same reaction with 2-propenyl methyl ketone and 1-propenyl methyl ketone to reveal the reaction scope and found that the former gave the expected saturated ketone in almost quantitative yield but no product was obtained when the latter was reacted at room temperature (Figure 3). However, we found that such a reaction proceeds smoothly at reflux temperature of THF to provide the product in 75 % yield.

At that time Brown's group at Purdue was investigating the same chemistry using acrolein and its homologs as a joint research project with us. Acrolein and 1-methyl acrolein gave corresponding saturated aldehydes almost quantitatively, but 2-methyl acrolein never produced the saturated aldehyde at room temperature (Figure 3). We informed Professor Brown's group of our results showing that 1-propenyl methylketone reacts with trialkylboranes at THF reflux temperature. They carried out the reaction with 2-methyl acrolein at reflux temperature but they also did not obtain any product. Finally, our group in Sapporo tried the same reaction using 2-methyl acrolein and obtained the corresponding aldehyde in 70% yield (Figure 3).

At Hokkaido Univ., Sapporo, Japan



At Purdue Univ., W. Lafayette, IN, USA

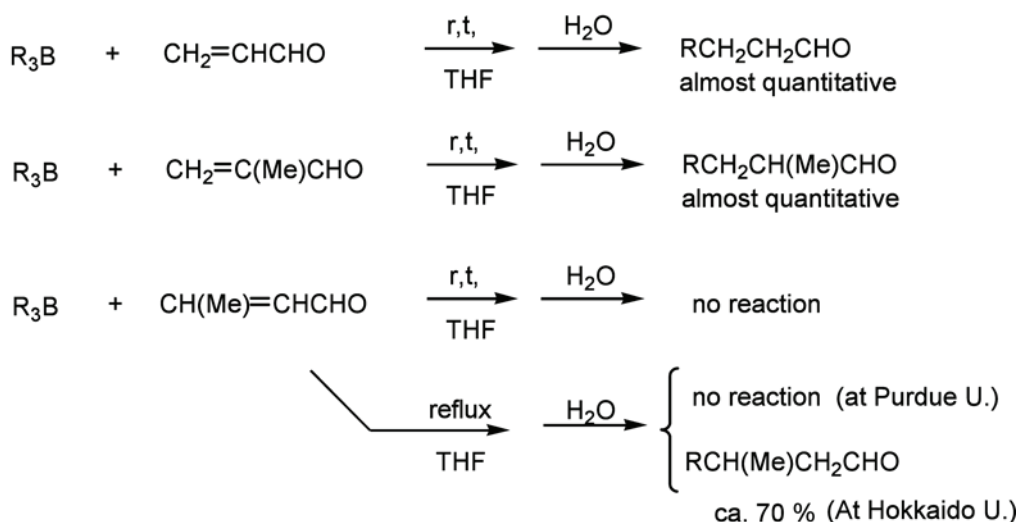


Figure 3

I still remember a letter from Professor Brown that I received at that time. He wrote: "Chemistry should be international. Why do we have such a large difference between two places, Sapporo, Japan and Indiana, the United States." Finally we found that the reason was due to the catalytic activity of oxygen for the reaction. Generally, organoborane reactions were carried out in inert gas such as nitrogen, because organoboranes are sensitive to oxygen. The nitrogen gas we used in Sapporo contained a small but effective amount as a catalyst. On the other hand, Purdue workers were unfortunately(?) able to use high purity nitrogen in the United States.

It was shown that the coordination mechanism (Figure 2) initially proposed should be changed to a free-radical chain mechanism (Figure 4), because it was discovered that galvinoxyl, an effective free-radical scavenger, completely inhibits the reaction and that the reaction can be accelerated by the addition of a catalytic amount of diacetyl peroxide or by photochemical activation. The reason why

acrolein gave good results in the reaction with trialkylboranes at Purdue is thought to be related to the chain length of the reaction.

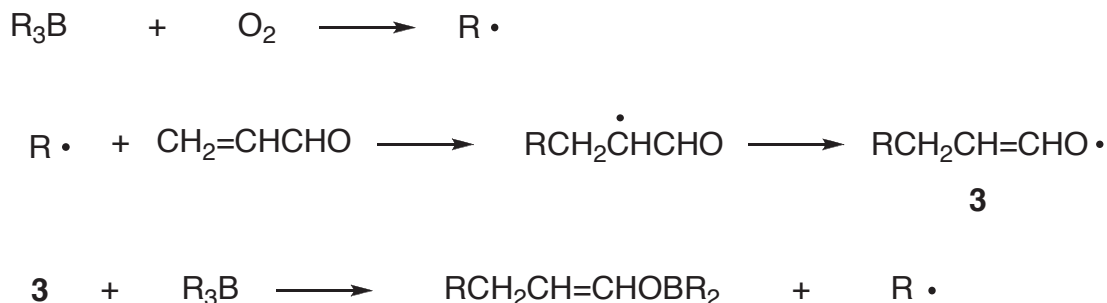


Figure 4

Since we incidentally discovered that organoboranes readily give alkyl radicals in the presence of a catalytic amount of oxygen, we next attempted to pursue the synthetic application of the reaction employing other substrates, as shown in Figures 5 and 6. It became apparent that the reactions shown in Figure 5 take place readily to produce expected products in excellent yields, whereas the reactions shown in Figure 6 afford poor results. However, such a difficulty can be overcome by a modified procedure (described in the following section).

