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Boranes in Organic Chemistry
2. β-Aminoalkyl- and β-sulfanylalkylboranes in organic synthesis

V.M. Dembitsky[1], G.A. Tolstikov[2*], M. Srebnik[1]

[1]Department of Pharmaceutical Chemistry and Natural Products, School of Pharmacy, P.O. Box 12065, The Hebrew University of Jerusalem, Jerusalem 91120, Israel

[2]Novosibirsk Institute of Organic Chemistry SB RAS, 9, Lavrentieva Ave., Novosibirsk, 630090, Russia

Abstract

Problems on using of β-aminoalkyl- and β-sulfanylalkylboranes in organic synthesis are considered in this review. The synthesis of boron containing α-aminoacids by Curtius rearrangement draws attention. The use of β-aminoalkylboranes available by enamine hydroboration are described.

Examples of enamine desamination with the formation of alkenes, aminoalcohols and their transformations into allylic alcohol are presented. These conversions have been carried out on steroids and nitrogen containing heterocyclic compounds.

The dihydroboration of N-vinyl-carbamate and N-vinyl-urea have been described. Examples using nitrogen and oxygen containing boron derivatives for introduction of boron functions were presented. The route to borylhydrazones by hydroboration of enehydrazones was envisaged.

The possibility of trialkylamine hydroboration was shown on indole alkaloids and 11-azatricyclo-[6.2.1^{1,8}0^{2,7}]2,4,6,9-undecatetraene examples.

The synthesis of β-sulfanyl-alkylboranes by various routes was described.

The synthesis of boronic thioaminoacids was carried out by free radical thiilation of dialkyl-vinylboronates. Ethoxyacetylene has been shown smoothly added 1-ethylthioboracyclopentane. Derivatives of 1,4-thiaborinane were readily obtained by divinylboronate hydroboration. Dialkylvinylboronates react with mercaptoethanol with the formation of 1,5,2-oxathioborepane derivatives. Stereochemistry of thiavinyl esters hydroboration leading to stereoisomeric β-sulfanylalkylboranes are discussed.

Examples of radical thiilation of various structural types vinylboronates were presented. In particular, 1,3,2-dioxaborinanes and 1,3,2-dioxaborolanes, containing by boron atom vinyl-, propenyl-, isopropenyl- or isopropylidene substituents have been used. Thiilation has been achieved by use of alkylmercaptanes, as well as mercaptamine derivatives. Alkylmercaptanes were able to replace the bromine substituent in tris-(2-bromoctyl)-borane. Dialkylvinylborates have been added hydrosulfite with the formation of 2-boronoethane sulfuric acids. A lot of examples of radical thiilation of vinylboronic acid dialkyl esters with mercaptoacids are presented. Under the azaisobutyric acid dinitryle conditions thioglycolic, β-mercaptopropionic, 2-mercaptoamberic acids and their esters as well as cysteine were added. Vinyl-, propenyl- and isopropenyl-dioxaborolanes were also participated in the thiilation with the formation of acetic, propionic or amberic acid thioethanoboronates.

The high reactivity of B,B,B-trivinyl-N,N,N-triphenylborazine in the reaction with thiophenol, leading to B-tris-(phenylmercaptoethyl)-N-phenylborazine was shown.

The problems of asymmetric hydroboration leading to chiral β-sulfanylalkylboranes were discussed briefly. In particular, an example, including dihydro-thiophene hydroboration, leading to (+)-R-thiofan-3-yl-diisopinocamphenylborane, and the interaction with acetaldehyde with the formation of (+)-R-3-thiophanyl-diethoxyborane was implemented. The reaction with 3,4-dihydrothiapyrane proceeds analogously.

A synthetic route to sulfono-norbornen-boronic acid esters by Diels-Alder reaction of cyclopentadiene with arylsulfanyl-vinylboronic acid esters has been discussed.

Introduction

β-Aminoalkyl- and β-sulfanylalkylboranes are rare groups of synthetic compounds and structurally similar groups with the corresponding structures B-C-C-NR_2 and B-C-C-SR. These compounds have been partially reviewed [1-6].

