

## Boranes in Organic Chemistry

### 3. $\alpha$ -, $\beta$ - and $\gamma$ -Haloalkylboranes: The Perspective Vehicles for Organic Synthesis

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#### Abstract

The methods of synthesis of  $\alpha$ - and  $\beta$ -haloalkylboranes, including chloration of alkylboronic acid esters, additive bromation and chloration of esters of vinyl- and alkenylboronic acids, addition of bromine to trivinylborazines have been considered.

The reactions of radical addition of polyhaloidmethanes to vinylboranes,  $\alpha$ - and  $\beta$ -unsaturated boronic esters, B-vinyl-B-arylboronic esters, B-trivinyl-B-triarylborazines were discussed. The hydroboration of acetylenic halogenides of dicycloalkylboranes, which led to halocontaining derivatives of dialkylvinylborane was separately considered. The examples of hydroboration of halogenides of allyl and vinyl types are presented. The reaction of dienic synthesis, which takes place between vinylchloroboranes or vinylboronic esters and tetra- or hexachlorocyclopentadienes has been discussed.

The reaction of alkenes and allenes with boron tribromide was described. The Markovnikov and non-Markovnikov hydrobromation of boron vinyl derivatives has been envisaged. The approaches to the synthesis of perfluoroalkylboranes on the base of hydroboration of perfluoroalkenes have been discussed. The methods of the synthesis of boronates, containing halogetaryl substituents, have been performed. The reactions of hydroboration of halogenides of allylic and propargylic types by 9-borabicyclononane have been shown. The regio- and stereoselectivity of the reaction has been discussed. The examples of the synthesis of boranes of the norbornene type were presented. The reaction of boroallylilation of allyl- and propargyl-halogenides leading to the derivatives of 3-bora-bicyclo[3,3,1]-nonane has been discussed.

Some directions of using of haloidalkylboranes in the synthesis have been discussed. The examples of nucleophilic substitution leading to oxyalkyl- and azidoalkylboranes have been presented. The route of obtaining of alcohols from  $\alpha$ -haloidalkylboranes has been shown. The general scheme of synthesis of  $\alpha$ -aminoboronic acids was performed. The general approach to the synthesis of allenes on the base of hydroboration products of propargyl halogenides has been discussed. The schemes of synthesis of 1,4-disubstituted-1,2,3-butatrienes are presented. The wide using reaction of introducing of vinylic group into substituent, bonding with boron atom in molecules of dialkylvinylboranes, was discussed. The reactions of new C-C bonds formation, based on the action of iodine on the alkylvinylboronates leading to 1,3-dienes and alkylidencyclanes have been shown. The route of the synthesis of cyclopropanes from  $\beta$ -haloidalkylboranes has been discussed.

#### Introduction

$\alpha$ -,  $\beta$ -,  $\gamma$ -Haloalkylboranes are rare groups of synthetic compounds with common structures such as **B-C-X**, **B-C-C-X**, **B-C-C-C-X** (X = F, Cl, Br or I) are mainly intermediate compounds in hydroboration reactions partly given in some reviews [1-9].

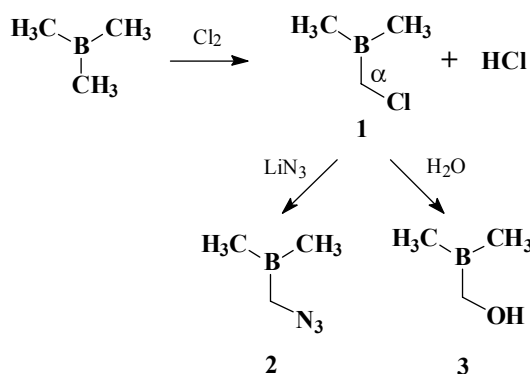
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#### $\alpha$ -Haloalkylboranes

##### *Reactions of chlorine with boranes*

Chlorine reacted with trimethylboranes at minus 95°C to give  $\alpha$ -chloro- $\alpha$ -boron derivative **1** [10]. Compound **1** reacted with lithium azide and with water to form the corresponding azide **2** and alcohol

3 [11] (Scheme 1).

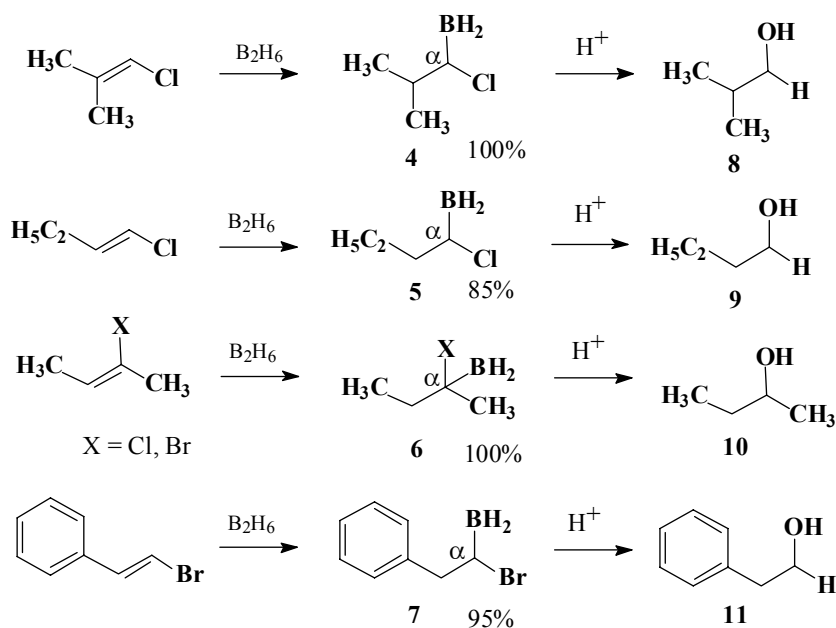


### Synthesis of haloalcohols via $\alpha$ -haloalkylboranes

The action of diborane on halogenated derivatives of unsaturated hydrocarbons was investigated for the first time by Stone et al. [12,13]. Treatment  $\alpha$ -halogenated boranes **4** – **7** proceeded corresponding haloalcohols **8** – **11** (Scheme 2). Pasto and Snyder [14] also found that in the hydroboration of vinyl halides, the boron atom was completely or predominantly in the  $\alpha$ -position.

### Addition tetrachloromethane to $\alpha,\beta$ -unsaturated esters

Reaction of addition of  $\text{CCl}_4$  to  $\alpha,\beta$ -unsaturated



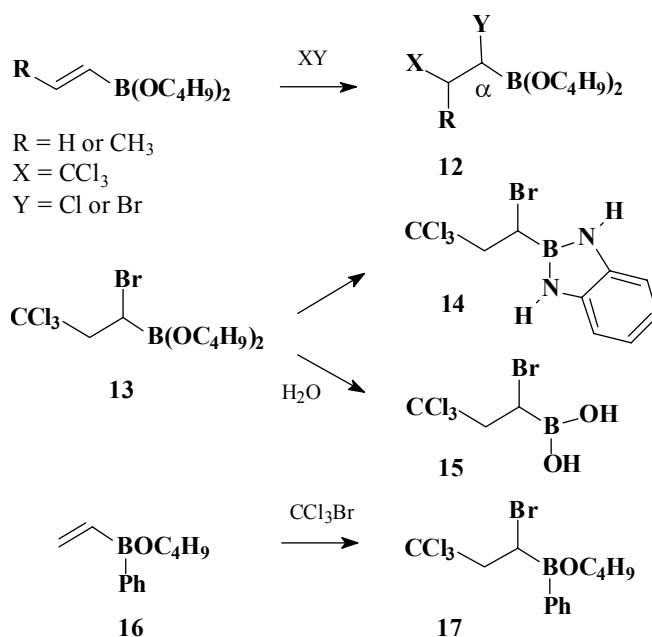
esters is common for all derivatives of dibutyl propene-2-boronate, in the presence of azobisisobutyronitrile as the initiator, as resulting are  $\alpha$ -haloalkylboranes **12** (Scheme 3) [15]. 1-Bromo-3,3,3-trichloropropane-1-boronic acid **15** could be obtained from 1-bromo-3,3,3-trichloro-dibutylpropane-2-boronate **13** by recrystallization from water, and **13** could be converted to its *o*-phenylenediamine **14** [16]. Light-initiated addition of bromotrichloro-methane to butyl B-phenyl-B-vinylborinate **16** proceeded readily butyl B-phenyl-B-(1-bromo-3,3,3-trichloro-1-propyl)borinate **17** [17,18].

### Formation of amidoboranes

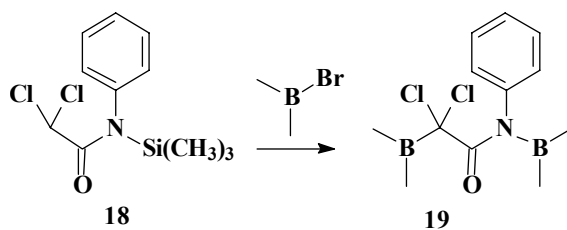
*N*-Trimethylsilylamides **18** reacted with bromodiorganylboranes quantitatively under formation of the corresponding amidoboranes, in certain cases these are in equilibrium with the dimeric forms [19]. Among these reactions in one case could be forming  $\alpha$ -haloalkyl compound **19** (Scheme 4). Thus, *N*-phenyl-*N*-trimethylsilyldichloroacetamide reacted with bromodimethylborane to form **19** [19].

### Hydroboration of cyclovinyllic derivatives

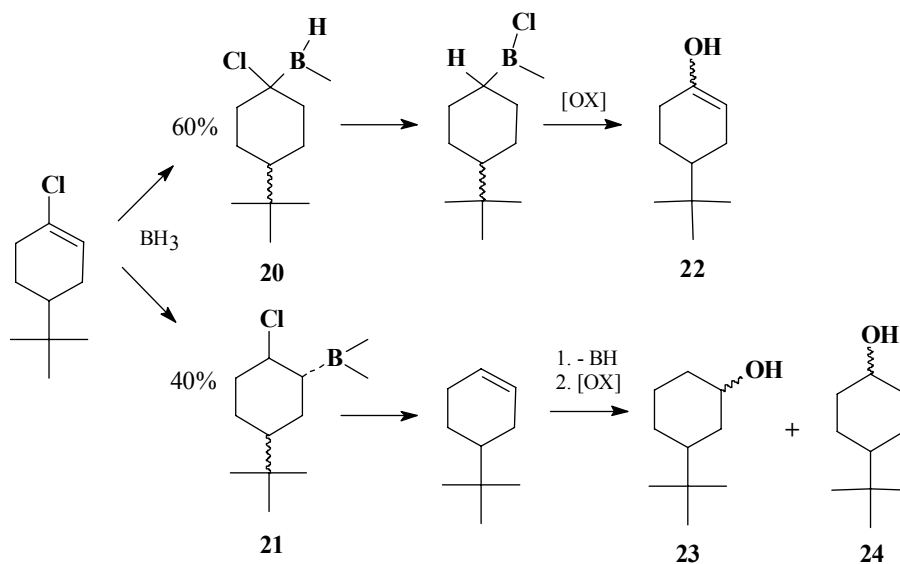
Pasto and Snyder also studied a series of vinyl halides to determine the placement of B – H in tetrahydrofuran with borane [14]. Hydroboration of 4-*t*-butyl-1-chlorocyclohexene at 25°C gave 60% 1-chlorocyclohexyl borane **20**, and 40% of the boron atom introduced at the  $\beta$ -position **21** (Scheme 5).



Scheme 3



Scheme 4

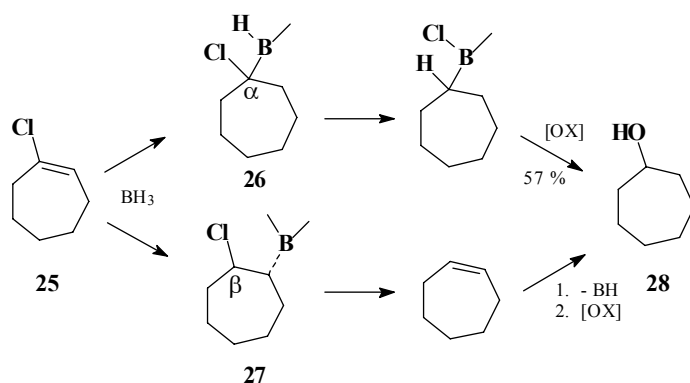


Scheme 5

Oxidation of **20** and **21** gives corresponding alcohols **22** – **24**.

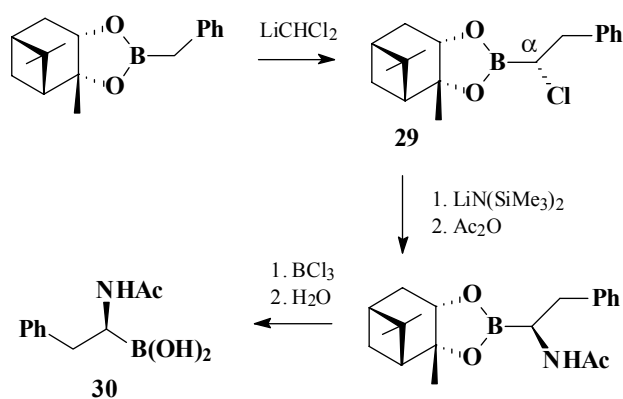
In the case of 1-chlorocycloheptene **25** two ad-

ducts were formed, at the  $\alpha$ - **26** and  $\beta$ -position **27** to chloride atom (Scheme 6) [14]. Oxidation of **26** and **27** gives one only compound **28**.



### Synthesis of optically active analogue of phenylalanine

An optically active boron analogue of phenylalanine has been obtained using the  $\alpha$ -haloboronic ester **29** [20]. The use of (+)-pinenediol for boronic acid protection allowed the preparation of an optically pure of **30** (Scheme 7).