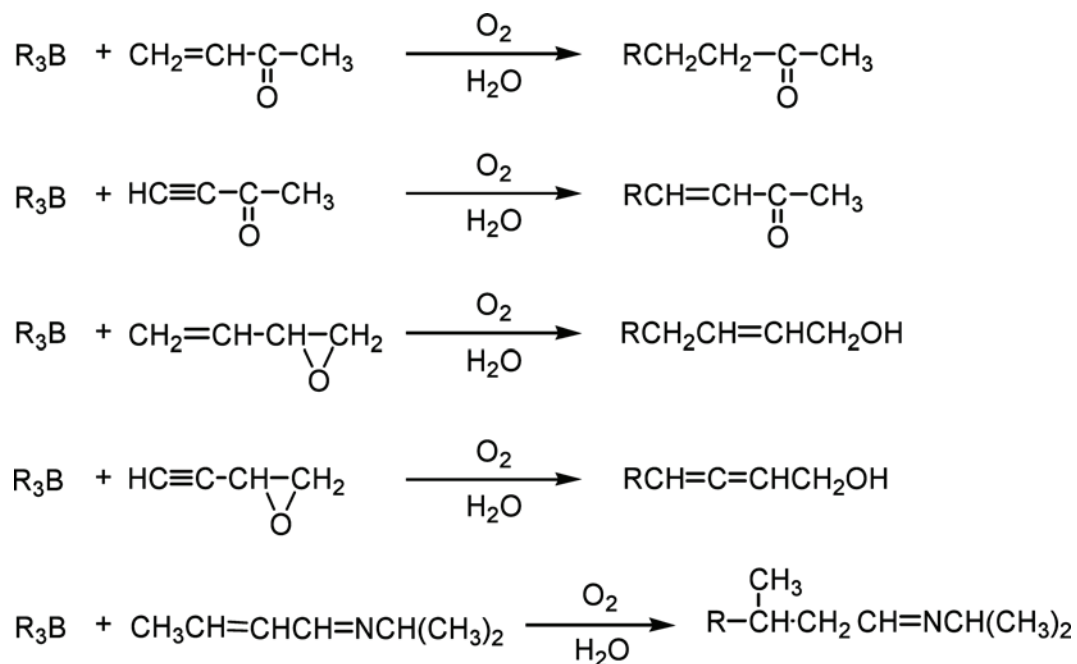


Figure 5

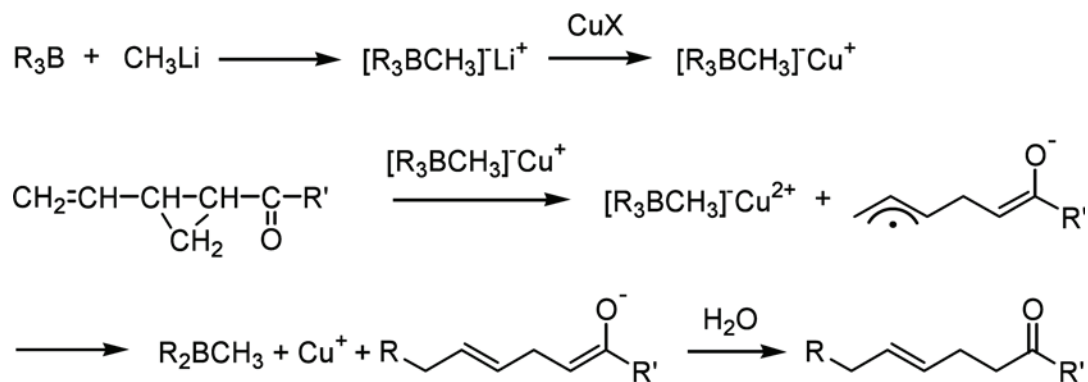


Figure 7

Copper(I) 1-alkenyltrimethylborates **4** are readily produced by the procedure depicted in Figure 8. They react smoothly with allyl bromide to give 1,4-alkadienes in greater than 90% yields, stereo- and regioselectively.

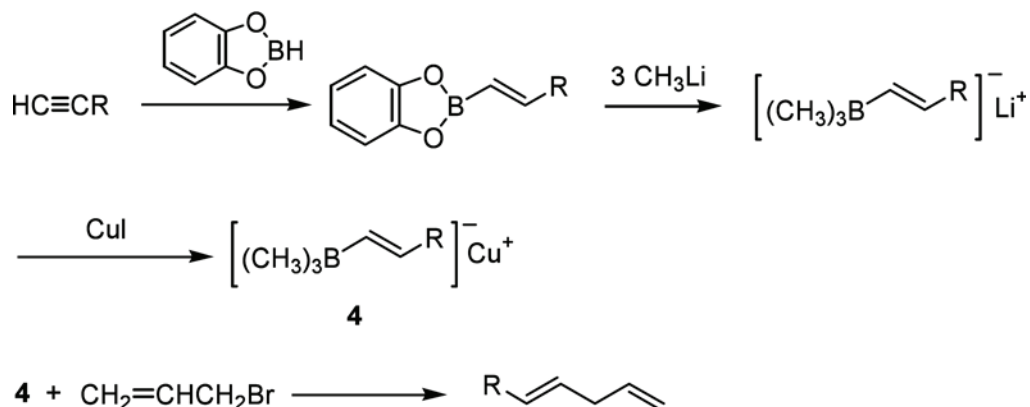


Figure 8

3. Synthesis *via* Tetracoordinated Organoborates, in which α -Carbons Have Heteroatoms Readily Removable as Leaving Groups²⁾

Because of the presence of a vacant p orbital on boron, organoboranes are accessible for nucleophilic attack to form tetracoordinated borate complexes **5** as shown in Figure 9. The R group on boron in **5** may migrate to X with the concurrent elimination of Y to give the product **7**. If the contribution of the resonance structure **6** is considerable, there is another possibility that a migration of R to X occurs without elimination of Y to yield the product **8**.

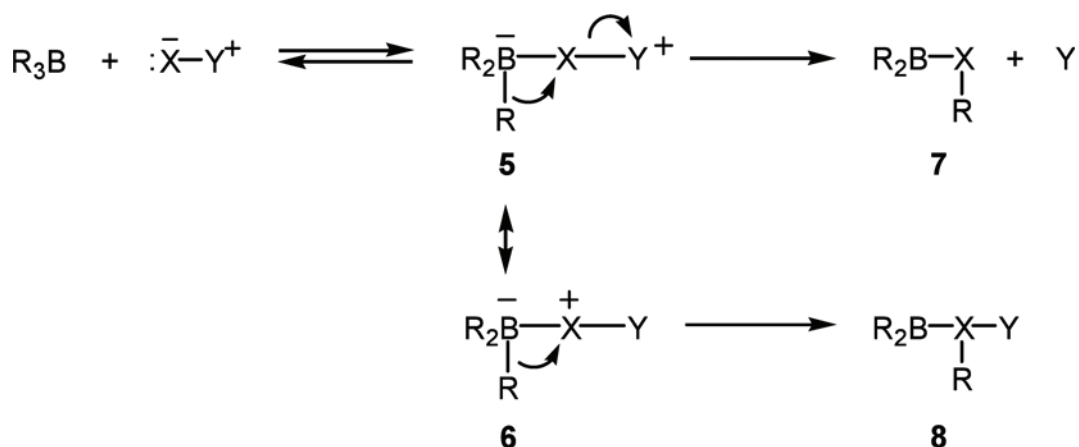


Figure 9

There have been many reports on organic synthesis by this type of reaction. One such synthetic reaction discovered by our research group is a selective synthesis of secondary amines by the reaction of trialkylboranes with alkyl azides. At the time of our initial planning, the desired synthesis was expected to be brought about through reaction with nitrenes generated by thermal treatment of alkyl azides (Figure 10). Actually, the secondary amines were produced in good yields, but it was confirmed that the reaction did not proceed through a nitrene intermediate but *via* a coordination process, because the reaction rate was determined to be second-order, first-order in both the organoborane and the alkyl azide, as shown in Figure 10. This reaction provides only pure secondary amines without any formation of primary and tertiary amines.

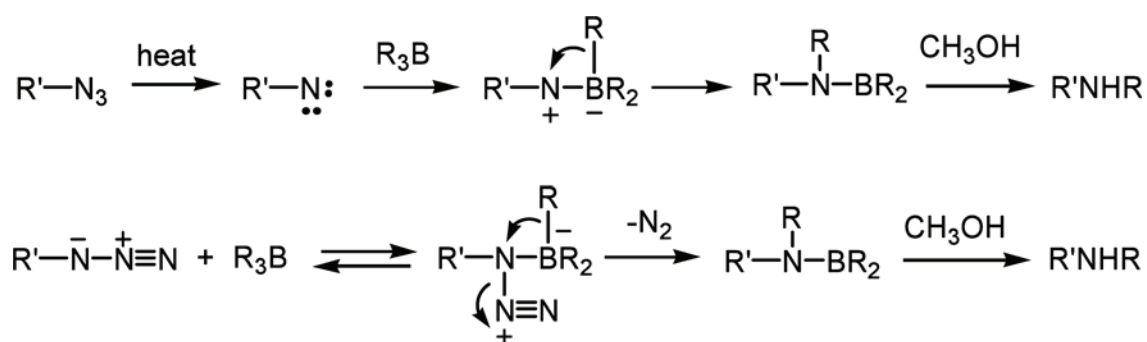


Figure 10

Instead of alkyl azides, when vinylic azides such as α -azidostyrene and 2-azido-1-alkenes are used, a different type of reaction occurs: alkyl group migration takes place from boron to the vinylic carbon followed by hydrolysis to give the corresponding ketones (Figure 11).

