Boranes in Organic Chemistry
3. α-, β- and γ-Haloalkylboranes: The Perspective Vehicles for Organic Synthesis

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Abstract

The methods of synthesis of α− and β−haloalkylboranes, including chlorination of alkylboronic acid esters, additive bromination and chlorination of esters of vinyl- and alkenylboronic acids, addition of bromine to trivinylborazines have been considered.

The reactions of radical addition of polyhaloidmethanes to vinylboranes, α− and β−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 boronallylation 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 α−haloidalkylboranes has been shown. The general scheme of synthesis of α−aminoboronic acids was perfomed. The general approach to the synthesis of alkenes 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 β−haloidalkylboranes has been discussed.

Introduction

α-, β-, γ-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].

α-Haloalkylboranes

Reactions of chlorine with boranes

Chlorine reacted with trimethylboranes at minus 95°C to give α-chloro-α-boron derivative 1 [10]. Compound 1 reacted with lithium azide and with water to form the corresponding azide 2 and alcohol
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3 [11] (Scheme 1).

Scheme 1

**Synthesis of haloalcohols via α-haloalkylboranes**

The action of diborane on halogenated derivatives of unsaturated hydrocarbons was investigated for the first time by Stone et al. [12,13]. Treatment α-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 α-position.

**Addition tetrachloromethane to α,β-unsaturated esters**

Reaction of addition of CCl₄ to α,β-unsaturated esters is common for all derivatives of dibutyl propene-2-borionate, in the presence of azobisisobutyronitrile as the initiator, as resulting are α-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-borinate 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 α-haloalkyl compound 19 (Scheme 4). Thus, N-phenyl-N-trimethylsilyldichloroacetamide reacted with bromodimethyl-borane to form 19 [19].

**Hydroboration of cyclovinylic 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 β-position 21 (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 α- 26 and β-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 α-haloboronic ester 29 [20]. The use of (+)-pinanediol for boronic acid protection allowed the preparation of an optically pure of 30 (Scheme 7).

α-, β-Haloalkylboranes

In some cases, the synthesis of α-haloalkylboranes was accompanied by β-haloalkylboranes. Conditions and/or reactants for the formation of α-, β-boryl alkyl halides differ from those used for obtaining α-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-(1RS,2SR)-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-propyleneborinane 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.
Bromination of chlordiisopropylaminovinylborane at minus 75°C in pentane gave (1,2-Dibromoethyl)-chloro-diisopropylaminoborane 38. (Scheme 9) [21].

![Scheme 9](image_url)

**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-dichloroethyl)-boronic acid 39 and dibutyl ester of (1,2-dibromoethyl)-boronic acid 40, respectively (Scheme 10).

![Scheme 10](image_url)

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

![Scheme 11](image_url)

**Bromination of borazine**

Seyferth and Takamizawa showed that in the reaction of B-trivinyl-N-triphenylborazine 43 with bromine in CCl₄, B-tris-(1,2-dibromoethyl)-N-triphenylborazine 44 was obtained [25] (Scheme 12).

![Scheme 12](image_url)

**α-β-Haloalkylboranes**

**Reactions of α-β-unsaturated butyl boronic esters**

Various α,β-boryl butyl halides 45 - 49 were obtained during the investigation of radical additions to α,β-unsaturated boronic esters [15]. A study of α,β-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.

Scheme 13

\[
\text{R} \quad \text{B(OC}_4\text{H}_9)_2 \quad \text{Cl} \quad \alpha \quad \gamma \quad \text{R}_1 \quad \text{R}_2 \quad \text{B(OC}_4\text{H}_9)_2
\]

- **45.** \(\text{R} = \text{R}_1 = \text{H}, \text{R}_2 = \text{Cl}\)
- **46.** \(\text{R} = \text{R}_1 = \text{H}, \text{R}_2 = \text{Br}\)
- **47.** \(\text{R} = \text{H}, \text{R}_1 = \text{CH}_3, \text{R}_2 = \text{Cl}\)
- **48.** \(\text{R} = \text{H}, \text{R}_1 = \text{CH}_3, \text{R}_2 = \text{Br}\)
- **49.** \(\text{R} = \text{CH}_3, \text{R}_1 = \text{H}, \text{R}_2 = \text{Br}\)