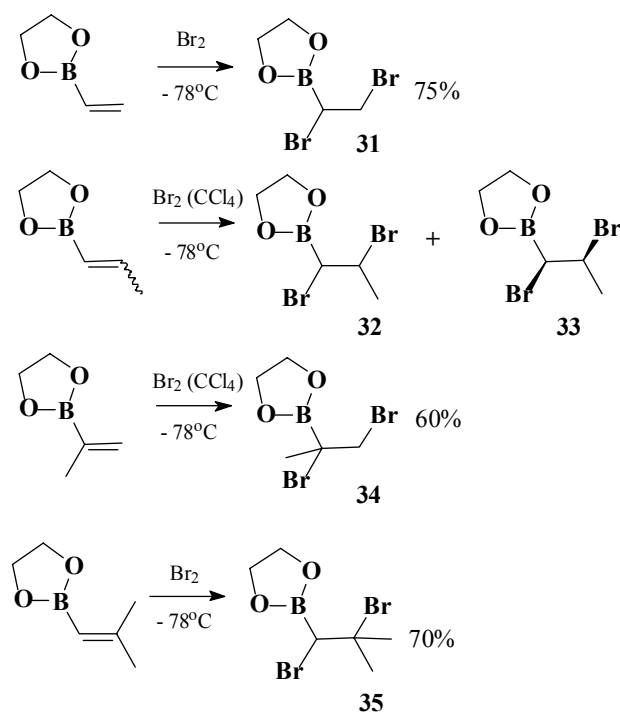
### $\alpha$ -, $\beta$ -Haloalkylboranes

In some cases, the synthesis of  $\alpha$ -haloalkylboranes was accompanied by  $\beta$ -haloalkylboranes. Conditions and/or reactants for the formation of  $\alpha$ -,  $\beta$ -boryl alkyl halides differ from those used for obtaining  $\alpha$ -boryl alkyl halides [1,2,5,6,8].

### Bromination of dioxaborolane derivatives

A series of brominations of dioxaborolane derivatives has been described by Coindard et al. [21]. Bromine reacted at minus 80–70°C with various dioxaborolane derivatives to give 2-(1,2-dibromo-ethyl)-[1,3,2]dioxaborolane **31**, two isomers of 2-(1,2-dibromo-propyl)-[1,3,2]dioxaborolane **32** and 2-

((1*RS*,2*SR*)-1,2-dibromo-propyl)-[1,3,2]dioxaborolane **33**, 2-(1,2-dibromo-1-methyl-ethyl)-[1,3,2]-dioxaborolane **34**, and 2-(1,2-dibromo-2-methyl-propyl)-[1,3,2]dioxaborolane **35** (Scheme 8).



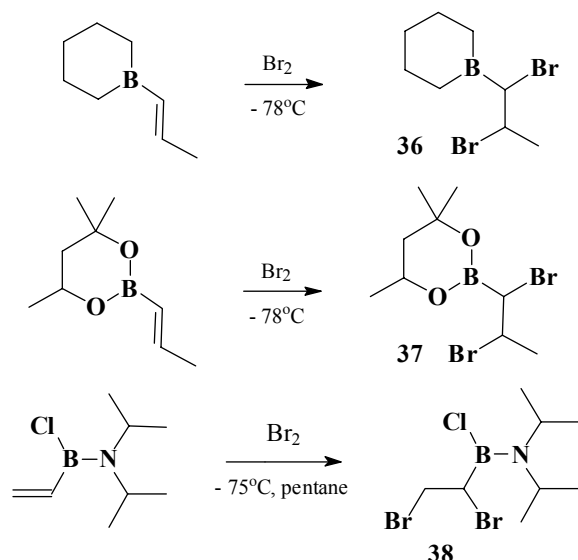
### Bromination of boron derivatives

The same bromination procedure was also applied to other boron compounds. Thus, bromination of propyleneborinane at minus 78°C provided 1,2-dibromo-propylborinane **36** (Scheme 9) [21].

Woods and Bengelsdorf [22] observed reaction between bromine and 4,4,6-trimethyl-2-vinyl-[1,3,2]dioxaborinane. The final product was identified as 2-(1,2-dibromo-ethyl)-4,4,6-trimethyl-[1,3,2]dioxaborinane.

borinane **37**.

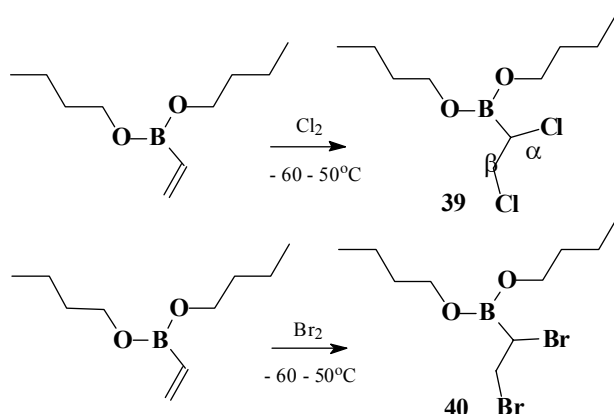
Bromination of chlordiisopropylaminovinyl-borane at minus 75°C in pentane gave (1,2-Dibromoethyl)-chloro-diisopropylaminoborane **38**. (Scheme 9) [21].



Scheme 9

### Halogenation of vinylboronic acid esters

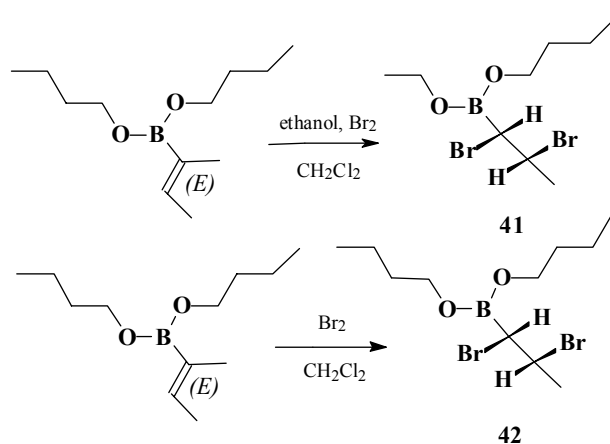
Mikhailov and Aronovich [23] found that both chlorine and bromine in hexane at -50°C reacted with dibutyl ester of vinylboronic acid to give dibutyl ester (1,2-dichloro-ethyl)-boronic acid **39** and dibutyl ester of (1,2-dibromo-ethyl)-boronic acid **40**, respectively (Scheme 10).



Scheme 10

Matteson and Liedtke [24] showed that the dibutyl ester of (*E*)-(1-methyl-propenyl)-boronic acid reacted with bromine and ethanol in benzene to form

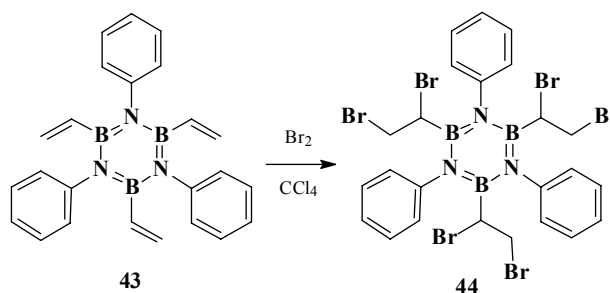
diethyl ester (1*RS*,2*SR*)-(1,2-dibromo-1-methyl-propyl)-boronic acid **41**. If the reaction was run without ethanol the dibutyl ester of (1*RS*,2*SR*)-(1,2-dibromo-1-methyl-propyl)-boronic acid **42** was found (Scheme 11).



Scheme 11

### Bromination of borazine

Seyferth and Takamizawa showed that in the reaction of B-trivinyl-*N*-triphenylborazine **43** with bromine in CCl<sub>4</sub>, B-tris-(1,2-dibromo-ethyl)-*N*-triphenylborazine **44** was obtained [25] (Scheme 12).



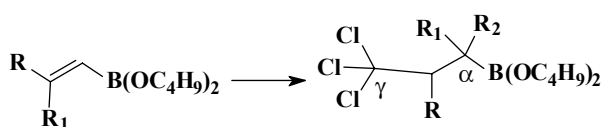
Scheme 12

### $\alpha,\gamma$ -Haloalkylboranes

#### Reactions of $\alpha,\beta$ -unsaturated butyl boronic esters

Various  $\alpha,\gamma$ -boryl butyl halides **45** - **49** were obtained during the investigation of radical additions to  $\alpha,\beta$ -unsaturated boronic esters [15]. A study of  $\alpha,\beta$ -unsaturated organoboron compounds furnished useful information for the synthesis of new organoborons which contain many different functional groups. Common principles of these reactions were

discovered by Matteson [15,18] and shown in Scheme 13.



45. R = R<sub>1</sub> = H, R<sub>2</sub> = Cl  
 46. R = R<sub>1</sub> = H, R<sub>2</sub> = Br  
 47. R = H, R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = Cl  
 48. R = H, R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = Br  
 49. R = CH<sub>3</sub>, R<sub>1</sub> = H, R<sub>2</sub> = Br

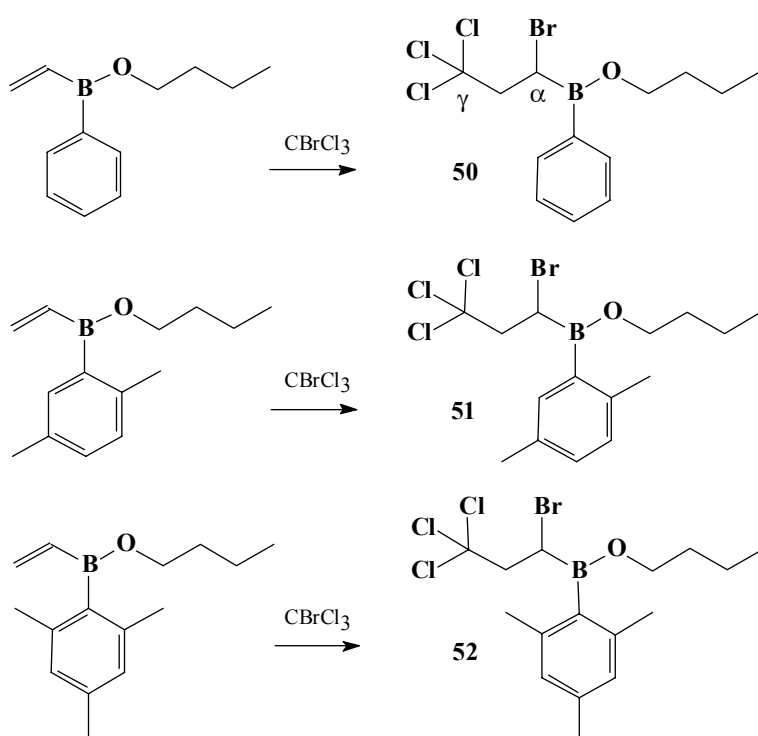
Scheme 13

### Synthesis of $\alpha,\gamma$ -halogenated borinates

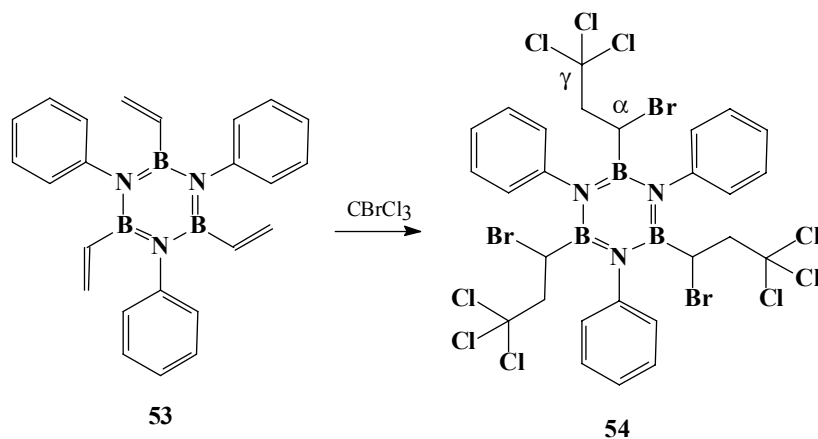
Matteson and Mah [26] built on their previous studies [15,18] and synthesized B-aryl-B(1-bromo-3,3,3-trichloro-1-propyl)borinates **50** - **52** via radical addition of bromotrichloromethane to B-aryl-B-vinylboronic esters (Scheme 14).

### Synthesis of $\alpha$ -bromo- $\gamma$ -trichloroorganoborazines

Seyferth and Takamizawa [25] synthesized of B-tris-(1-bromo-3,3,3-trichloro-propyl)-*N*-triphenylborazine **54** from B-trivinyl-*N*-triphenylborazine **53** and trichlorobromomethane (Scheme 15).