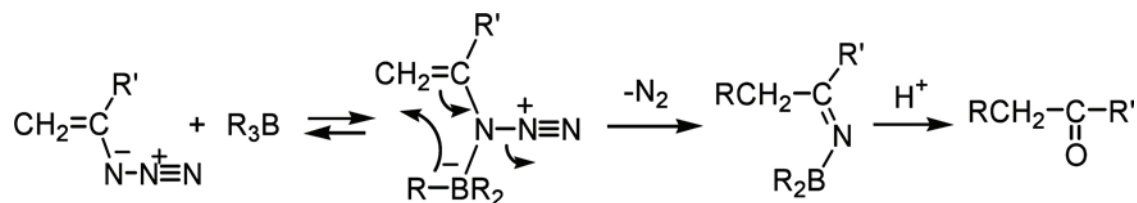


Figure 11

Organoboranes were recognized to have high versatility for the synthesis of organic compounds having various functional groups. However, there has been no report of successful direct synthesis of carboxylic acids from organoboranes. In order to find a means for such synthesis, we examined the reactions of organoboranes with sodium cyanide, 2-oxazolines, and catecholdichloromethene ether. However, all of the reactions were found to yield only symmetric ketones (by migration of two alkyl groups) instead of carboxylic acids. Fortunately, it was finally discovered that the reaction of trialkylboranes with the dianion of phenoxyacetic acid, which is readily available, occurs smoothly and is followed by acidification to give corresponding carboxylic acids in good yields (Figure 12). This reaction is also applicable to the direct synthesis of olefinic carboxylic acids *via* the selective monohydroboration of alkadienes (Figure 12).

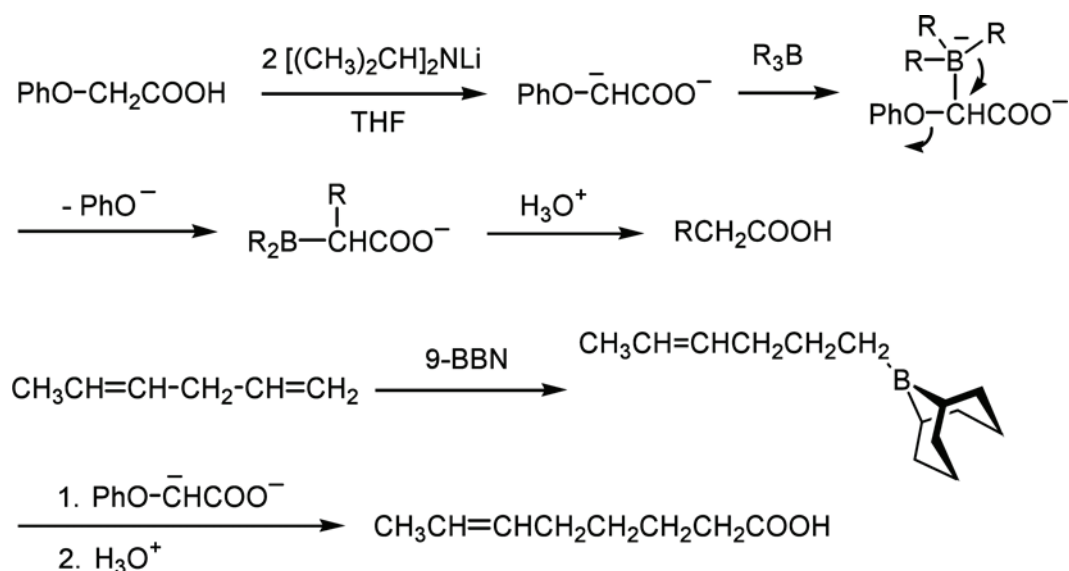


Figure 12

4. Synthesis via 1-Alkynylborates and 1-Alkenylborates²⁾

As one of the modified patterns of new R-X bond formation (Figure 9), the following reactions are

In connection with the reaction of 1-alkenylborates, we attempted the isopropenylation of C=C bonds. Our first expectation was that an organoborane would react with isopropenyllithium to form tetracoordinated organoborates, iodination of which, followed by elimination of the B-I moiety, would give the isopropenyl derivatives. As anticipated, the reaction was found to proceed smoothly to afford corresponding products in good yields (Figure 15).

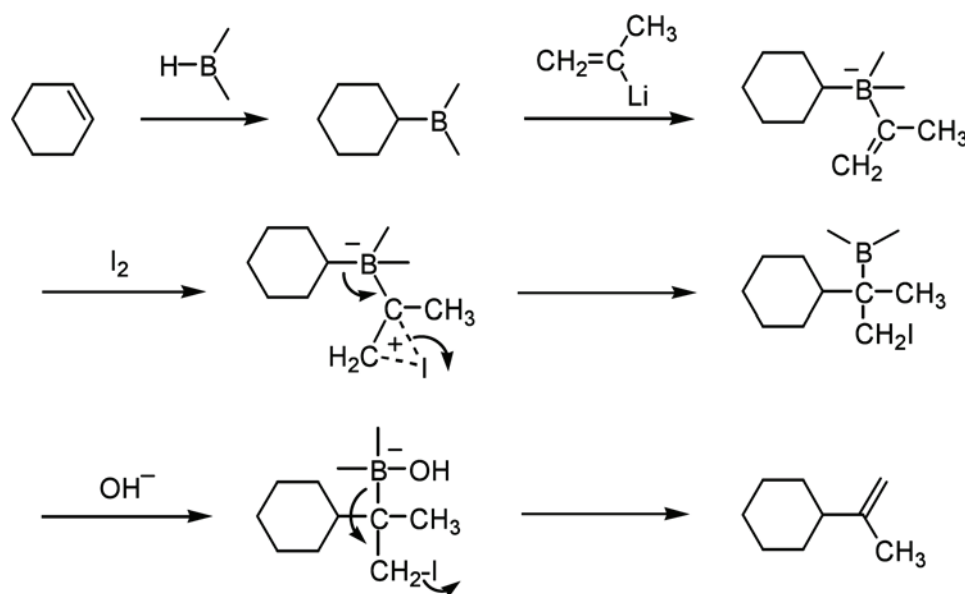


Figure 15

5. Synthesis *via* Electrochemical Conditions of Organoboranes³⁾

Trialkylboranes are readily electrolyzed by using graphite as an anode and a platinum plate as the cathode in a methanol solution containing sodium methoxide and sodium perchlorate to give the corresponding methoxyalkanes in relatively good yields. The reaction is considered to occur through the formation of alkyl cations. Some of such reactions were reported.

6. Synthesis *via* Palladium-Catalyzed Cross-Coupling Reaction of Organoboron Compounds with Organic Electrophiles (Suzuki Coupling)⁴⁾

1) Coupling Reaction of 1-Alkenylboron Compounds

Stereoselective syntheses of conjugated (*E,E*)-, (*E,Z*)-, (*Z,E*)-, and (*Z,Z*)-alkadienes are of considerable importance in organic chemistry. Recently a number of new methods utilizing various organometallic compounds in the presence of transition metal complexes for the preparation of conjugated dienes have been attempted. However, the scope of many of these reactions is limited by the nature of the organometallic reagent involved or the procedure employed, e.g., some of them require stoichiometric amounts of metal complexes, and they can be best utilized only for the syntheses of

symmetric dienes or unfunctionalized alkadienes because of the strong reducing property of organometallics.