*corresponding authors. E-mail: gtolstik@nioch.nsc.ru

β-Aminoalkylboranes (B – C – C – NR_2)

Synthesis of boron containing analogue of amino acids

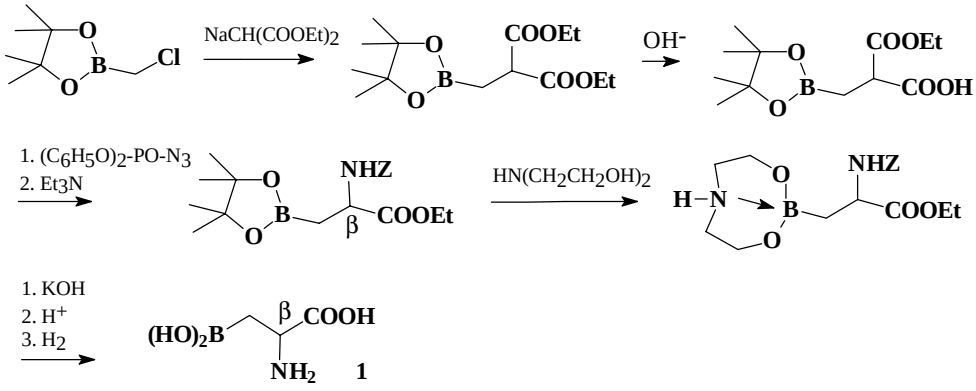
In certain cases, β-aminoalkylboranes could be isolated. For example in the synthesis of boron-containing amino acids. Curtius rearrangement gave the β-boryl alkyl amine, which is an analogue of aspartic acid **1** (Scheme 1) [7].

Hydroboration of enamines

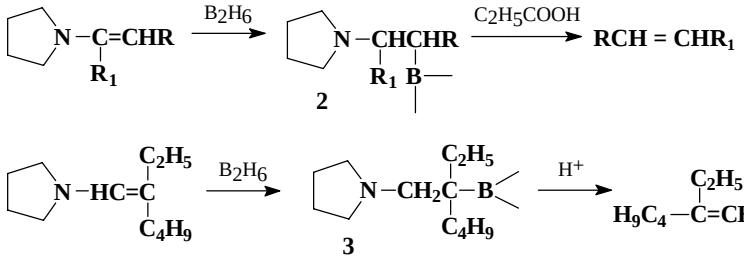
Aliphatic enamines easy react with diborane to form intermediate β-boryl alkyl amines. Thus, Lewis and Pearce [8,9] showed that pyrrolidine enamines of 3-pentanone and 4-heptanone reacted with diborane to give intermediate complexes which in boiling diglyme lead to 2-pentene and 3-heptene, respectively. On the other hand, if R and R_1 are ethyl and butyl, for instance in 2-ethyl-1-N-pyrrolidyl-heptane, 2-ethyl-hexene was formed in 42% (Scheme 2), where **2** and **3** are β-aminoalkylboranes.

The enamines of cyclic ketones were hydroborated in the β-position in all cases. 1-*N*-piperidylcyclohexene **4** reacted with diborane to give *trans*-2-N-piperidyl-cyclohexyl-borane **5**, which under acidic conditions converted to cyclohexene **6** with yields of 88-98% (Scheme 3) [8,9].

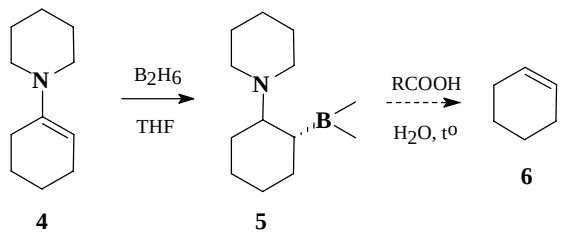
4-*tert*-Butyl-1-N-pyrrolidylcyclohexene **7** reacted with diborane to form an equimolar mixture of the isomeric β-aminoorganoboranes **8** and **9** which were smoothly converted to 4-*tert*-butylcyclohexene **10** by protolysis (Scheme 4) [9].