Scheme 14



Scheme 15

## $\beta$ -Haloalkylboranes

### Hydroboration of Acetylenes

Dihydroboration of acetylenes proceeds to place two boron atoms preferentially on the terminal carbon atom has been investigated [27]. A careful reexamination of the dihydroboration of 1-hexyne using deuterium as a tracer has confirmed the original conclusion [28]. These vinylboranes evidently have rich possibilities for organic synthesis. Thus, the hydroboration of substituted propargyl chlorides provides the convenient route for terminal allenes were  $\beta$ -haloalkyl boranes **55**, are the postulated intermediates, in yields of 64-73% (Scheme 16) [29]. Hydroboration of functional alkynes is also possible, and when the functionality is close to the triple bond, further reaction of the boranes may lead to useful synthetic procedure, [30-32] where intermediate **56** is  $\beta$ -chloroalkylborane.  $\beta$ -Heterosubstituted alkylboranes can induce  $\beta$ -elimination **57** to form allenes

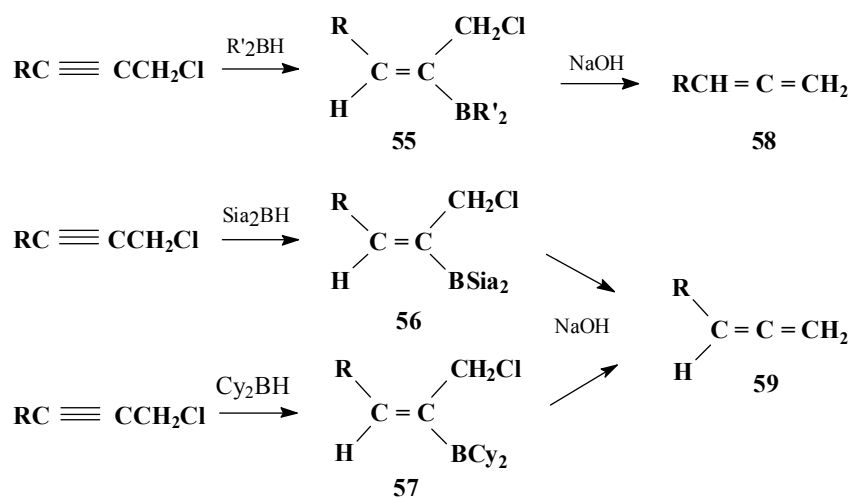
**58** and **59** [33].

The same synthetic route achieved the stereoselective synthesis of *trans*-1,4-disubstituted-1,2,3-butatrienes **62** where  $\beta$ -**61**, and  $\alpha$ -haloalkylboranes **60** are the intermediates (Scheme 17) [34-36]. Propargylboranes produced by rearrangement of allenylboranes react with allyl bromines in the presence of copper iodides in highly specific fashion to yield 1,5-enynes only.

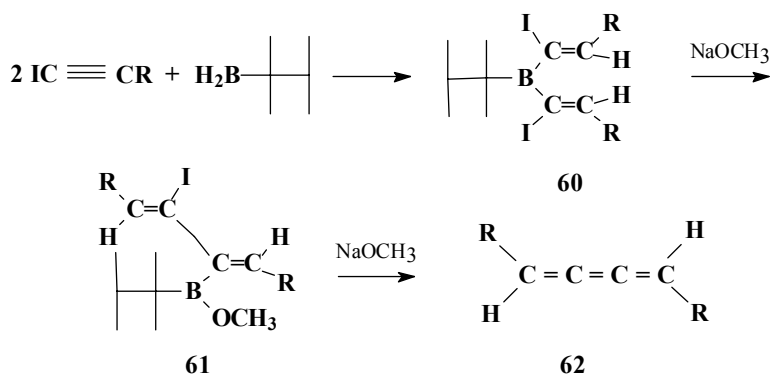
Diisopinocampheylborane **64** reacts with 1,4-dichloro-but-2-yne **63** in tetrahydrofuran at -40-(+) 20°C, providing (3-chloro-1-chloromethyl-propenyl)-bis-(2,6,6-trimethyl-bicyclo[3.1.1]hept-3-yl)-borane **65** (Scheme 18) [37].

### Allylic derivatives

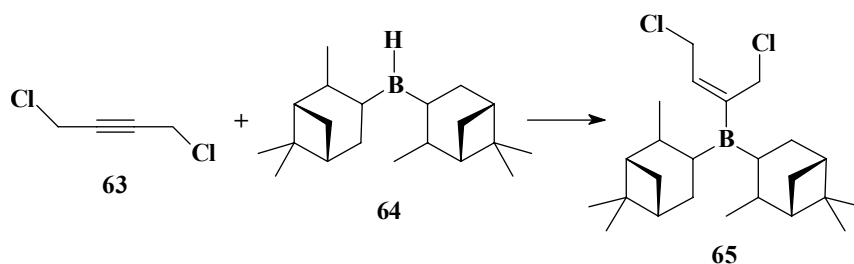
Hydroboration of allylic compounds can provide  $\beta$ -substituted organoboranes [36,38]. The products depend on the functional groups. The amount of  $\beta$ -substituted organoborane increases with increasing electronegativity of the substituents.



Scheme 16

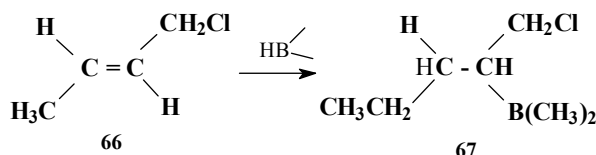


Scheme 17



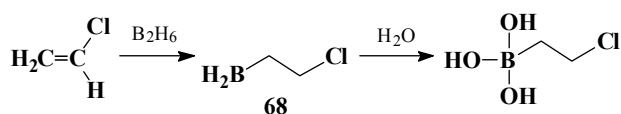
Scheme 18

Hydroboration of crotylchloride **66** gave about 90% of  $\beta$ -chloroalkylborane **67** [39]. When X is a good leaving group, such as Cl, elimination occurs to give 1-butene, which then undergoes hydroboration. This reaction was conducted in ethyl ether (Scheme 19) [39].



Scheme 19

$\beta$ -Haloalkylboranes may be prepared by reaction with unsaturated compounds [12,13]. It was reported that tetrafluoroethylene reacts with diborane at room temperature and rapidly at 80°C, with formation of ethyldifluoroborane, diethylfluoroborane, and a polymeric product. Thus the first  $\beta$ -elimination of  $\beta$ -haloalkylborane was found by Hawthorne and Dupont [40]. They obtained  $\beta$ -chloroethylborane dichloride **68** in low yield (Scheme 20).

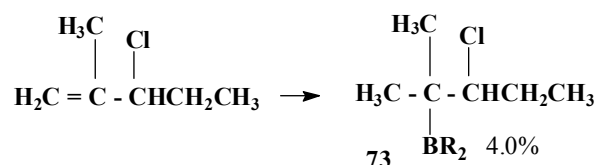
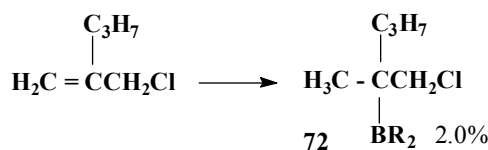
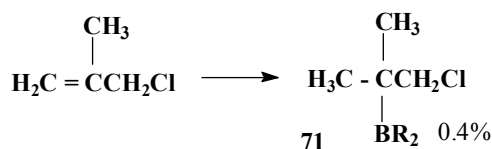
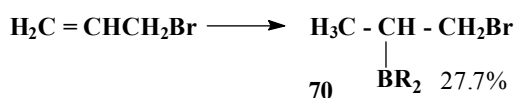
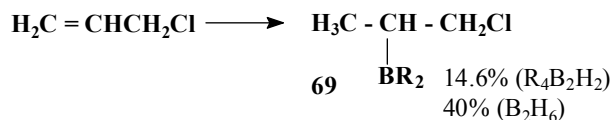


Scheme 20

Tetraalkyldiboranes are hydroborate 3-haloolefins more selectively than diborane. According to Köster et al. [41,42] who found that in the reaction of 3-haloolefins with tetraethyl- and tetrapropylborane, the boron preferred the terminal carbon atom, and less so formed  $\beta$ -halo-alkylboranes **69** – **73** (Scheme 21).

#### *Intramolecular transfer reactions of alkenylboranes with inorganic electrophiles*

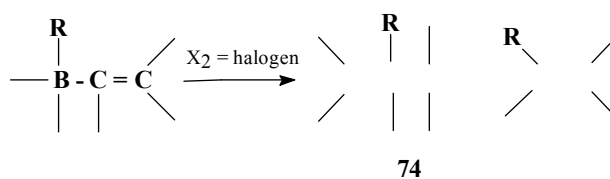
The predilection of organoboranes to undergo to



Scheme 21

*intra*-molecular transfer reactions is well known [3,6]. Alkenylboranes react with halogens [29] or acids [43,44] to undergo 1,2-migration of an alkyl group from boron atom to the  $\alpha$ -alkenyl carbon. Halogen induced migration products undergo  $\beta$ -elimination to give highly stereospecific alkenes, and also  $\beta$ -haloalkylboranes **74**. Typical reactions are indicated below (Scheme 22).

Reaction of alkenylboranes **75** with iodine in the

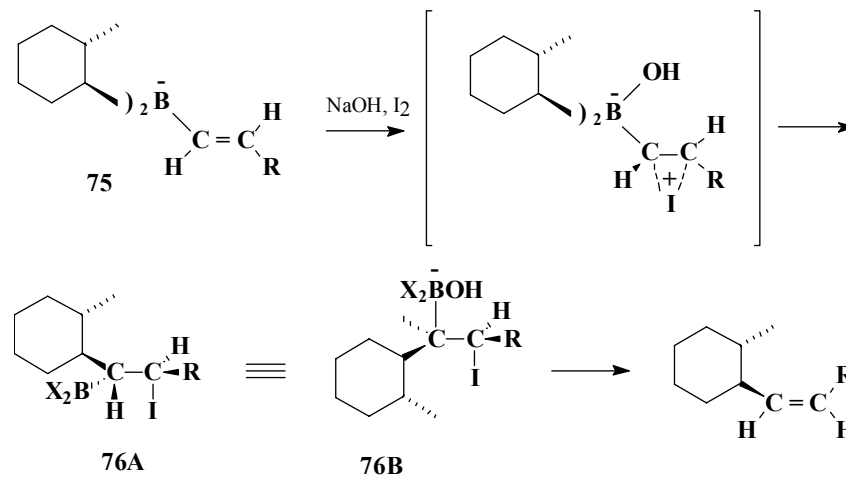


Scheme 22



presence of excess base, usually sodium hydroxide, gave configurationally inverted alkenes [45], and formed as intermediate  $\beta$ -haloalkyl boranes com-

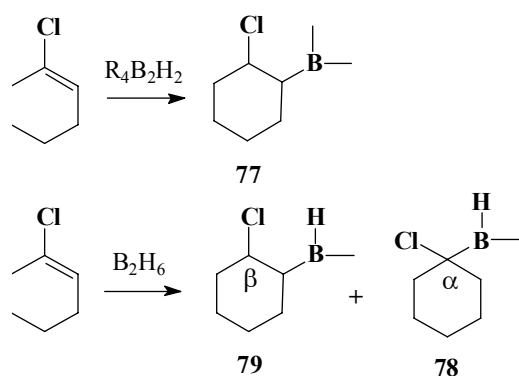
pounds **76A** and **76B** (Scheme 23). A major drawback of the iodine induced alkene synthesis is that it utilizes one or two alkyl groups.



Scheme 23

### Reactions of cyclovinyl derivatives with organoboranes

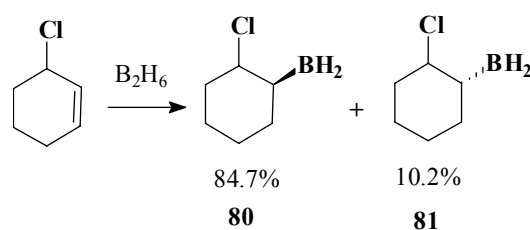
Köster et al. [41,42] obtained cyclohexyldialkylborane from 1-chlorocyclohexene and tetraalkylborane, *via* intermediate  $\beta$ -boryl alkyl chloride **77** (Scheme 24). In diborane THF two organoboranes with  $\alpha$ - **78** and  $\beta$ -position **79** chlorine with boron atom were obtained [14].



Scheme 24

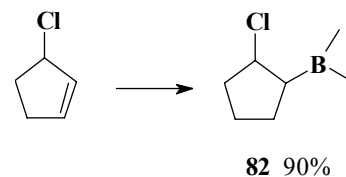
According to Pasto and Hickman [39] who carried out detailed studies of the hydroboration of 3-chlorocyclohexene with diborane in diethyl ether and tetrahydrofuran, the boron atom attacks mainly in 2 position with the formation of the *trans*-isomer **80** (85-87%) and *cis*-isomer **81** (10%), and two minor

3-*cis*- (1.5%) and 3-*trans*- (3.6%) isomers (Scheme 25).



Scheme 25

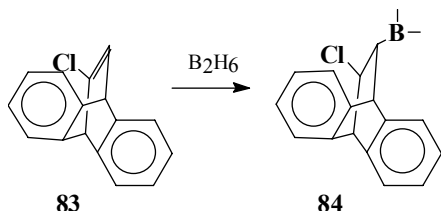
The presence of substituents can introduce marked directive influences on the reaction of hydroboration [38,46,47]. Hydroboration of 3-chlorocyclopentene with tetraethylborane in butyl ether at 0-10°C leads mainly to 2-chlorocyclopentylboranes **82** (Scheme 26) [48].



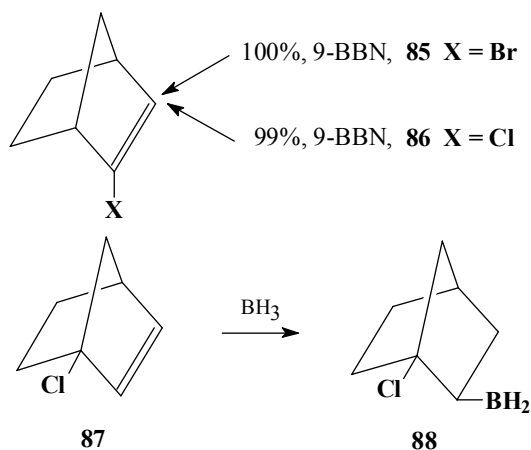
Scheme 26

Cristol et al. [49] have reported that the hydroboration of 7-chlorodibenzobicyclo[2.2.2]-octatriene **83**

under the action of diborane in diethyl ether gave  $\beta$ -haloalkylborane **84** (Scheme 27). These results indicate that in this system the boron adds predominantly in  $\beta$ -position to the chlorine substituent.