On the other hand, it is well-known that 1-alkenyldiorganoboranes are readily prepared by the monohydroboration of 1-alkynes with diorganoboranes such as disiamylborane [bis(3-methyl-2-butyl)borane] and catecholborane. This reaction makes (*E*)-1-alkenyldiorganoboranes with high stereoselectivity (more than 99%), quantitatively. Highly pure (*Z*)-1-alkenyldiorganoboranes (more than 98%) are prepared *via* monohydroboration of 1-halo-1-alkynes with disiamylboranes or dicyclohexylborane, followed by treatment with *t*-butyllithium (Figure 16).

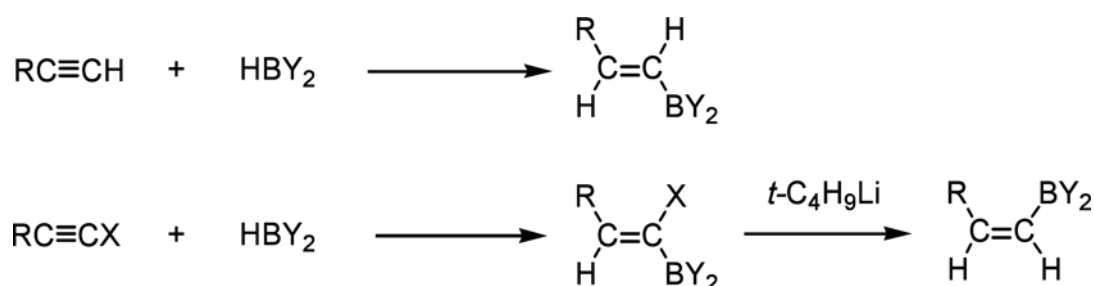


Figure 16

Accordingly, if such 1-alkenyldiorganoboranes react with 1-alkenyl halides or 1-alkynyl halides, they will provide convenient procedures for the synthesis of conjugated dienes or enynes. In spite of efforts by many workers all over the world to find such cross-coupling reactions, no results of a successful study had been reported at the time we intended to pursue this study.

The common mechanism of transition metal-catalyzed cross-coupling reactions between organometallics and organic halides involves sequential (a) oxidative addition, (b) transmetalation, and (c) reductive elimination. Initially, we presumed that one of the reasons 1-alkenylboranes cannot react with 1-alkenyl halides is in step (b), because the transmetalation process between $\text{R}'\text{PdX}$ and 1-alkenylboranes does not occur smoothly due to the weak carbanion character of organic groups in organoboranes. Consequently, we thought that if the organoborates formed from 1-alkenylboranes and basic species are used instead of alkenylboranes themselves, there is a possibility that the transmetalation can take place readily. Actually we found that (*E*)-1-alkenyldisiamylboranes react with (*E*)- and (*Z*)-1-alkenyl halides in the presence of a catalytic amount of tetrakis (triphenylphosphine) palladium and base to produce the corresponding (*E,E*)- and (*E,Z*)-conjugated alkadienes stereo- and regioselectively in excellent yields, whereas (*Z*)-1-alkenyldisiamylboranes give only corresponding dienes in about 50% yields. Fortunately, it was discovered later that such coupling reactions afford high yields when (*Z*)-1-alkenyldialkoxyboranes are used in the place of (*Z*)-1-alkenyldisiamylboranes (Figure 17).

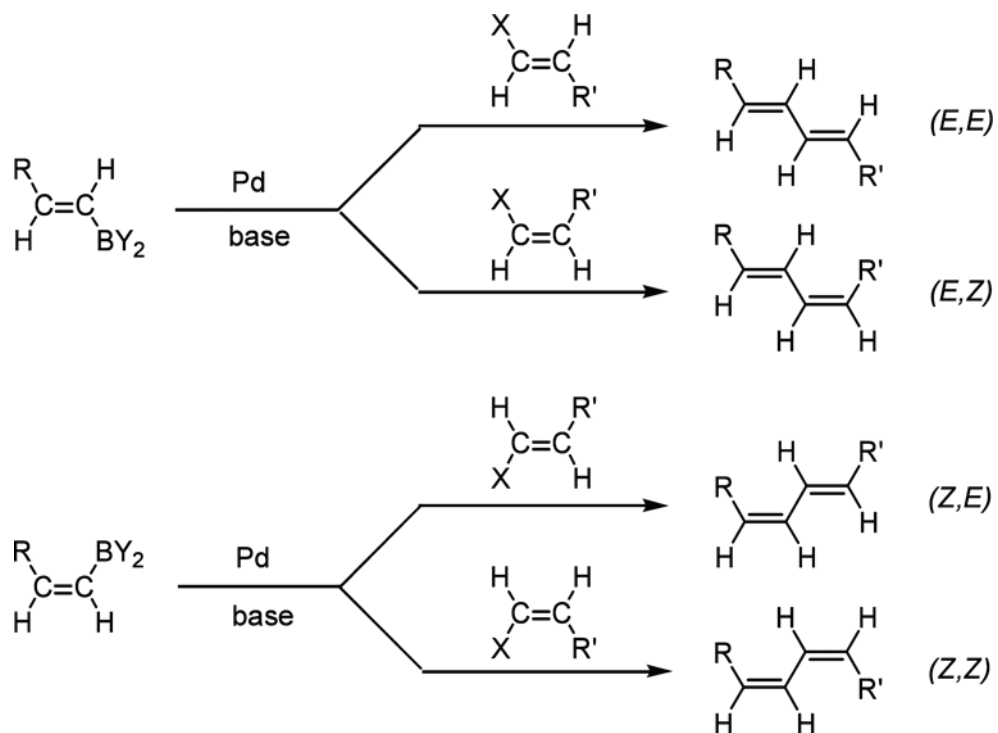


Figure 17

Experimental evidence concerning the reaction mechanism suggests that the reaction can be accommodated by an oxidative addition of $R'X$ to $Pd(0)$ followed by an exchange of the halide ion with the base, transmetalation with 1-alkenylborates, and reductive elimination as shown in Figure 18.