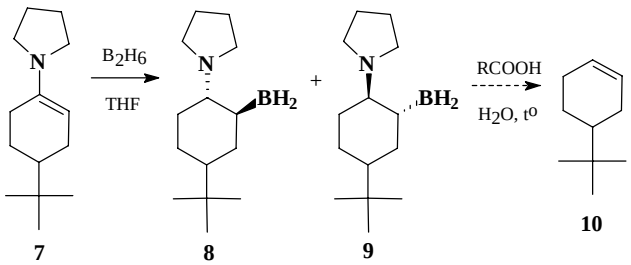
Scheme 1



Scheme 2

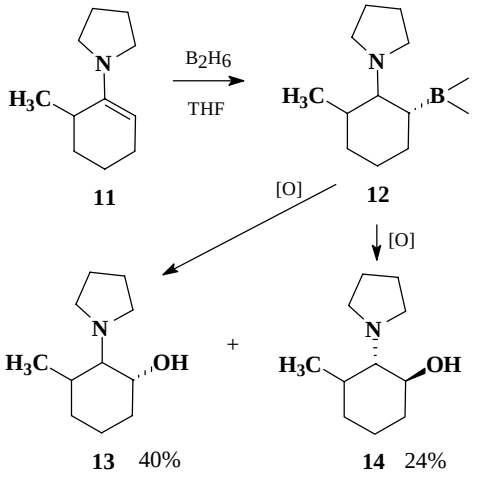


Scheme 3



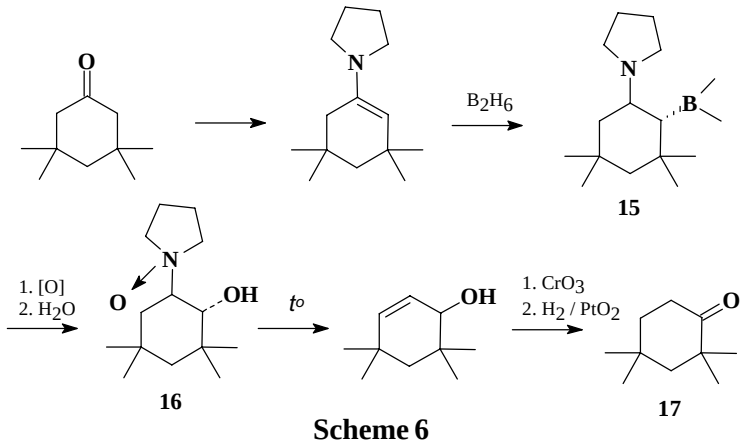
Scheme 4

The hydroboration of the enamines of α-substituted cyclohexanone **11** formed β-amino- alkylborane **12** and oxidation leads to stereoisomeric amino alcohols **13** and **14** (Scheme 5) [10].



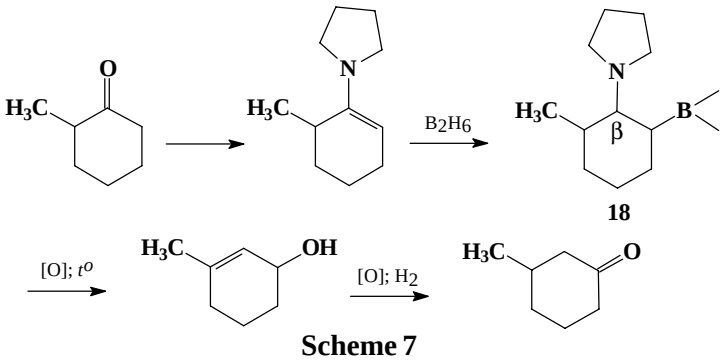
Scheme 5

Alkyl-substituted amino alcohols **16** can possible to convert symmetrically substituted cyclohexanones to the asymmetrically substituted compound **17** *via* β-aminoalkyl- borane **15** (Scheme 6) [11-13].



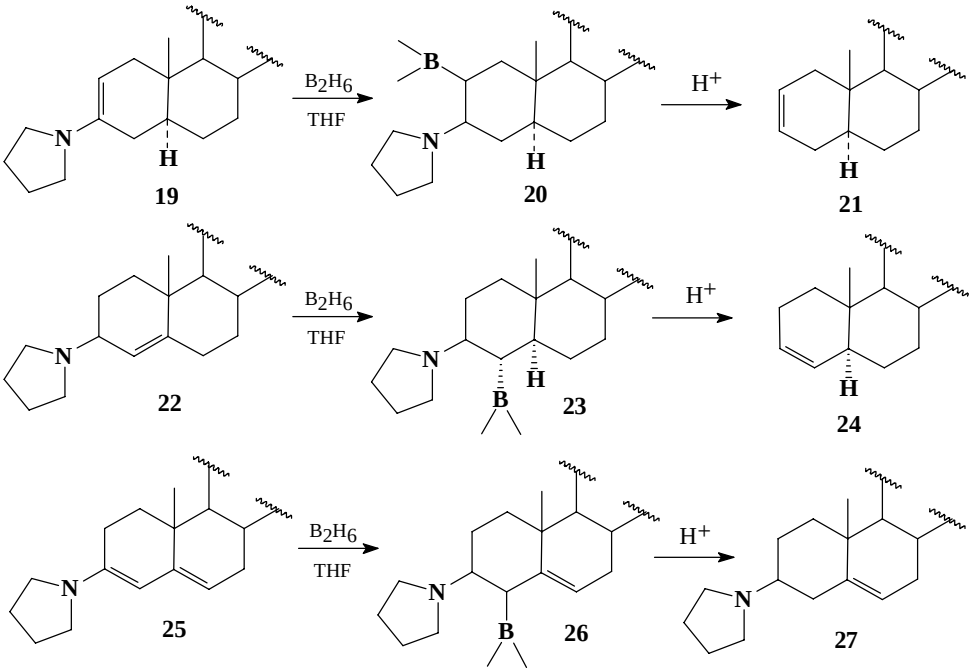
Scheme 6

A keto group in an adjacent position could also be obtained on a series of asymmetrically substituted cyclic ketones *via* β-aminoalkylborane **18** (Scheme 7) [11,13].