Scheme 27



Scheme 28

### Reactions of norbornanes with halides

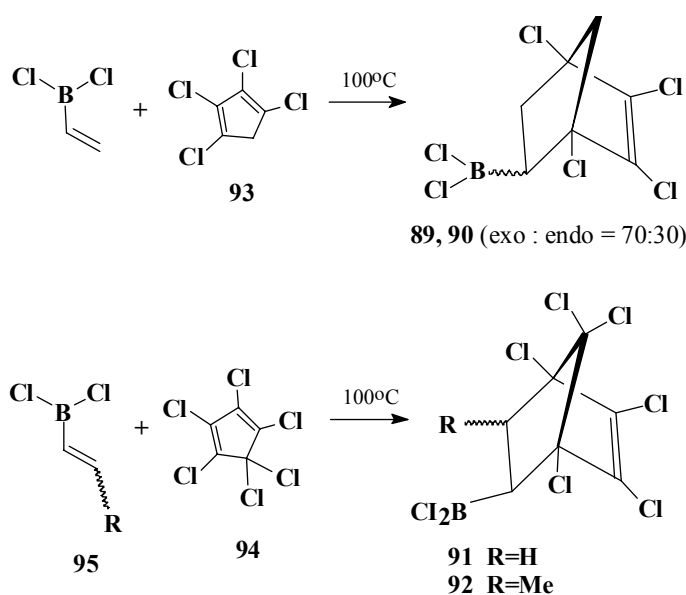
The effects of heterosubstituents can be overcome through hydroborating agents of specific structure, for instance 3-butenyl derivatives [50], propionic acid esters [51], propargyl chloride [52], allyl [53], allyl sulfonates [54] and also for 2-bromonorbornene [55]. A high degree of selectivity was found for 9-BBN in case of 2-bromo-**85** and/or 2-chloronorbornanes **86**.

However, hydroboration of 1-chloronorbornane **87** gave the corresponding chlorohydrin **88** in 63% yield (Scheme 28) [56].

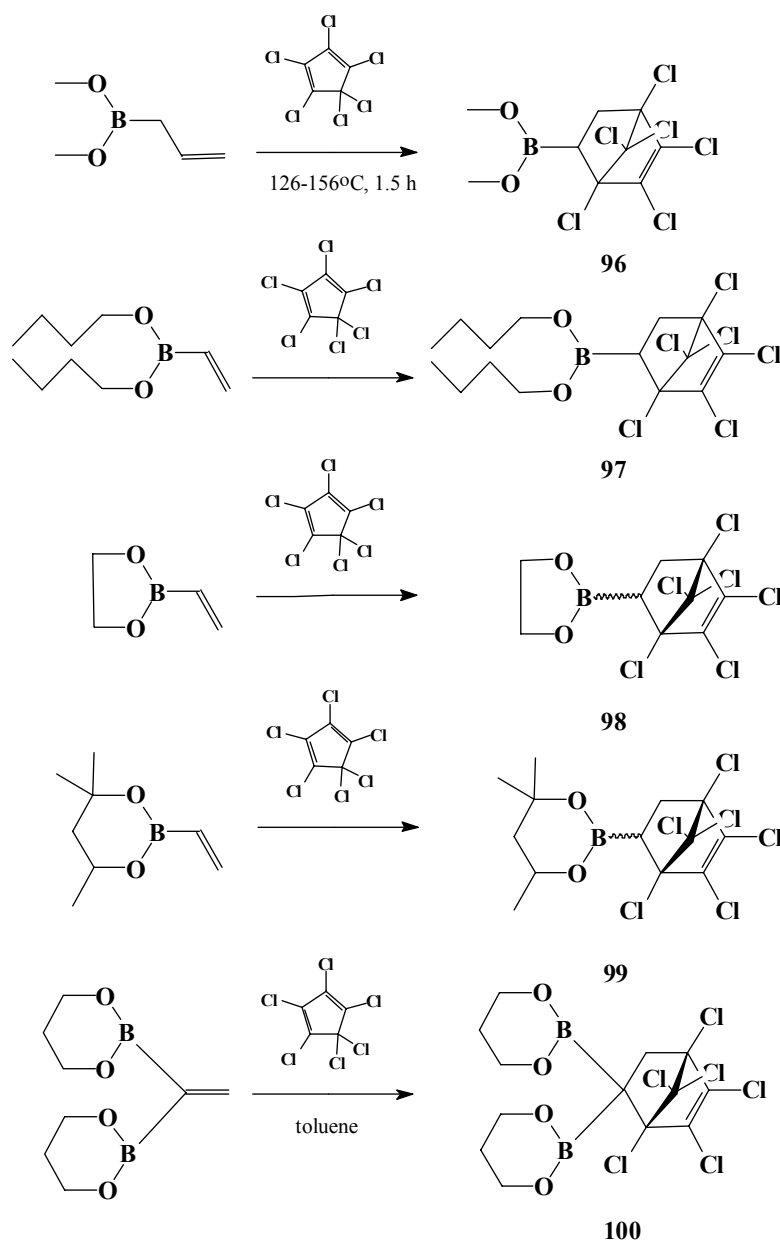
Usually alkenyldialkylboranes do not appear to have been used in the Diels-Alder reaction [3] although haloalkenylboranes have been reacted with dienes to form Diels-Alder adducts [57] including  $\beta$ -haloalkylboranes (Scheme 29) **89** - **92**. Coindard and Braun [57] have studied several reactions of

chlorinated dienes with vinylboranes. In some cases the authors obtained norbornane derivatives. Thus, dichlorovinylborane in benzene at 100°C reacted with 1,2,3,4-tetrachloro-cyclopenta-1,3-diene **93** to give dichloro-(1.4.5.6-tetrachloro-5-norbornen-2-yl)-borane **89, 90**. In the same manner, dichlorovinylborane reacted with 1,2,3,4,5,5-hexachloro-cyclopenta-1,3-diene **94** to give dichloro-(1.4.5.6.7.7-hexachloro-5-norbornen-2-yl)borane **91**. Reaction between dichloropropenylborane **95** and 1,2,3,4,5,5-hexachloro-cyclopenta-1,3-diene gave **92** (Scheme 29).

$\beta$ -Haloalkylboranes such as halide derivatives of norbornane **96** - **100** could be obtained from different boryl allyl and/or vinyl derivatives by reaction with 1,2,3,4,5,5-hexachloro-cyclopenta-1,3-diene (Scheme 30).



Scheme 29



Scheme 30

According to Michailov and Bubnov [6] and Mikhailov [9] the ester of allylboronic acid reacts easily with 1,2,3,4,5,5-hexachloro-cyclopenta-1,3-diene, providing 2-(1,4,5,6,7,7-hexachloro-bicyclo[2.2.1]hept-5-en-1-yl)methyl-boronic acid **96** [58]. The same authors used dibutyl ester of vinylboronic acid and obtained the corresponding dibutyl ester of 1,4,5,6,7,7-hexachloro-norbornen-(5)-boronic acid **97**.

Coindard and Braun [57] used 2-vinyl-[1,3,2]dioxaborolane which reacted with hexachloro-cyclopentadiene to give 2-(1,4,5,6,7,7-hexachloro-norborn-5-en-2-endo-yl)-[1,3,2]dioxaborolane **98**.

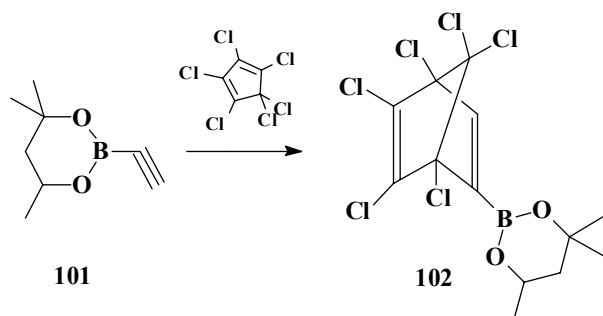
Woods and Bengelsdorf [59] showed that 4,4,6-

trimethyl-2-vinyl-[1,3,2]dioxaborinane reacts with 1,2,3,4,5,5-hexachloro-cyclopenta-1,3-diene to give 2-(1,4,5,6,7,7-hexachloro-norborn-5-en-2-endo-yl)-4,4,6-trimethyl-[1,3,2]dioxaborinane **99**.

Reaction between of 2,2'-ethene-1,1'-diyl-bis-[1,3,2]dioxaborinane and hexachloro-cyclopentadiene provided 2,2'-(1,4,5,6,7,7-hexachloro-norborn-5-ene-2,2'-diyl)-bis-[1,3,2]dioxaborinane **100** [4,60].

Interesting experimental data have been obtained by Wood and Strong [61]. They used the reaction of acetylenic analogues **101** of **99**, which react with 1,2,3,4,5,5-hexachloro-cyclopenta-1,3-diene to form 2-(4,4,6-trimethyl-1,3,2-dioxaborinane-2-yl)-1,4,5,

6,7,7-hexachlorobicyclo-[2.2.1]hepta-2,5-diene **102** (Scheme 31).

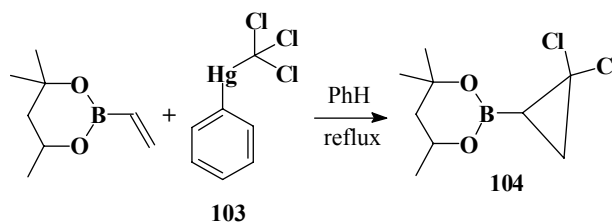


Scheme 31

### Pericyclic reactions with alkenylboranes

In addition to the Diels-Alder reaction, alkenylboranes can participate in various pericyclic reactions which typical alkenes undergo. Thus, Woods and Bengelsdorf [59] using vinylboronic ester (4,4,6-trimethyl-2-vinyl-[1,3,2]dioxaborinane) showed that it reacted with phenyltrichloro-methylmercury **103**

to undergo a cyclopropane reaction, where **104** was identified as 2-(2,2-dichloro-cyclopropyl)-4,4,6-trimethyl-[1,3,2]dioxaborinane (Scheme 32).



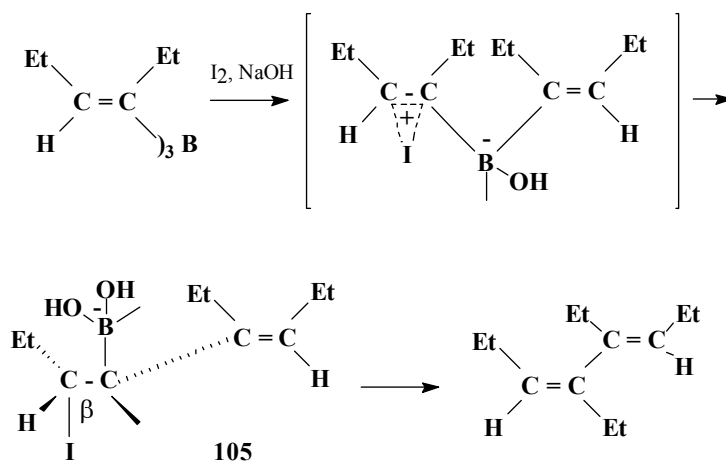
Scheme 32

### Synthesis of conjugated (Z,E)-dienes

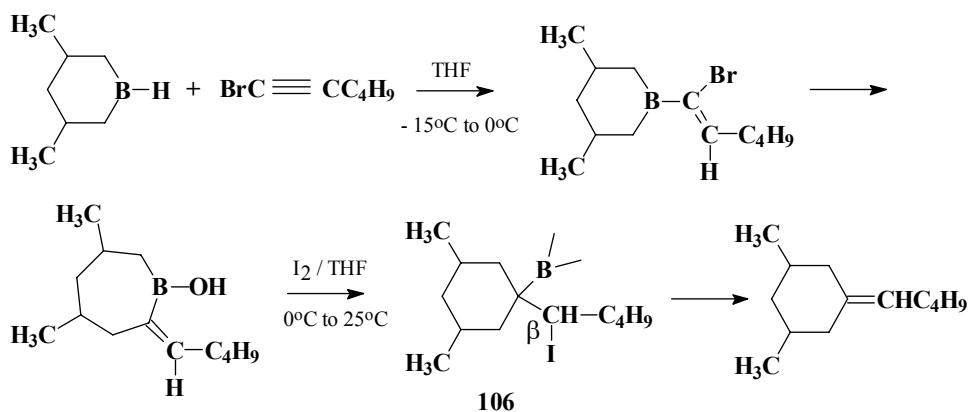
$\beta$ -Haloalkylboranes **105** arise in the synthesis of symmetrical (Z,E)-dienes according to procedure described by Zweifel et al. (Scheme 33) [62].

### Synthesis of exocyclic olefins

The reaction of 3,5-dimethylborinane with 1-bromo-1-hyxyne afforded intermediate  $\beta$ -iodoalkylborane **106** (Scheme 34) [45].



Scheme 33

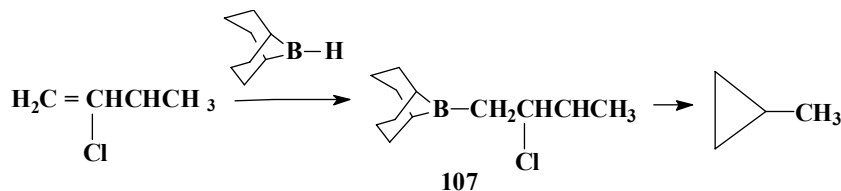


Scheme 34

### *$\beta$ -Haloalkylboranes in formation of cyclopropane ring*

Hawthorne [64] and later Brown and Rhodes [65]

shown that 9-BBN is a good agent in hydroboration and synthesis of cyclopropane rings in 80-85% yield via  $\beta$ -chloroalkylboranes as the major intermediate **107** (Scheme 35).