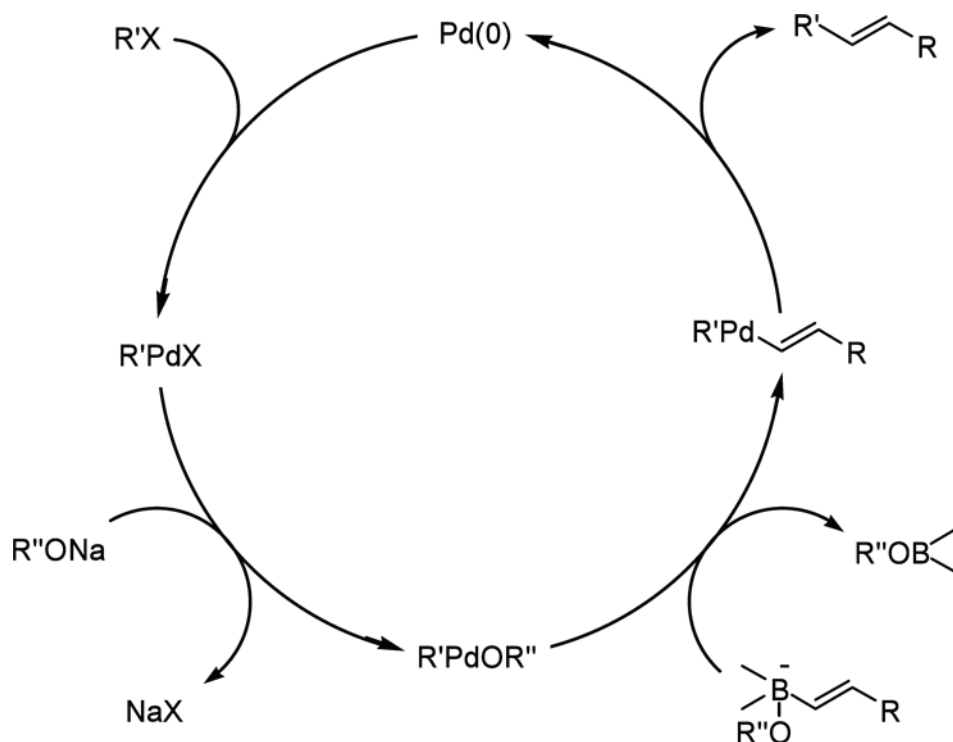


Figure 18

The reaction of aryl halides with 1-alkenylboranes provides a convenient new method for the stereoselective synthesis of arylated alkenes under such conditions. The same cross-coupling reaction of 1-alkenylboranes with allylic or benzylic halides occurs smoothly to give 1,4-alkadienes or allylbenzenes, respectively, in excellent yields.

2) Coupling Reaction of Arylboron Compounds. Synthesis of Biaryls

The reaction of aryl halides with copper at high temperature is called the Ullmann reaction, which is of broad scope and has been used to prepare many symmetrical biaryls. However, when a mixture of two different aryl halides is used, three possible coupled products can be produced. Consequently, the development of a selective and general method for synthesis of all kinds of biaryls has been desired. The first method to prepare biaryls by the cross-coupling of arylboranes with haloarenes was reported in 1981 by our group (Figure 19). The reaction proceeds even under heterogeneous conditions to give the corresponding coupled products selectively in high yields.

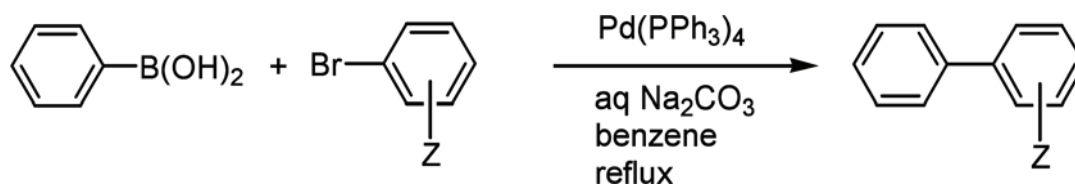
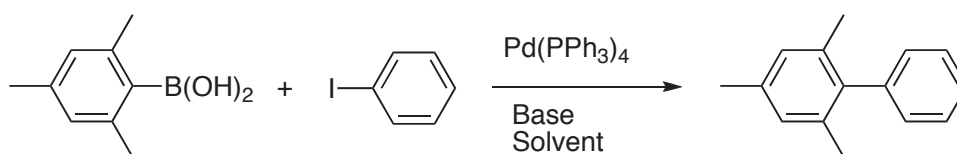


Figure 19

Aromatic-aromatic (or heteroaromatic) couplings between aromatic boronic acids or esters and aromatic electrophiles providing symmetrical and unsymmetrical biaryls selectively in high yields have been used most frequently. The importance of biaryl units as components in many kinds of compounds, pharmaceuticals, herbicides, and natural products, as well as engineering materials, such as conducting polymers, molecular wires and liquid crystals, has attracted enormous attention from the chemical community. Although steric hindrance of aryl halides is not a major factor for the formation of substituted biaryls, the reaction with sterically hindered areneboronic acids resulted in low product yields. Aromatic boronic acids which have electron-withdrawing functional groups possess same difficulty. Fortunately, this difficulty can be largely overcome by employing modified reaction conditions. (Table 1 and Figure 20).

Table I. Reaction of Mesitylboronic Acid with Iodobenzene under Different Conditions



Base	Solvent	Temp/°C (Time 8h)	Yield/% ^a
Na ₂ CO ₃	Benzene/H ₂ O	80	25(6)
Na ₂ CO ₃	DME/H ₂ O	80	50(1)
K ₃ PO ₄	DME/H ₂ O	80	70(0)
NaOH	DME/H ₂ O	80	95(2)
Ba(OH) ₂	DME/H ₂ O	80	99(2)

^aGLC yields of the coupling product based on iodobenzene and the yields of mesitylene are shown in the parentheses.

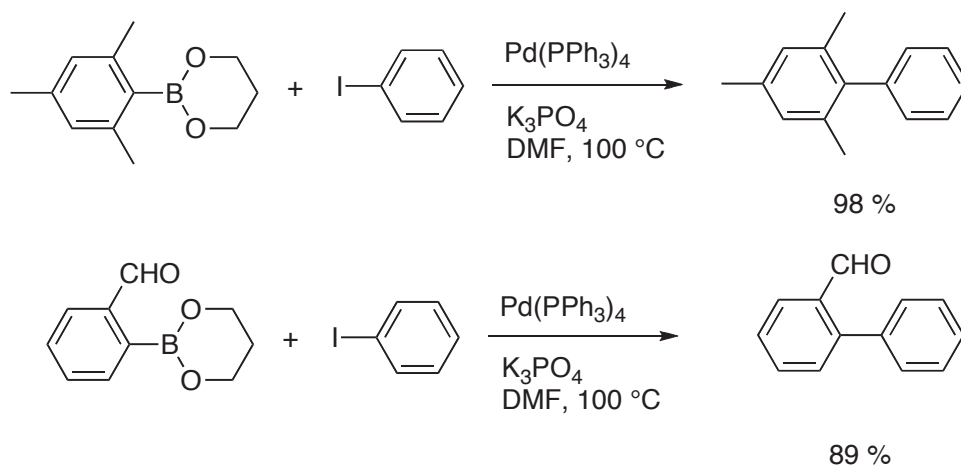


Figure 20

Polycondensation reactions of aryldiboronic acids with dihaloarenes have been utilized for production of aromatic, rigid-rod polymers, which play an important role in a number of diverse technologies.

3) Coupling Reaction of (sp³)C-B Compounds

Organometallic compounds with alkyl groups having (sp³)carbons containing β-hydrogens were

severely limited for coupling reaction due to competitive side reactions. We examined the coupling reactions between alkylboron compounds and various organic halides in the presence of a base and $\text{Pd}(\text{Ph}_3)_4$, and we found that no cross-coupling reaction of B-alkyl-9-borabicyclo[3.3.1]nonanes (B-R-9-BBN), readily obtainable from alkenes by hydroboration, with 1-halo-1-alkenes or haloarenes occurred under the standard coupling conditions but that the coupling proceeds smoothly by using a catalytic amount of $\text{PdCl}_2(\text{dppf})$ and bases to provide the expected coupled products in excellent yields. Because the reaction is tolerant of a variety of functionalities on either coupling partner, stereochemically pure functionalized alkenes and arenes can be obtained under mild conditions (Figure 21).