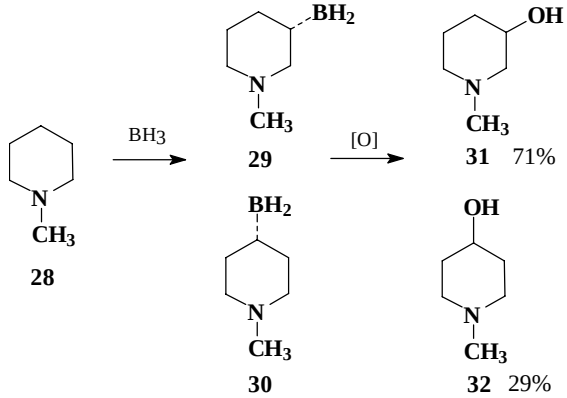
Scheme 7

An analogous conversion has been carried out in the steroids series. Thus, 3-*N*-pyrrolidyl-2-cholestene **19** was converted to 2-cholestene **21** *via* 3-β-*N*-pyrrolidyl-2-α-cholestanylborane **22** [9] (Scheme 8). Also 3-β-*N*-pyrrolidyl-4-cholestene **22** formed a β-aminoalkylborane **23** with a *trans*-diequatorial location of the substituents, which is converted to 3-cholestene **24** by protonolysis [9]. 3-*N*-Pyrrolidyl-3,5-cholestadiene **25** was converted to 3-β-*N*-pyrrolidyl-5-cholestene **27** *via* β-aminoalkylborane **26** [14].



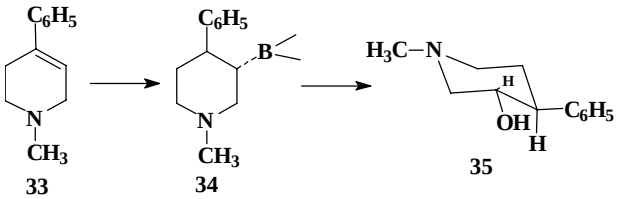
Scheme 8

Hydroboration of 1-*N*-methyl-1,2,3,6-tetrahydropyridine **28** gave a mixture of 1-*N*-methyl-3-piperidinol **31** and 1-*N*-methyl-4-piperidinol **32** *via* the corresponding β-aminoalkylborane **29** and γ-aminoalkylborane **30** (Scheme 9) [15-17].



Scheme 9

The hydroboration-oxidation of 1-*N*-methyl-4-phenyl-1,2,3,6-tetrahydropyridine **33** provided *trans*-1-*N*-methyl-4-phenyl-3-piperidinol **35** *via* the β-aminoalkylborane **35** (Scheme 10) [18].