Scheme 35

### *The Zweifel olefin synthesis*

The Zweifel synthesis in the original form provides a stereospecific synthesis of (*Z*)-alkenes [45] via  $\beta$ -boryl alkyl iodide complexes **108** and **109** (Scheme 36).

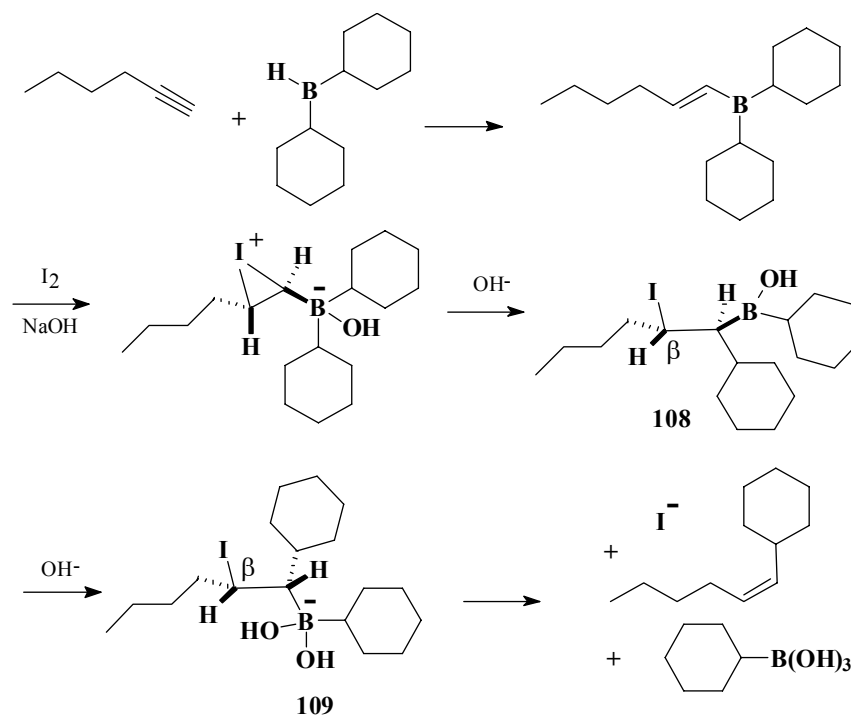
### *Bromoboration of unsaturated compounds*

The reaction of boron tribromide with hex-1-ene formed bromo-bis-(2-brom-hexyl)-boran **110** (Scheme 37) [66]. Also boron tribromide reacted at 90°C during seven hours with *trans*-hex-3-ene to form bromo-bis-(2-brom-1-ethyl-butyl)-boran **111** [66]. In

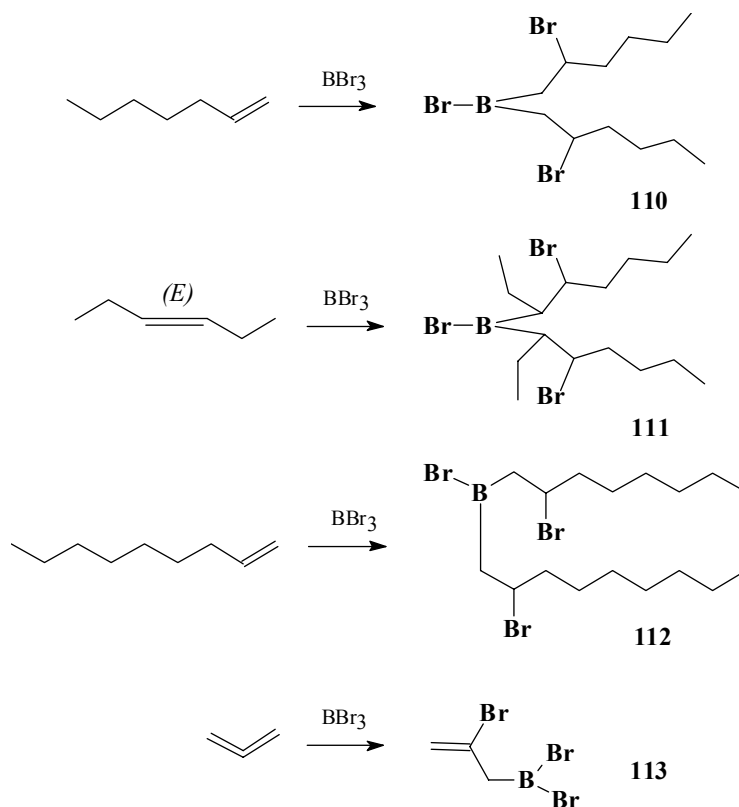
a similar fashion, oct-1-ene reacted with hex-1-ene to give bromo-bis-(2-brom-octyl)-boran **112**.

Joy et al. [67] studied the reaction of boron halides (Cl and Br) with some organoboron compounds. The authors showed that bromoboration of propadiene gave 2-brom-3-dibromboryl-prop-1-en **113**.

Tanigawa et al. [68] have described the synthesis of two stannan derivatives such as *trans*-cinnamyltriethyl- and *trans*-cinnamyltriphenyltin and their reactions with tribromoborane. The reaction of *trans*-cinnamyltriethyl- and/or *trans*-cinnamyl-triphenyltin **114** with tribromoborane proceeded with the preferential transfer of the *trans*-cinnamyl group transi-



Scheme 36

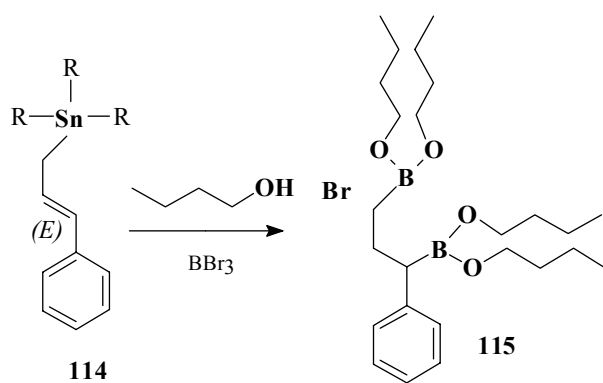


Scheme 37

tion state through a four-centered cyclic transition state or a six-membered cyclic transition state. The resulting *trans*-cinnamyl dibromoborane was attacked further by excess tribromoborane to afford 1-phenyl-2-bromo-1,3-bis(dibutoxyboryl)propane **115** (Scheme 38).

### Reactions boron compounds with hydrogen bromide

Matteson and Liedtke [24] demonstrated reaction of dibutyl ester vinylboronic acid with hydrogen bro-



R=Alkyl, aryl, or vinyl

Scheme 38

mid. Dibutyl-2-bromo-ethan-boronate **116** was found as final product (Scheme 39).

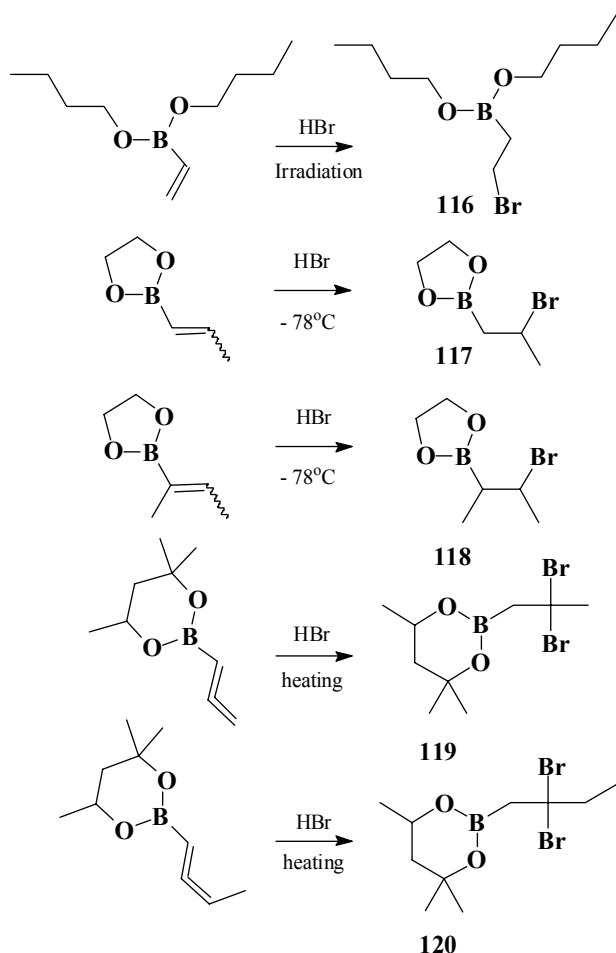
Incorporation of bromide in the  $\beta$ -position was found in the reaction between 2-propenyl-[1,3,2]dioxaborolane and 2-(1-methyl-propenyl)-[1,3,2]dioxaborolane with hydrogen bromide [21]. In both cases the corresponding  $\beta$ -boryl alkyl bromides such as 2-(2-bromo-propyl)-[1,3,2]dioxaborolane **117** and 2-(2-bromo-1-methyl-propyl)-[1,3,2]dioxaborolane **118** were obtained (Scheme 39).

According to Mikhailov et al. [69] liquid HBr reacts with 4,4,6-trimethyl-2-propadienyl-[1,3,2]dioxaborinane and 2-buta-1,2-dienyl-4,4,6-trimethyl-[1,3,2]dioxaborinane, to form 2-(2,2-dibromo-propyl)-4,4,6-trimethyl-[1,3,2]dioxaborinane **119** and 2-(2,2-dibromo-butyl)-4,4,6-trimethyl-[1,3,2]dioxaborinane **120** respectively (Scheme 39). In both cases they found that the reactions were endothermic.

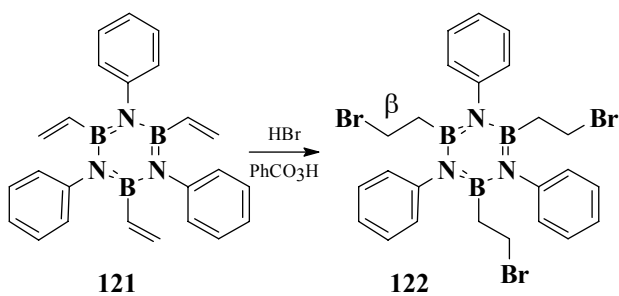
Also it was found that B-trivinyl-*N*-triphenylborazin **121** reacted with HBr in benzene and produced B-tris-(2-bromoethyl)-*N*-triphenylborazin **122** (Scheme 40) [25].

### Formation of $\beta$ -fluoroalkylboranes in cyclization reactions

$\beta$ -Fluoroalkylboranes can be forming during cy-



Scheme 39

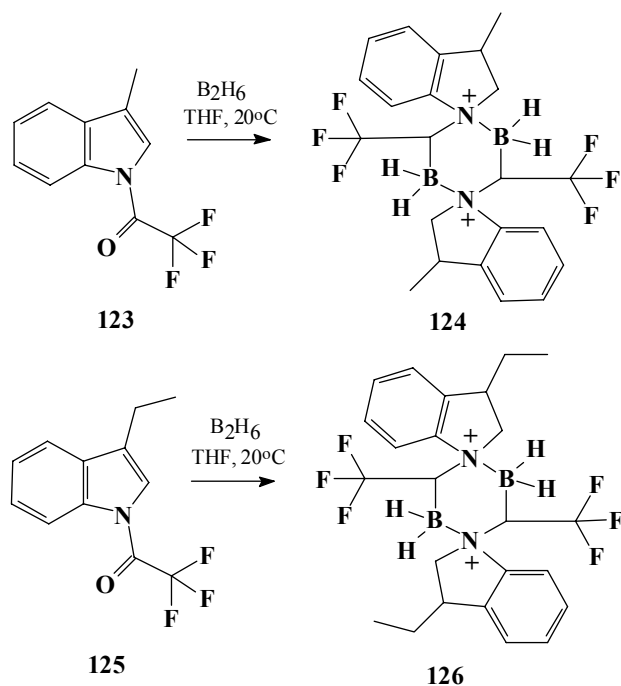


Scheme 40

clization reactions. Diborane reacts with 2,2,2-trifluoro-1-(3-methyl-indol-1-yl)-ethanone **123** to form dimeric 2,2,2-trifluoro-1-[1'-(3'-methyl-indolino)]-ethylborane **124**. Also 1-(3-ethyl-indol-1-yl)-2,2,2-trifluoro-ethanone **125** reacts with diborane resulting in the formation of dimeric 2,2,2-trifluoro-1-[1'-(3'-ethylindolino)]-ethylborane **126** (Scheme 41) [70].

### Markovnikov hydroboration in the formation of $\beta$ -fluoroalkylboranes

Fluoro-containing compounds are widely being



Scheme 41

used in biology and medicine, analytical and organic chemistry [71]. Recently Brown et al. [72] have demonstrated the Markovnikov hydroboration of perfluoroalkylethylenes **127** - **132** (Scheme 42). In all cases investigated, authors have been found that boron atom incorporated in  $\beta$ -position of fluorine only.