**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**


Scheme 14

Scheme 15

**β-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 β-haloalkyl boranes, 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 is β-chloroalkylborane. β-Heterosubstituted alkylboranes can induce β-elimination 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 β-61, and α-haloalkylboranes 60 are the intermediates (Scheme 17) [34-36]. Propargylboranes produced by rearrangement of allylboranes 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 β-substituted organoboranes [36,38]. The products depend on the functional groups. The amount of β-substituted organoborane increases with increasing electronegativity of the substituents.

![Scheme 16](image1.png)

![Scheme 17](image2.png)
Hydroboration of crotyl chloride 66 gave about 90% of β-chloroalkylborane 67 [39]. When X is a good leading group, such as Cl, elimination occurs to give 1-butene, which then undergoes hydroboration. This reaction was conducted in ethyl ether (Scheme 19) [39].

\[ \text{Scheme 19} \]

β-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 β-elimination of β-haloalkylborane was found by Hawthorne and Dupont [40]. They obtained β-chloroethylborane dichloride 68 in low yield (Scheme 20).

\[ \text{Scheme 20} \]

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 tetrapropyl diborane, the boron preferred the terminal carbon atom, and less so formed β-halo-alkylboranes 69 – 73 (Scheme 21).

\[ \text{Scheme 21} \]

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

The predilection of organoboranes to undergo to 

\[ \text{Scheme 22} \]

*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 α-alkenyl carbon. Halogen induced migration products undergo β-elimination to give highly stereospecific alkenes, and also β-haloalkylboranes 74. Typical reactions are indicated below (Scheme 22).

Reaction of alkenylboranes 75 with iodine in the 

\[ \text{Scheme 22} \]
presence of excess base, usually sodium hydroxide, gave configurationally inverted alkenes [45], and formed as intermediate β-haloalkyl boranes compounds 76A and 76B (Scheme 23). A major drawback of the iodine induced alkene synthesis is that it utilizes one or two alkyl groups.

Reactions of cyclovinylic derivatives with organoboranes

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

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).

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

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 β-haloalkylborane 84 (Scheme 27). These results indicate that in this system the boron adds predominantly in β-position to the chlorine substituent.

**Reactions of norbornanes with halides**

The effects of heterosubstituents can be overcome through hydroborating agents of specific structure, for instance 3-butenyl derivatives [50], propiolic 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 haloalkenyloboranes have been reacted with dienes to form Diels-Alder adducts [57] including β-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).

β-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).
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-2endo-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-2endo-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'-((4,4,6,7,7-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-dioxaborinan-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

β-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 β-iodoalkylborane 106 (Scheme 34) [45].

Scheme 33

Scheme 34
**β-Haloalkylboranes in formation of cyclopropane ring**

Hawthorne [64] and later Brown and Rhodes [65] have shown that 9-BBN is a good agent in hydroboration and synthesis of cyclopropane rings in 80-85% yield via β-chloroalkylboranes as the major intermediate 107 (Scheme 35).

\[
\begin{align*}
\text{BH}_2 + \text{B(OH)}_3 & \rightarrow \text{BH} + \text{B(OH)}_3 \\
\text{H}_2\text{C} = \text{CHCHCH}_3 + \text{Cl} & \rightarrow \text{CH}_3 + \text{BCH}_2\text{CHCHCH}_3
\end{align*}
\]

Scheme 35

The Zweifel olefin synthesis

The Zweifel synthesis in the original form provides a stereospecific synthesis of (Z)-alkenes [45] via β-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-
tion state through a four-centered cyclic transition state or a six-membered cyclic transition state. The resulting trans-cinnamyldibromoborane 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 bromide. Dibutyl-2-brom-ethan-boronate 116 was found as final product (Scheme 39).

Incorporation of bromide in the β-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 β-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 endotermic.