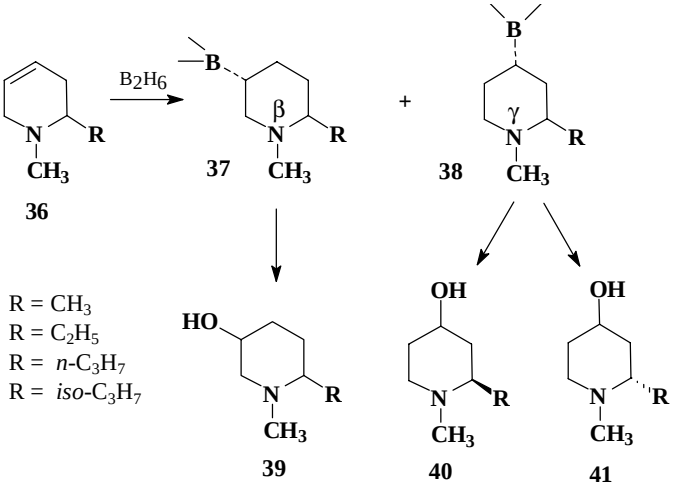


Scheme 10

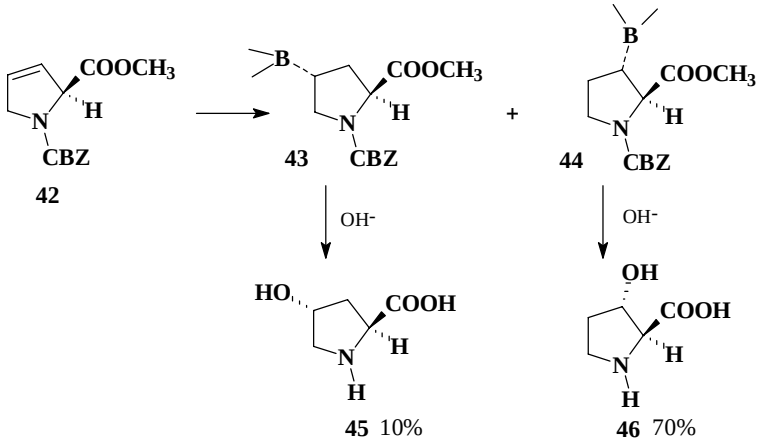
The reaction of 4-alkyl-substituted 1-*N*-methyl-1,2,3,6-tetrahydropyridines **36** with diborane proceeded in a similar manner [19] and gave a 50% mixture of isomeric alcohols **39** - **41** [84]. The reaction undergoes *via* the corresponding β-aminoalkylborane **37** and γ- aminoalkylborane **38** (Scheme 11) [19,20].

The hydroboration of *N*-carbobenzyloxy-3,4-dehydro-DL-proline methyl ester **42** proceeded to give 10% *trans*-hydroxy-DL-proline **45** and 70% *cis*-hydroxy-DL-proline **46** *via* the corresponding β-aminoalkylborane derivatives **43** and **44** (Scheme 12) [21].

2,3-Dicarbomethoxy-2,3-diazabicyclo[2.2.1]hept-



Scheme 11

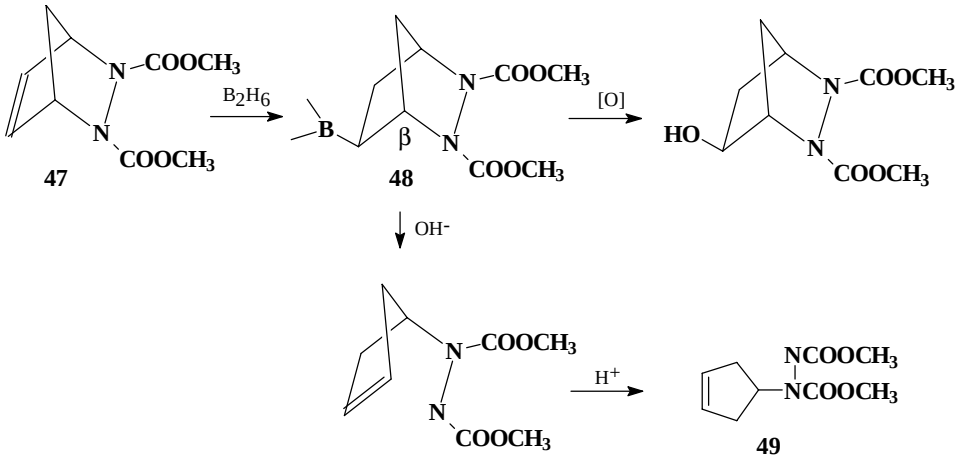


Scheme 12

5-ene **47** reacted with diborane followed by oxidation with hydrogen peroxide in alkaline medium where β-elimination from **48** leads to 4-(N,N'-dicarbomethoxyhydrazo)-cyclopentene **49** (Scheme 13) [21-23].

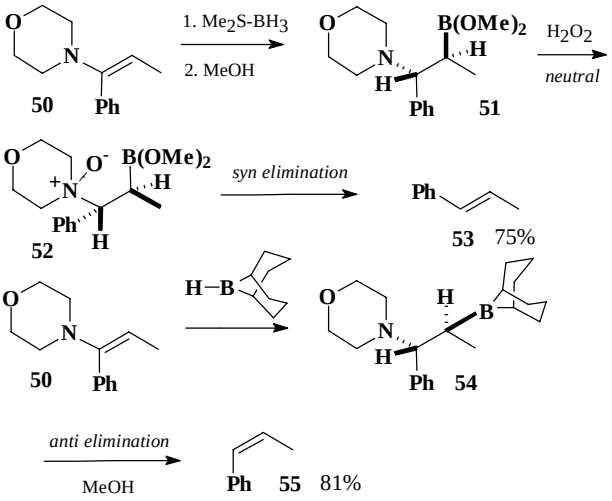
Synthesis of alkenes from enamines

β-Aminoborane intermediates **51**, **52** and **54** formed isomerically pure enamines under hydrobor-