### Synthesis of $\beta$ -iodoalkylboranes

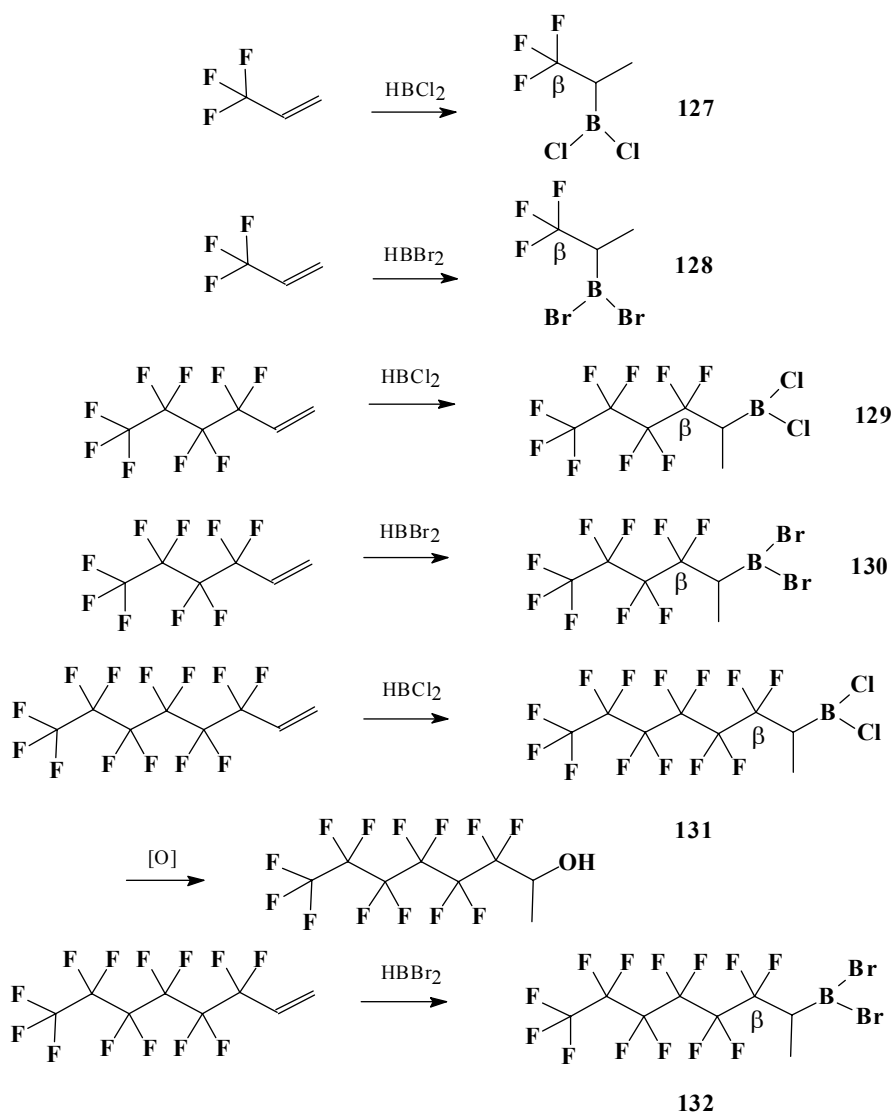
Mongéot [73] has been prepared of  $\beta$ -iodoalkylboranes using  $\text{BI}_3$  in the reaction with ethene. Resulting of formation was obtained **133** (Scheme 43).

A halide substitution reaction was described by Matteson and Liedtke [24]. The authors showed that dibutyl-2-bromo-ethyl-boronate **134** reacted with  $\text{NaI}_3$  and resulted in the formation of dibutyl-2-iodo-ethyl-boronate **135** (Scheme 44).

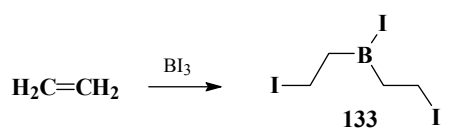
### Reactions with heterocycle compounds

Lawesson [74] described the reaction of bromothiophenes and tributylborate. Under various conditions dibutyl(4-bromo-3-thienyl)boronate **136** was obtained (Scheme 45).

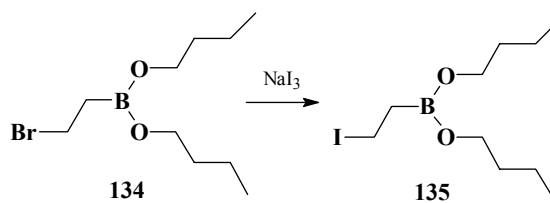
In case of the nitrogen-containing compounds, 2-chloro-8-methoxy-quinoline **137** was described, which reacted with trimethyl borate in the presence of lithium tetramethylpiperidide in tetrahydrofuran to form 2-chloro-8-methoxyquinolin-3-boronic acid **138** (Scheme 46) [75].



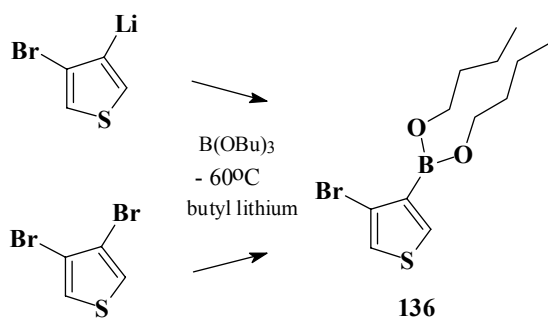
Scheme 42



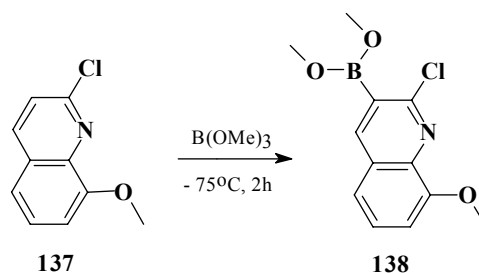
Scheme 43



Scheme 44



Scheme 45

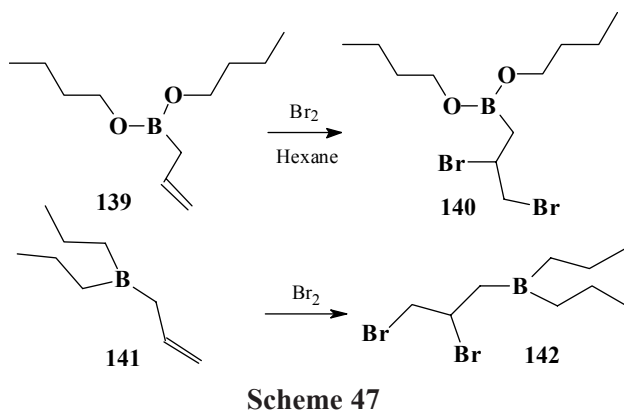


Scheme 46



### $\beta$ -, $\gamma$ -Bromination of allylboranes

$\beta$ -,  $\gamma$ -Bromination of dibutylallylboronate **139** or dipropyl allylborane **141** produced the corresponding  $\beta$ -bromoalkylboranes such as dibutyl-2,3-dibromopropylboronate **140** [23] and 2,3-dibromopropyl-dipropylborane **142** (Scheme 47) [76].



### $\gamma$ -Haloalkylboranes

#### Reactions with allyl chlorides

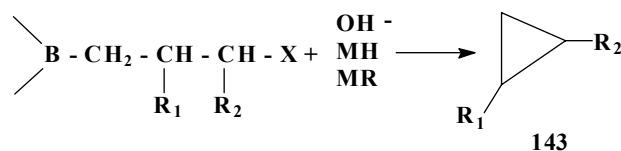
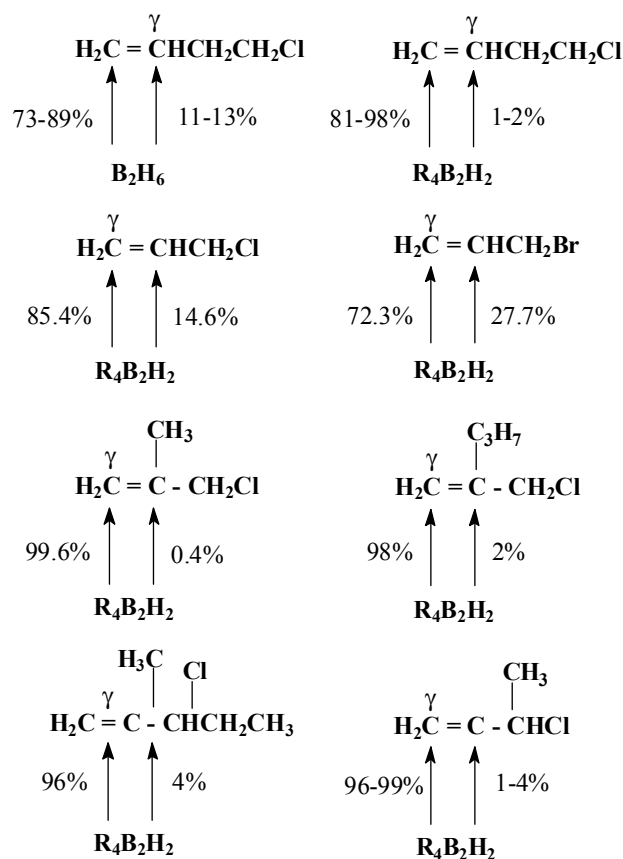
If the chloride atom located in a  $\gamma$ -position then hydroboration of alkenes involves predominant placement of the boron atom at the least substituted site of the double bond when diborane or tetraalkyldiboranes were added [7,8,9]. During reaction of hydroboration-oxidation of chloroalkenes usually forming of different 3-butenyl derivatives *via*  $\gamma$ -boryl alkyl chlorides [47].

Tetraalkyldiboranes react with 3-haloolefins more selectively than diborane. According to Koster et al. [41,42] in reaction of  $\gamma$ -haloolefines with tetraethyl- and also tetrapropylidiborane, the boron atom incorporated predominantly to the terminal carbon atom as indicated below (Scheme 48).

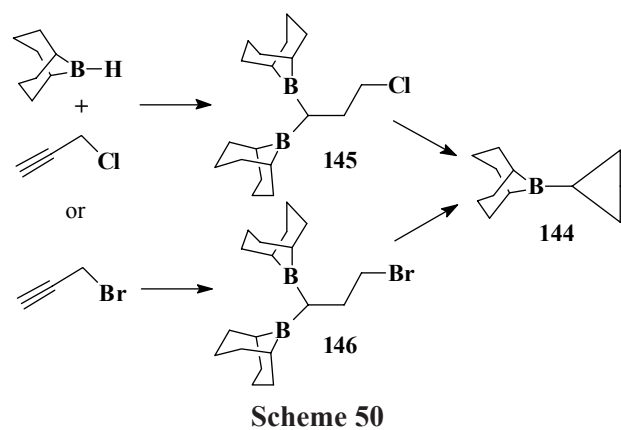
The organoboranes obtained from tetraalkyldiboranes and/or allyl chlorides react with aqueous alkali, or metal hydrides and form cyclopropane rings **143** with different alkyl fragments (X = halides) according to following general reaction (Scheme 49) [5,6,41].

#### $\gamma$ -Haloalkylboranes in formation of cyclopropane ring

$\gamma$ -Haloalkylboranes are the major intermediate products during formation of cyclopropanes from the



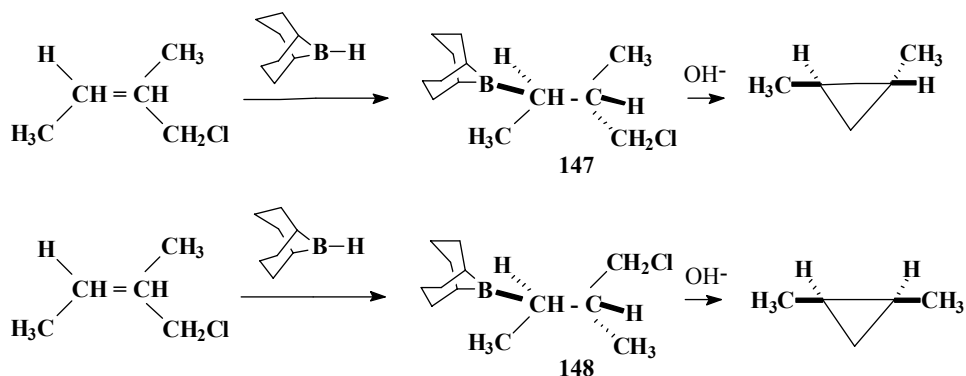
hydroboration of allyl halides [40]. If the 9-BBN is used as the hydroborating agent of acetylenes or olefins the yield of cyclopropane **144** is increased [65].  $\gamma$ -Haloalkylboranes **145** is intermediate (Scheme 50).



Matos and Soderquist [77] using propargyl bromide for dihydroboration with 9-BBN-H followed by treatment of the adduct with aqueous sodium hydroxide obtained the hydroxy(cyclopropyl)borate complexes, which underwent efficient palladium-catalyzed cross-coupling to produce a variety of aryl

and vinyl cyclopropanes in good to excellent yields *via* formation of  $\gamma$ -bromoalkylborane **146** [78].

Synthesis with inversion of configuration was observed by Goering and Trebeath [79]. Scheme 51 shows reactions illustrating the behaviour of the diastereometric  $\gamma$ -chloroalkylboranes **147** and **148**.