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 β-fluoroalkylboranes in cyclization reactions

β-Fluoroalkylboranes can be forming during cy-
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]. In all cases investigated, authors have been found that boron atom incorporated in \(\beta\)-position of fluorine only.

**Synthesis of \(\beta\)-iodoalkylboranes**

Mongeot [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 \(\text{NaI}\) 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].
β-, γ-Bromination of allylboranes

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

γ-Haloalkylboranes

Reactions with allyl chlorides

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

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

The organoboranes obtained from tetraalkyl diboranes 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].

γ-Haloalkylboranes in formation of cyclopropane ring

γ-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 hydroboring agent of acetylenes or olefines the yield of cyclopropane 144 is increased [65]. γ-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 γ-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 γ-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 γ-chloroalkylboranes 150 and 151. And even the relatively interred 1-phenyl-2-methylallylic chlorine 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 γ-borylalkyl 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 γ-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 BSia2 to form cyclopropane 161 via γ-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 NaOH and to form the corresponding cyclopropane derivatives 164 via γ-boryl alkyl chloride 165 (Scheme 56). The cyclization 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 diboronbromopropane 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).
Hydroboration of vinyl halides

Myrtenyl chloride and bromide (X = Cl or Br) underwent hydroboration-oxidation to form primarily 2-β-halomethyl-3α-hydroxynorpinanes 171 via intermediate γ-boryl alkyl halides 172 (Scheme 59) [86].

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

Derivatives of boraadamantane analogues

3-Methoxy-7-chloromethyl-3-borabicyclo[3.3.1]non-6-ene 175 was carried out with of B₂H₆, H₃B-THF and/or H₃B-N(C₂H₅)₃ proceed final adduct of 176 (Scheme 61) [6,87,88].

7-chloromethyl-3-methoxy-3-bora-bicyclo[3.3.1]non-6-ene 177 was hydroborated with Et₄B₂H₂ gives of 4-chloro-1-bora-adamantane 178 (Scheme 62). 2-Methylbutane was used as the solvent in this reaction [9,89,90].

Chloronorbornane derivatives

The substituent effects of chlorine in norbornane
derivatives was reported by Fry and Farnham [56]. Hydroboraton of 1-chloronorbornane 179 indicated that 32-37% of boron was incorporated in 3-position to form γ-chloroalkylborane 180 (Scheme 63) [56].

Chloroboration of unsaturated compounds was carried out by Joy et al. [67]. Norbornadiene 181 reacted with trichlororborane at -80°C to produce 6-chloro-2-nortricyclodichloroborane 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 of catechol (Scheme 64).

**Dienoic condensation of allylboronic acid**

The dimethyl ester of allylboronic acid 185 condensed easily with hexachlorocyclopentadiene, providing the γ-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 H₂O₂ 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-hexachlorobicyclo[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 127-145°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°C for 2 hrs lead to the γ-chloraalkyl 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 γ-boryl alkyl chloride and bromide 196 compounds, respectively (Scheme 68) [91].

**Vinylboranes in Diels-Alder Reactions**

Formation of γ-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-buta-1,3-diene, providing two
The first synthesis of γ-fluoroalkyl derivatives of borazole was reported by Gridina et al. [93]. N-1,3,5-Triphenylborazol 201 reacted with the organomagnesium derivative of 3,3,3-trifluoro-chloropropane (C₃H₄ClF₃Mg) to produce B-mono-(3,3,3-trifluoro-propyl)-N-1,3,5-triphenylborazol 202 (Scheme 70).

**Synthesis of γ-fluoroalkylboranes**

The study of the reactions of diboron, diboron tetrafluoride, and diboron tetrachloride with unsaturated hydrocarbons provided various γ-haloalkylboranes [95]. Thus, the 4-chloro-but-1-ene 203 reacted with diborane tetrafluoride for 24 hrs at 100°C, to give 4-chloro-1,2-bis-difluoroboranyl-butane 204.
A series of 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 γ-haloalkylboranes 207 – 209 (Scheme 73) in 72 – 99% yields, respectively.

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Received 29 March 2002.