Scheme 13

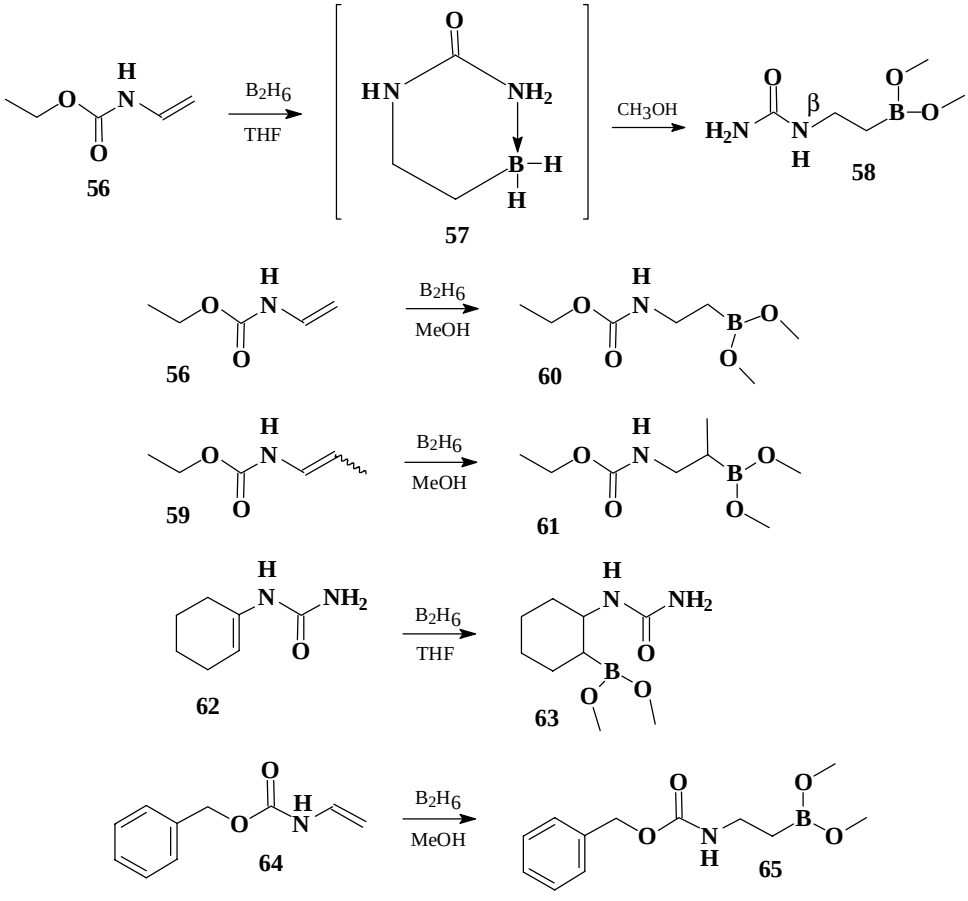
ation reactions [24]. Morpholine enamine of propiophenone **50** reacted with dimethylsulfoboron hydride to give derivatives of boronic acid which could be converted to the amine oxide without affecting the boronic ester [25] and than eliminated to (*E*)-1-phenylpropene **53**. If the hydroboration was carried out with 9-BBN, an intermediate β-aminoalkylborane **54** was formed which β-eliminated in an *anti* manner to give (*Z*)-1-phenylpropene **55** (Scheme 14) [26,27].



Scheme 14

Synthesis of β-aminoalkylboranes from urea derivatives

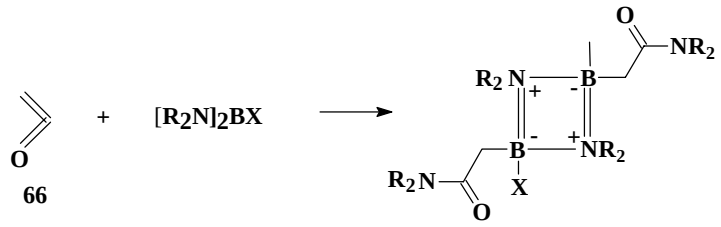
Lewis and Pearce [8] reported that when diborane in tetrahydrofuran was treated with *N*-cyclohex-1-enylpiperidine and the resulting organoborane hydrolyzed, there was obtained an almost quantitative yield of *trans*-2-*N*-piperidylcyclohexylboronic acid **57**. Similarly, Butler and Soloway [28] hydroborated *N*-vinylurea **56** and realized an 80% yield of dimethyl β-ureidoethylboronate **58** after treating the intermediate with excess methanol (Scheme 15). Derivatives of propenylurea **59** reacted with diborane to give the corresponding β-aminoalkylboranes **60** and **61**. The cyclohex-1-enyl-urea **62** reacted with diborane in tetrahydrofuran to form β-aminoalkylborane **63**. Benzyl-vinylcarbamate **64** with diborane gave the benzyl ester of (2-dihydroxyboranyl-ethyl)-carbamic acid **65** [28].