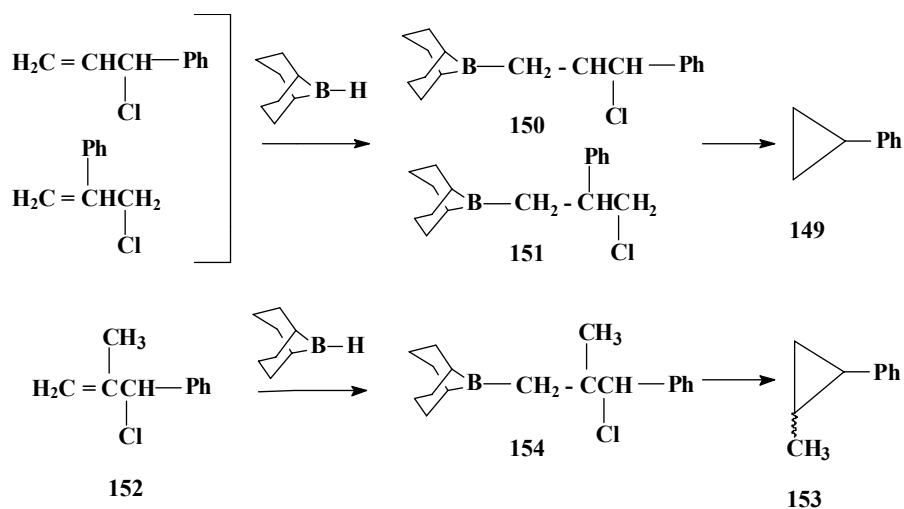


Scheme 51

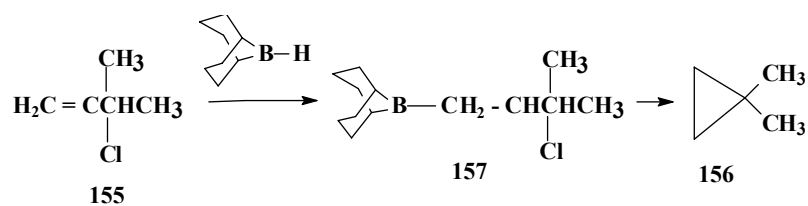
1-Phenylallyl chloride and 2-phenylallyl chloride were converted into phenyl-cyclopropane **149** in 91% and 92% yields respectively, [41] *via*  $\gamma$ -chloroalkylboranes **150** and **151**. And even the relatively interred 1-phenyl-2-methylallylic chloride **152** was converted

into a cyclopropane **153** *via* **154** (Scheme 52) [80, 81,82].

Also 1,1-dimethylallyl chloride **155** was converted into the corresponding cyclopropane **156** without difficulty *via*  $\gamma$ -boryl alkyl chloride **157** (Scheme 53) [65].



Scheme 52



Scheme 53

Hydroboration of 1,1-dichloropropene **158** with 9-BBN resulted in cyclopropanation **159** thought to proceed *via* the  $\gamma$ -boryl alkyl chloride derivative **160** (Scheme 54) [65,83].

Disiamylborane proved to be useful in selective hydroboration of chloro unsaturated compounds. For example, 1-chloropropene reacted with  $\text{BSi}_2$  to form cyclopropane **161** *via*  $\gamma$ -boryl alkyl chloride **162** [53, 84]. The same compound **161** could be obtained using diborane where **163** was as intermediate (Scheme 55) [64,65]. Previously, Brown and Gallivan [38] showed that boron predominated at the 1-position (60%) in 1-chloropropene.

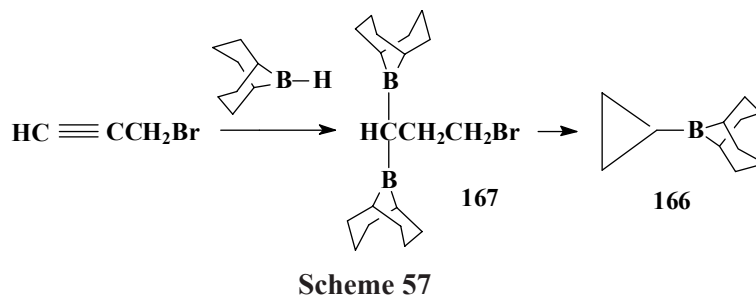
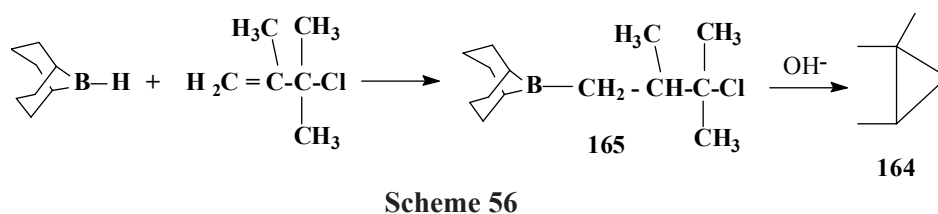
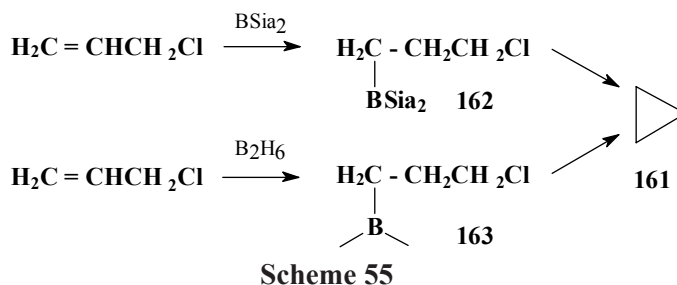
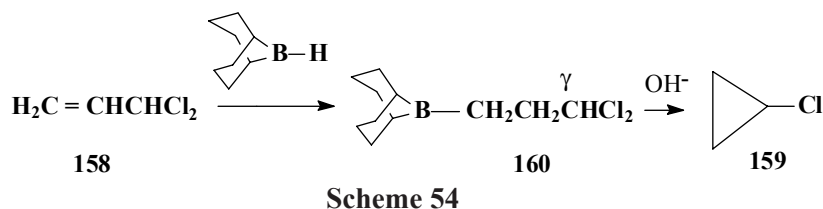
Brown and Rhodes [65] reported that 9-BBN reacted with appropriate branched allylic chlorides, to undergo cyclization with aqueous  $\text{NaOH}$  and to form the corresponding cyclopropane derivatives **164** *via*  $\gamma$ -boryl alkyl chloride **165** (Scheme 56). The cycliza-

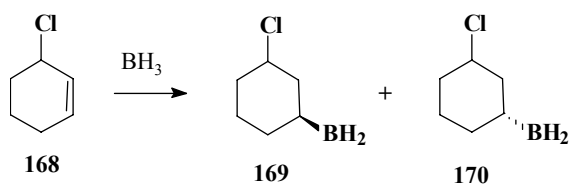
tion of hydroborated allylic chlorides to form the corresponding cyclopropanes was discovered by Hawthorne and Dupont [40] and subsequently applied to the synthesis of a variety of cyclopropanes by Hawthorne [64].

Reaction of bromoacetylene derivative with 9-BBN proceed B-cyclopropyl-9-BBN **166** from open-chain diboronbromopropene intermediate **167** has also been reported (Scheme 57) [85].

### Hydroboration of 3-chlorohexene

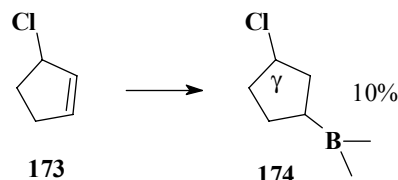
A detailed study of the hydroboration of 3-chlorocyclohexene has been described by Pasto and Hickman [39]. The hydroboration of 3-chlorocyclohexene **168** gave rise to a mixture of four isomeric chlorocyclohexylboranes, 1.5 to 3.6% *cis*-3- **169** or *trans*-3-isomers **170** (Scheme 58).





Scheme 58

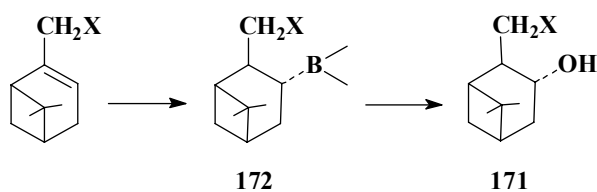
Köster et al. [42] found that the hydroboration of 3-chlorocyclopentane **173** with tetraethyldiborane in dibutyl ether at 0-10°C provided  $\gamma$ -chlorocyclopentylboranes **174**, the major adduct being  $\beta$ -chlorocyclopentylboranes (90%) (Scheme 60 see also Scheme 26).



Scheme 60

### Hydroboration of vinyl halides

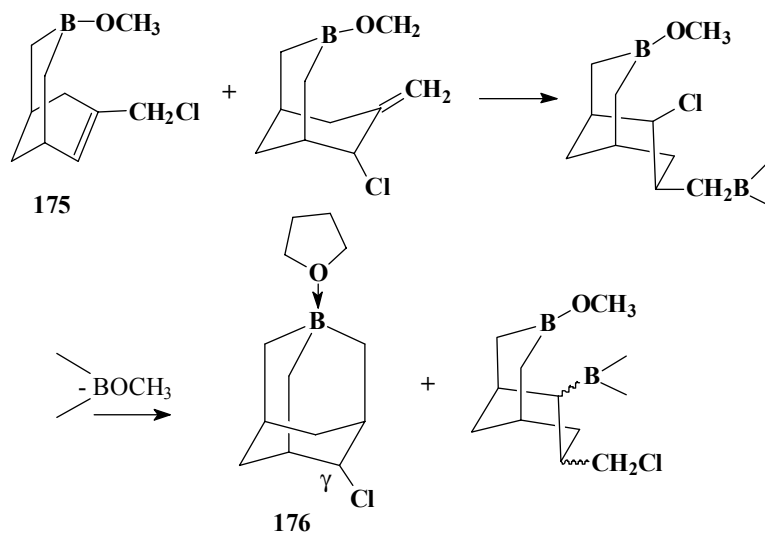
Myrtenyl chloride and bromide (X = Cl or Br) underwent hydroboration-oxidation to form primarily 2- $\beta$ -halomethyl-3 $\alpha$ -hydroxynorpinanes **171** via intermediate  $\gamma$ -boryl alkyl halides **172** (Scheme 59) [86].



Scheme 59

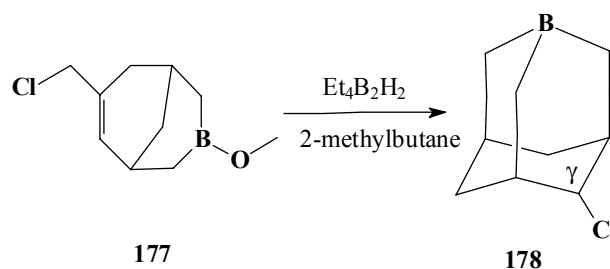
### Derivatives of boraadamantane analogues

3-Methoxy-7-chloromethyl-3-borabicyclo[3.3.1]non-6-ene **175** was carried out with  $\text{B}_2\text{H}_6$ ,  $\text{H}_3\text{B}\cdot\text{THF}$  and/or  $\text{H}_3\text{B}\cdot\text{N}(\text{C}_2\text{H}_5)_3$  proceed final adduct of **176** (Scheme 61) [6,87,88].



Scheme 61

7-chloromethyl-3-methoxy-3-bora-bicyclo[3.3.1]non-6-ene **177** was hydroborated with  $\text{Et}_4\text{B}_2\text{H}_2$  gives of 4-chloro-1-bora-adamantane **178** (Scheme 62). 2-Methylbutane was used as the solvent in this reaction [9,89,90].

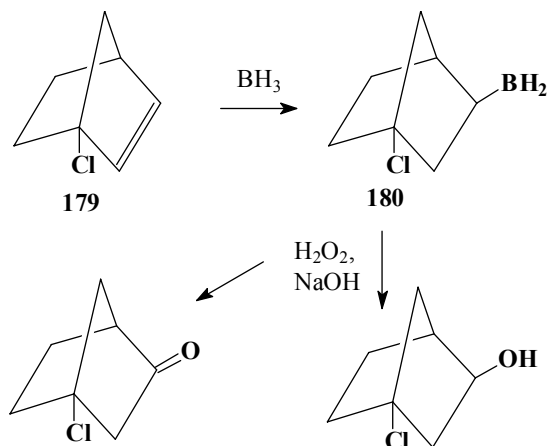


Scheme 62

### Chloronorbornane derivatives

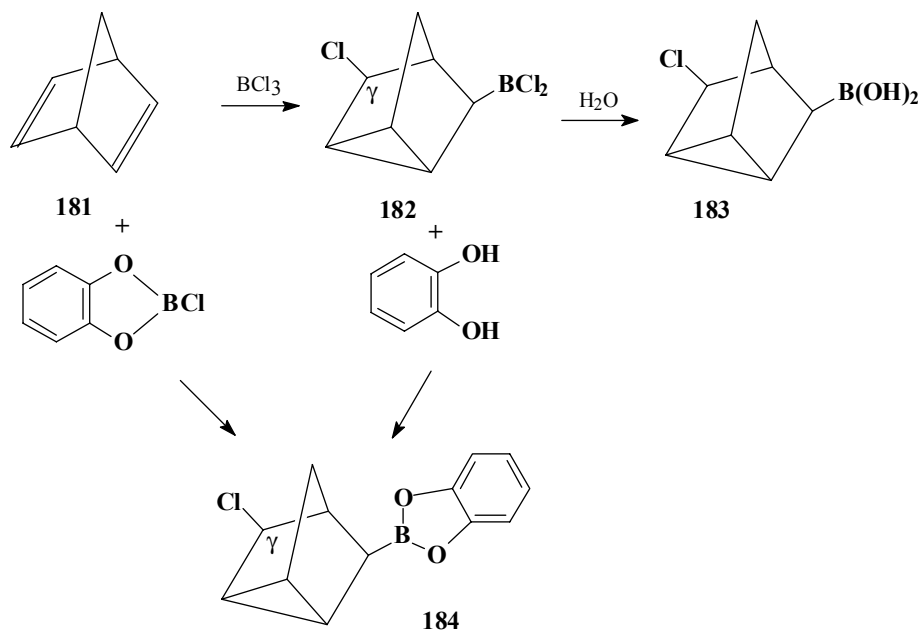
The substituent effects of chlorine in norbornane

derivatives was reported by Fry and Farnham [56]. Hydroboration of 1-chloronorbornane **179** indicated that 32-37% of boron was incorporated in 3-position to form  $\gamma$ -chloroalkylborane **180** (Scheme 63) [56].