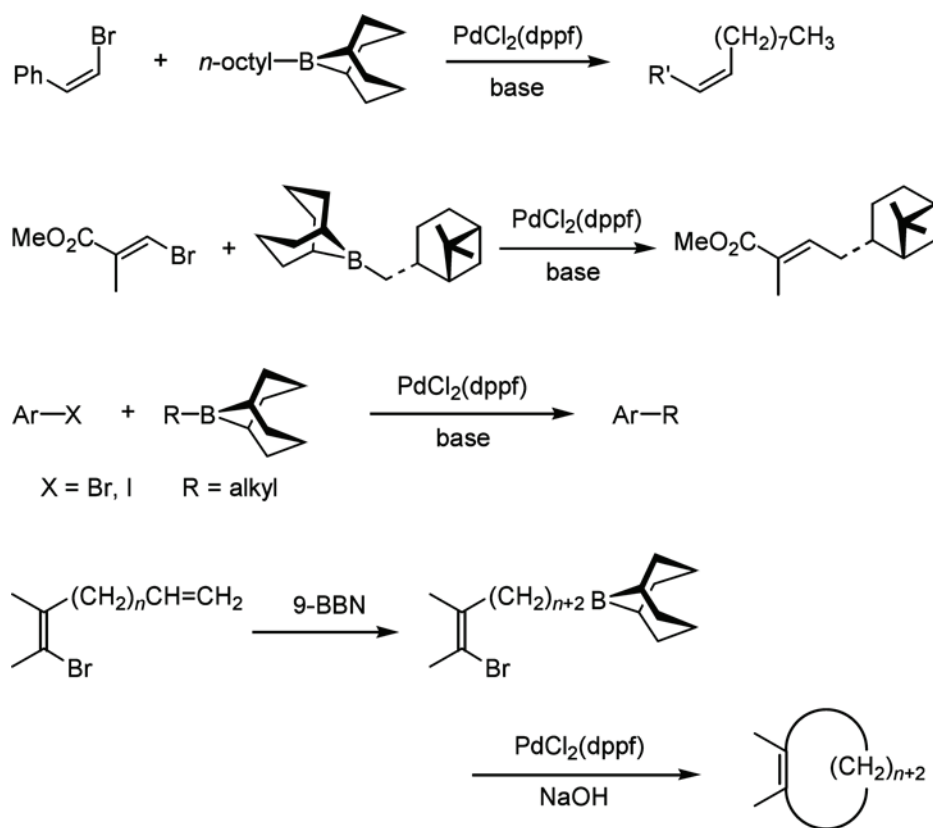


Figure 21

More recently, it has become apparent that palladium-catalyzed coupling reactions of 1-alkenyl, aryl and alkylboron compounds with aryl or 1-alkenyl triflates, instead of corresponding organic halides, take place with ease to give expected coupled products in high yields under mild conditions. The reactivity of triflates and halides in the reaction decreases in the order of $\text{I} > \text{Br} > \text{OTf} > \text{Cl}$. Thus, the sequential cross-coupling of **10** with two alkylborane derivatives obtained from two different alkenes affords the differently disubstituted benzene derivatives selectively (Figure 22).

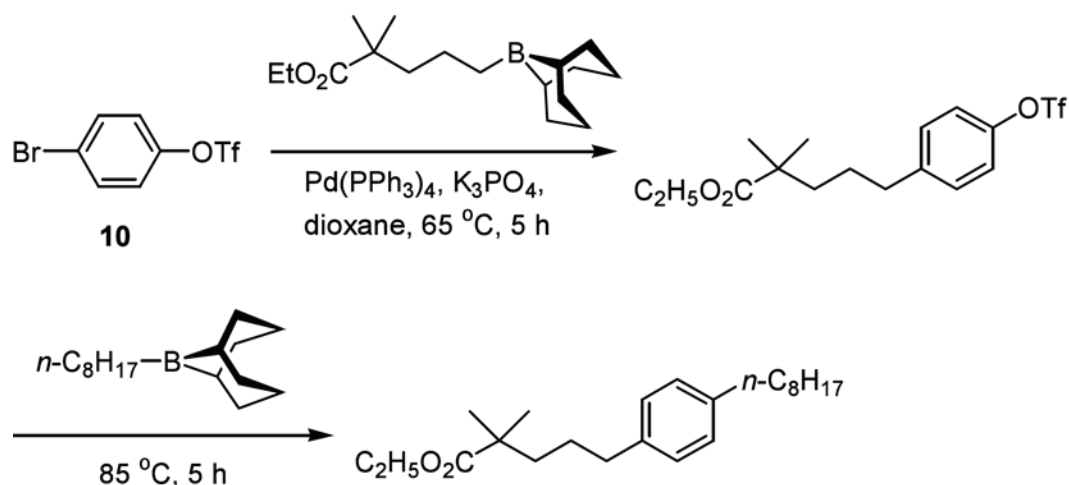


Figure 22

Thus, palladium-catalyzed cross-coupling reactions between different types of organoboron compounds with sp^2 -, sp^3 -, and sp -hybridized carbon-boron bonds and various organic electrophiles in the presence of a base provide a powerful and useful synthetic methodology for the formation of many different types of carbon-carbon bonds (Figure 23).

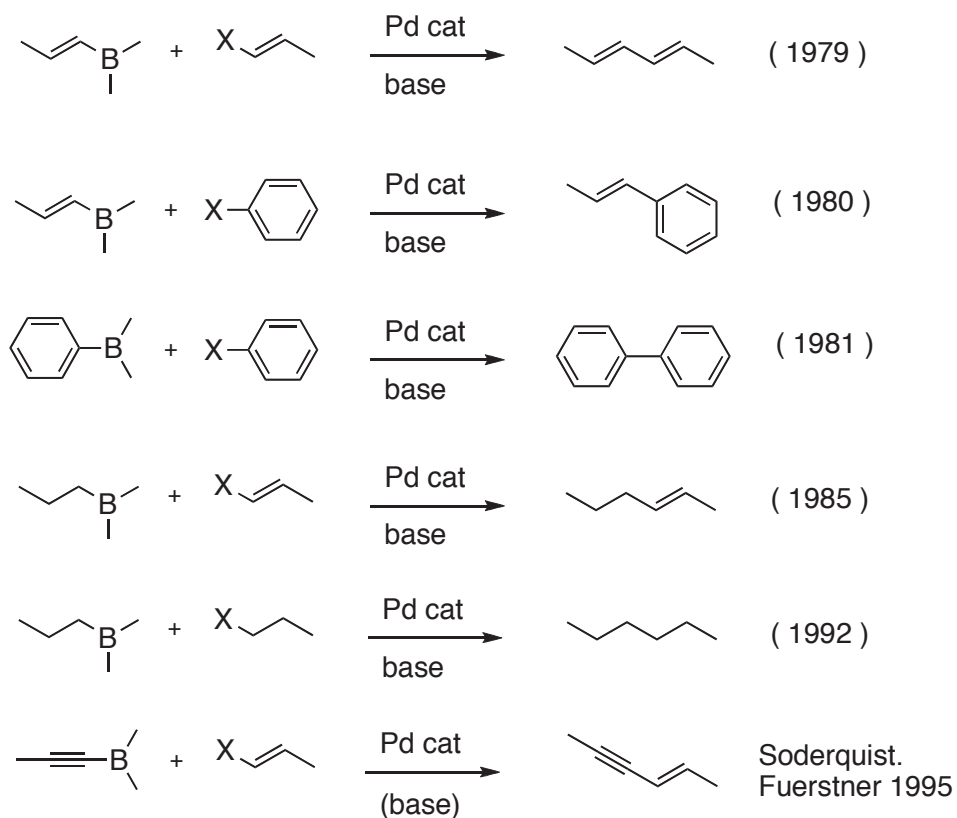


Figure 23

The coupling reaction offers several advantages:

- (1) Availability of reactants
- (2) Mild reaction conditions
- (3) Water stability
- (4) Easy use of the reaction both in aqueous and heterogeneous conditions
- (5) Tolerance of a broad range of functional groups
- (6) High regio- and stereoselectivity
- (7) Insignificant effect toward steric hindrance
- (8) Use of very small amounts of catalysts
- (9) Utilization as one-pot synthesis
- (10) Non-toxic reaction
- (11) Easy separation of inorganic boron part

7. Synthesis *via* Haloboration Reaction)⁵⁾

In connection with the development of the cross-coupling reaction of organoboron compounds with 1-alkenyl halides, as described in the previous section, we tried to find a novel selective synthetic method for the preparation of alkenyl halides. As such a synthetic method, one can anticipate the hydrometalation or carbometalation of 1-alkynes followed by metal-halogen exchange reaction.

Haloboration reaction of unsaturated hydrocarbons with BX_3 appears to have first been reported by Lappert. There has been no report, however, on application of haloboration to organic synthesis. Recently, we discovered that B-X-9-BBN ($X = Br, I$) reacts with 1-alkynes stereo- regio-, and chemoselectively. The reasons we chose the reagent as a haloborating agent are as follows: 1) when BX_3 is employed, there is a possibility for BX_3 to react with 1, 2, or 3 equivalent(s) of an alkene, 2) steric bulkiness of the borabicyclo[3.3.1]nonane moiety in B-X-9-BBN may increase the reaction selectivity and 3) the easy preparation of B-X-9-BBN was already reported, as depicted in Figure 24.

It was proved that although B-Br-9-BBN:SM₂ complex (**11**) itself does not react, the free B-Br-9-BBN (**12**) readily generated on treatment with BBr₃ reacts with 1-alkynes to afford the corresponding bromoboration products (**13**), which are converted to 2-bromo-1-alkenes (**14**) by protonolysis with acetic acid (Figure 24).

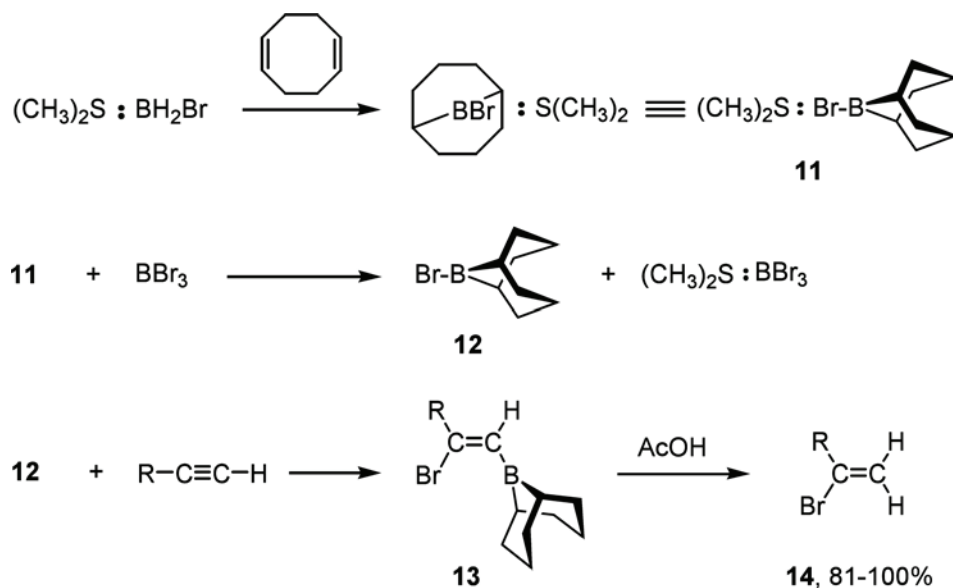


Figure 24

To establish the stereochemistry of the reaction, experiments (Figure 25) were carried out, and the results obtained definitely indicate that haloboration proceeds *via* Markovnikov *cis* addition of Br-B to the terminal triple bond. In addition, it was ascertained that bromoboration using B-Br-9-BBN occurs only at terminal $\text{C}\equiv\text{C}$ bonds, but not at internal $\text{C}\equiv\text{C}$ or terminal and internal $\text{C}=\text{C}$ bonds. Furthermore, since many functional groups can tolerate the reaction conditions, the haloboration is applicable to 1-alkynes with those functional groups. B-I-9-BBN can also be employed for the reaction, whereas B-Cl-9-BBN is very inert as a haloboration agent.

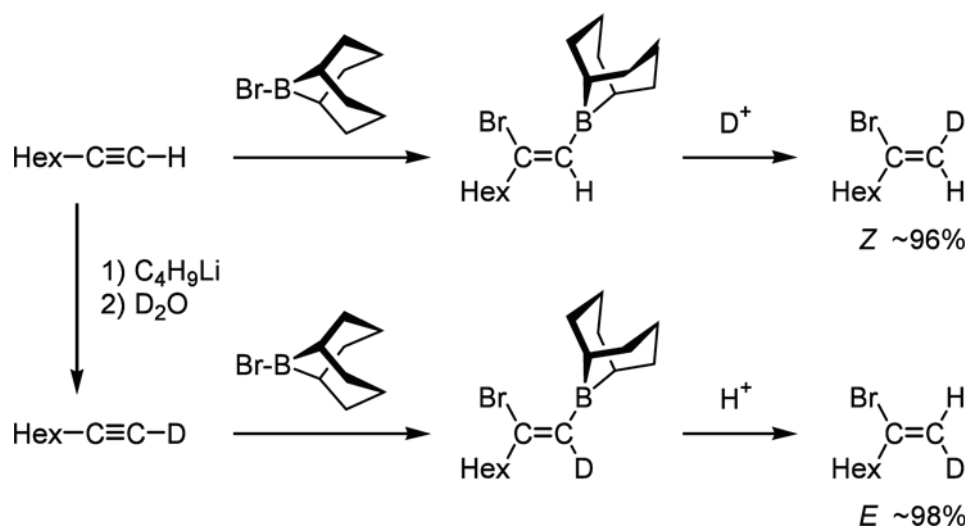


Figure 25

The haloboration adducts thus obtained are valuable intermediates to give various organic