Scheme15

Reactions of boranediamines with ketene

Paetzold and Kosma [29,30] have studied the products formed by aminoboration of ketene. The aminoboration of ketene **66** with $HalB(NR_2)_2$ **67** – **70** leads to β-aminoalkylboranes **71** - **74** with common structure $[(R_2N)HalB\text{-}CH_2\text{-}CONR_2]_2$ (Scheme 16). For details of this reaction see our review [31].



67. R=Me; X=CI
68. R=Et; X=CI
69. R=Me; X=I
70. R+Me; X=Br

71. R=Me; X=CI
72. R=Et; X=CI
73. R=Me; X=I
74. R=Me; X=Br

Scheme 16

Synthesis of derivatized porphyrins

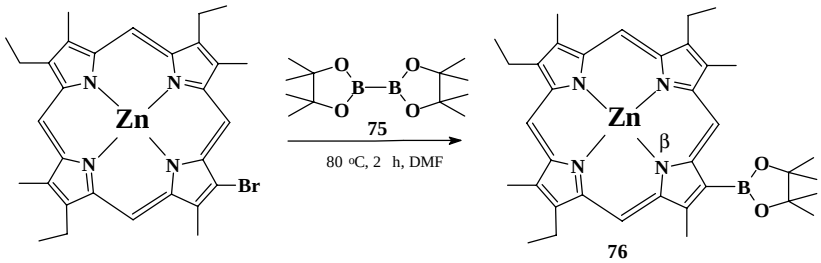
In studies of modified porphyrin complexes, β-aminoalkylborane was obtained [32]. The authors used 4,4,5,5,4',4',5',5'-octamethyl-[2,2']bi[[1,3,2]dioxaborolanyl] **75** for reaction with bromo Zn^{+2} complex and obtained compound **76** (Scheme 17).

A Suzuki coupling method

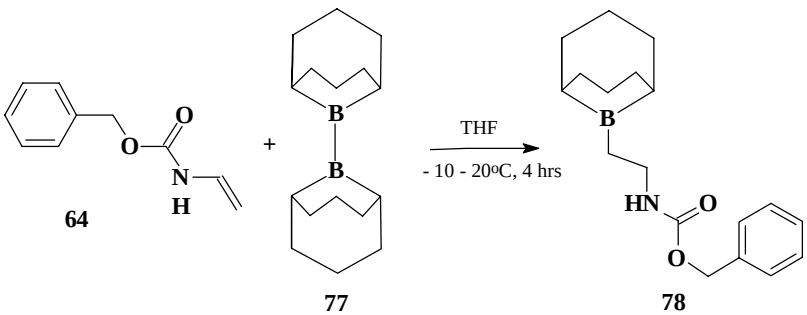
A Suzuki coupling method for direct introducing a protected β-aminoethyl group into arenes and alkenes was reported by Kamatani and Overman [33]. It was shown that benzyl-vinylcarbamate **64** reacted with [9,9']bi[9-bora-bicyclo[3.3.1]nonyl] **77** in tetrahydrofuran to form the benzyl ester of [2-(9-bora-bicyclo[3.3.1]non-9-yl)-ethyl]carbamic acid **78** (Scheme 18).