Scheme 63

Chloroboration of unsaturated compounds was carried out by Joy et al. [67]. Norbornadiene **181** reacted with trichloroborane at  $-80^\circ\text{C}$  to produce 6-chloro-2-nortricyclyl-dichloroborane **182**. It could be transformed to the corresponding boronic acid **183**. A similar compound, 2-(*cis*- and *trans*-6'chloro-2'-nortricyclyl)benzo-1,3,2-dioxaborole **184** was obtained when 1,5-cyclooctadiene **180** reacted with 2-chloro-1,3,2-benzodioxaborole, **182**, in the presence



Scheme 64

of catechol (Scheme 64).

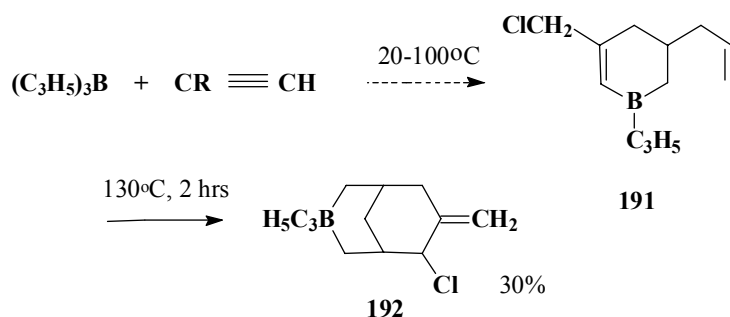
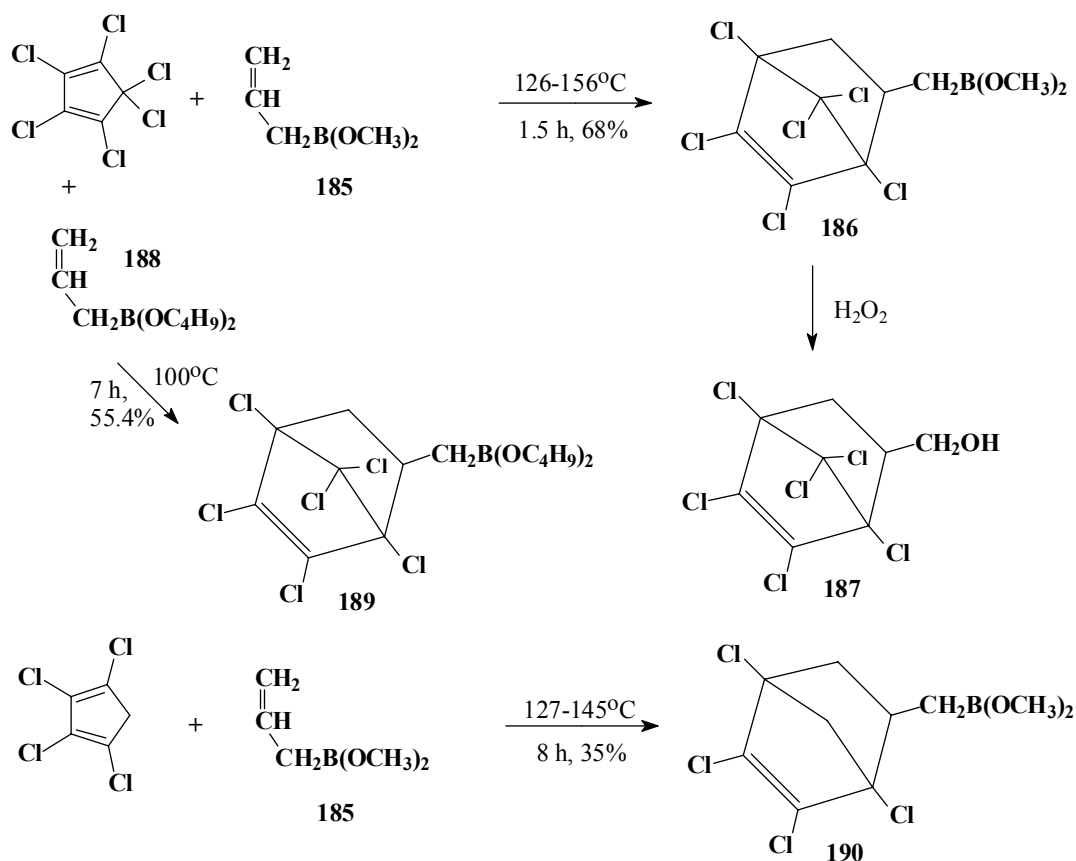
### *Dienoic condensation of allylboronic acid*

The dimethyl ester of allylboronic acid **185** condensed easily with hexachlorocyclopentadiene, providing the  $\gamma$ -boryl alkyl chloride **186**, named as 2-(1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hept-5-en-2-yl)methylboronate (Scheme 65) [6,9,89]. Oxidation of **186** by  $\text{H}_2\text{O}_2$  gave the corresponding alcohol **187**. The *n*-dibutyl ester of allylboronic acid **188** condensed with hexachlorocyclopentadiene to give 2-(1,4,5,6,7,7-hexachloro-bicyclo[2.2.1]hept-5-en-2-yl)butylboronate **189** [9,58]. Also the dimethyl ester of allylboronic acid **185** condensed with 1,2,3,4-tetrachlorocyclopentadiene at  $127\text{--}145^\circ\text{C}$  during 8 hrs gave the dimethyl ester of 2-(1,4,5,6-tetrachlorobicyclo[2.2.1]hept-5-en-2-yl)methylboronate **190** [6].

### *Allyl compounds of binuclear boracyclanes*

Halogenated acetylene react with trialkylboranes at room temperature. 3-Chloromethyl-1,5-diallyl-1-boracyclohex-2-ene **191** was prepared by keeping a mixture of propargyl chloride and triallylborane (1/1 v/v) at room temperature for a month [9]. Heating 3-chloromethyl-1,5-diallyl-1-boracyclohex-2-ene **191** to  $130^\circ\text{C}$  for 2 hrs lead to the  $\gamma$ -chloroalkyl borane **192**, 3-*n*-propyl-7-methylene-6-chloro-3-borabicyclo[3.3.1]nonane (Scheme 66).

Reaction between triallylboranes and propargyl

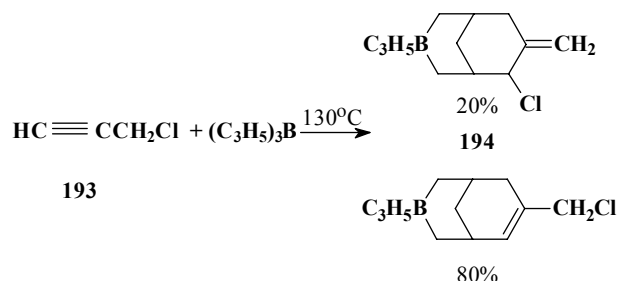


chloride **193** was carried out and a mixture of two compounds in the ratio 1:4 were obtained. One was identified as 3-*n*-propyl-7-methylene-6-chloro-3-borabicyclo[3.3.1]nonane **194** (Scheme 67) [87,88,90].

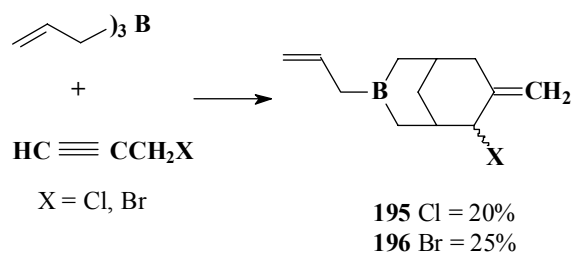
In the case a substantial part was halides (Cl or Br) of the allylic halide unit in the product is rearranged to give  $\gamma$ -boryl alkyl chloride **195** and bromide **196** compounds, respectively (Scheme 68) [91].

### Vinylboranes in Diels-Alder Reactions

Formation of  $\gamma$ -haloalkylboranes in Diels-Alder reactions were observed by Singleton et al. [92].



Thus, 9-vinyl-9-bora-bicyclo[3.3.1]nonane **197** reacted with 2-chloro-but-1,3-diene, providing two



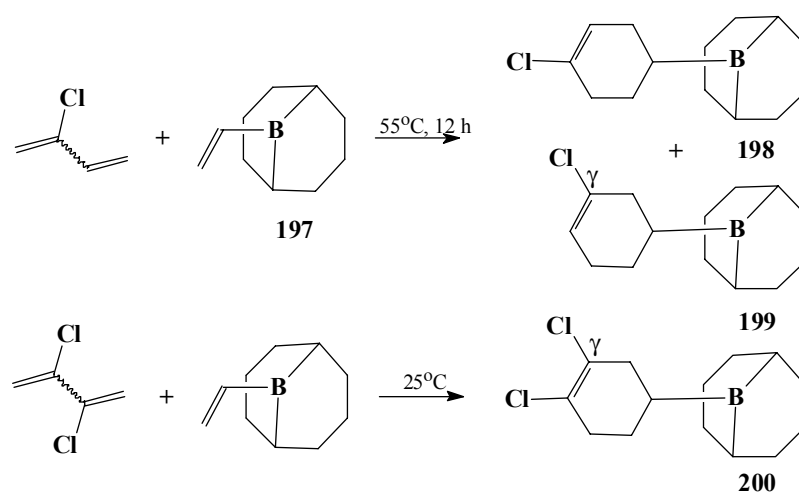
Scheme 68

isomers, 9-(4-chloro-cyclohex-3-enyl)-9-bora-bicyclo[3.3.1]nonane **198** and 9-(3-chloro-cyclohex-3-enyl)-9-bora-bicyclo[3.3.1]nonane **199**, in a ratio of

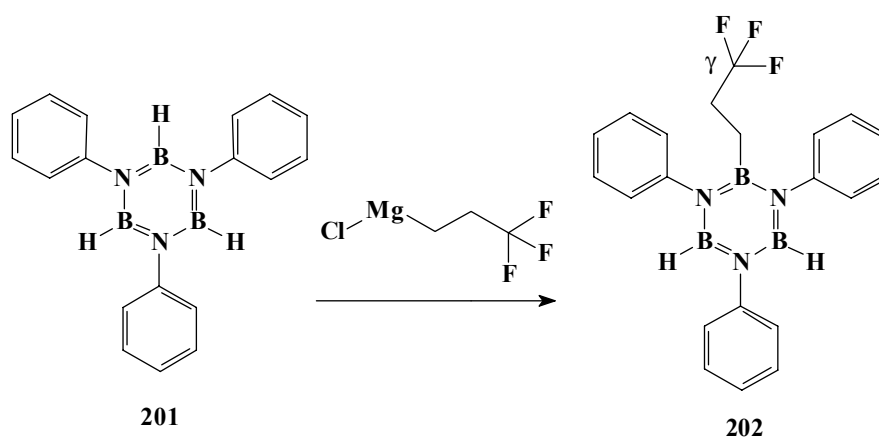
90:10 (75%). In the case of the 2,3-dichloro-but-1,3-diene, 9-(3,4-dichloro-cyclohex-3-enyl)-9-bora-bicyclo[3.3.1]nonane **200** was obtained (Scheme 69).

### Synthesis of $\gamma$ -fluoroalkylboranes

The first synthesis of  $\gamma$ -fluoroalkyl derivatives of borazole was reported by Gridina et al. [93]. *N*-1,3,5-Triphenylborazole **201** reacted with the organomagnesium derivative of 3,3,3-trifluoro-chloropropane ( $\text{C}_3\text{H}_4\text{ClF}_3\text{Mg}$ ) to produce B-mono-(3,3,3-trifluoropropyl)-*N*-1,3,5-triphenylborazole **202** (Scheme 70).



Scheme 69



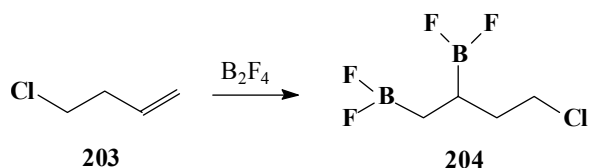
Scheme 70

### Synthesis of $\gamma$ -haloalkylboranes from alkenes

The study of the reactions of diboron, diboron tetrafluoride, and diboron tetrachloride with unsat-

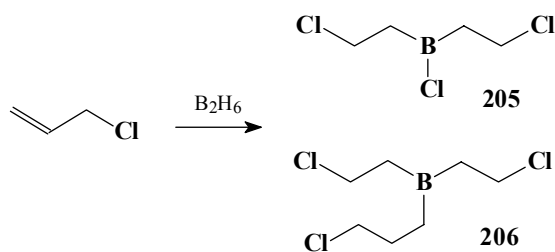
urated hydrocarbons provided various  $\gamma$ -haloalkylboranes [95]. Thus, the 4-chloro-but-1-ene **203** reacted with diborane tetrafluoride for 24 hrs at  $100^\circ\text{C}$ , to give 4-chloro-1,2-bis-difluoroboranyl-butane **204**

(Scheme 71).



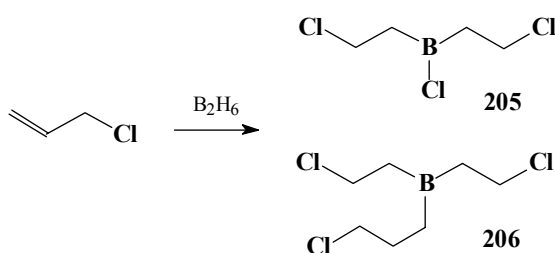
Scheme 71

Reaction of 3-chloropropene with diborane provided two compounds, tris-(3-chloropropyl)-borane **206** and chloro-bis-(3-chloropropyl)-borane **205**. (Scheme 72) [40].



Scheme 72

A series studies on the interaction between halogen olefins and diborane were reported by Köster et al. [41,42]. According to these studies, dipropylborane easily reacted with halogen olefins such as 3-chloro-2-methylpropene to produce the corresponding  $\gamma$ -haloalkylboranes **207** – **209** (Scheme 73) in 72 – 99% yields, respectively.



Scheme 73

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