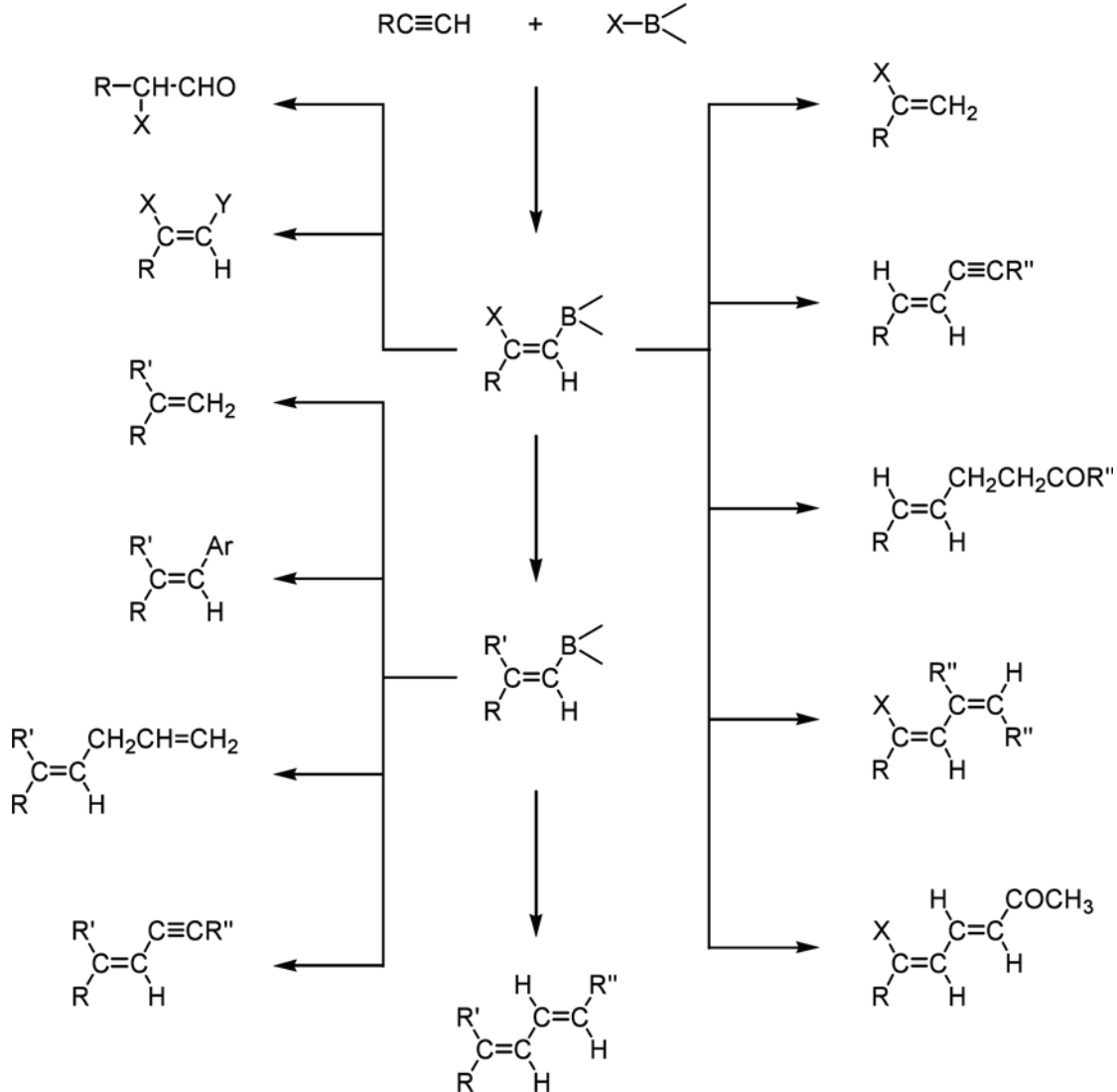


Figure 26

CONCLUSION

As shown in this article, all kinds of organoboron compounds including (sp²)C-B, (sp³)C-B and (sp)C-B bonds can be used in coupling reactions with various organic electrophiles to provide corresponding coupled products readily in high yields stereo- and regioselectively. Such reactions have a number of advantages. Today, the Suzuki coupling reaction continues to evolve, with many new possibilities reported during the past three decade. For example, solid-phase Suzuki coupling has been developed using either resin-bound aryl halides with solution-phase boronic acids or *vice versa*. Such approaches play an important role in the combinatorial and parallel methodologies now used to explore chemical reactivity, especially in medicinal chemistry. Increasingly, industry is seeking to use more

environmentally-friendly processes. These often require ingenious solutions to which Suzuki coupling is well-suited. Research groups around the world are investigating modifications of the reaction that work in aqueous media or with trace amounts of catalysts.

We can expect to see many more interesting versions of the Suzuki coupling in the future.

ACKNOWLEDGEMENTS

I wish to thank the late Professor Herbert C. Brown. My study on borane chemistry began in Professor Brown's laboratory at Purdue University in 1963 under his guidance. I also thank my many co-workers who helped me explore the riches of the New Boron Continent described in this article.

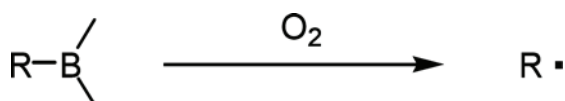
REFERENCES

1. CL-1
2. CL-2
3. CL-3
4. CL-4
5. CL-5

Classified List (CL)

Papers Numbers (abbreviated references) will be shown in Publication List indicated later

CL-1: Organoboranes as Sources of Organic Radicals

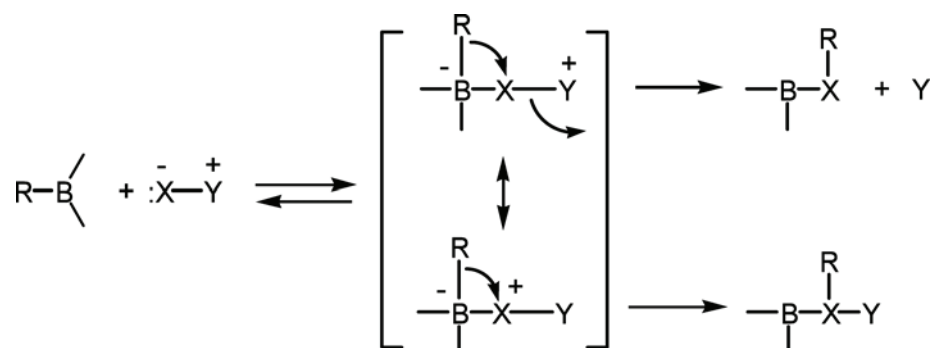


Paper No. Abbreviated References

- 2 *JACS*, **1967**, 89, 5708.
- 10 *JCS Chem. Comm.*, **1969**, 1009.
- 11 *JACS*, **1970**, 92, 710.
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- 18 *JACS*, **1971**, 93, 1508.
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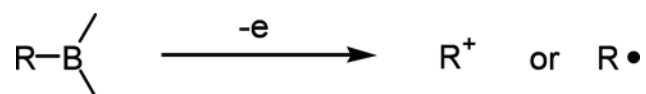
CL-2: Organoboranes as Carbanion Sources



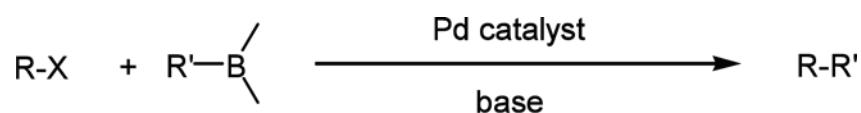
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CL-4: Coupling Reactions of Organoboranes with Organic Electrophiles (Suzuki Coupling)

R, R' = alkyl, 1-alkenyl, aryl, 1-alkynyl, allyl and benzyl

Paper No. Abbreviated References

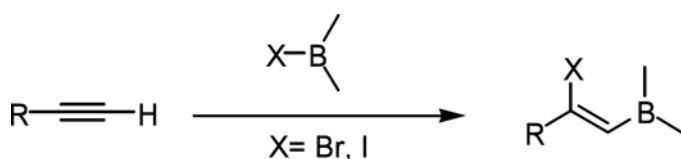
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CL-6: Other Investigations (Hydroboration, Isomerization, Displacement Reaction, etc)

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