Synthesis of isonitrile-triphenylboranes

Bittner et al. [34] by the reactions of triphenyl-

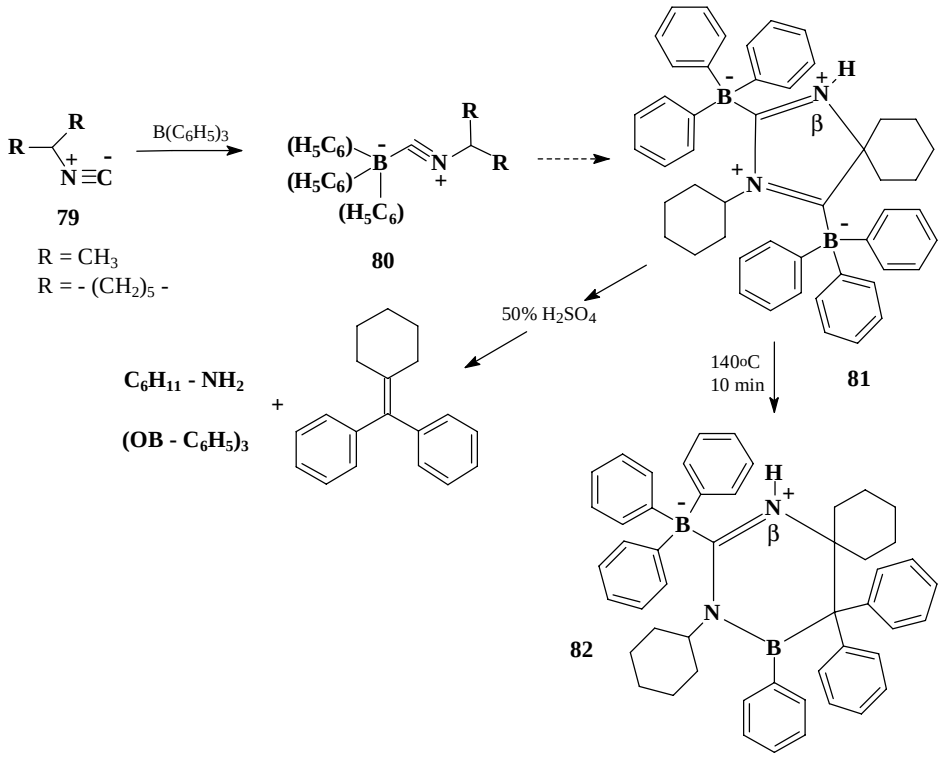


Scheme 17



Scheme 18

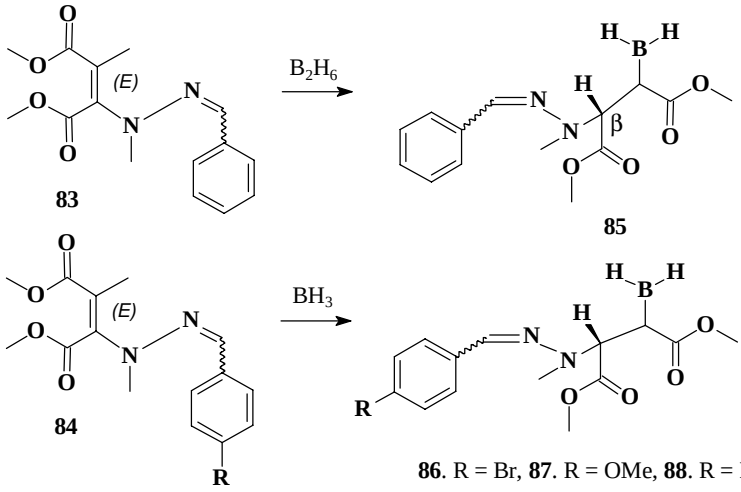
boranes **80** with isonitriles **79** obtained **81.** When heated **81** was transformed to (3-cyclohexyl-4,5,5-triphenyl-1,3-diaza-4-bora-spiro[5.5]undec-1-en-2-yl)-triphenylborate **82** (Scheme 19).



Scheme 19

Synthesis of borylhydrazones

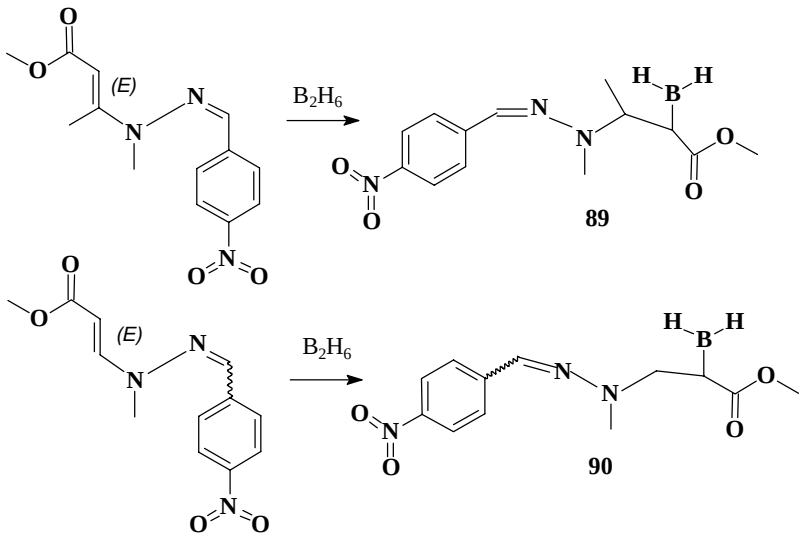
Hydroboration of enehydrazones **83** and **84** under different conditions gave a series of stable boranes **85 - 88** [35]. Thus, the dimethyl ester of 2-(*N*'-benzylidene-*N*-methylhydrazino)-but-2-enedioic acid **83** reacted with diborane in bis-(2-methoxy-ethyl)ether to form the dimethyl ester of 2-(*N*'-benzylidene-*N*-methyl-hydrazino)-3-boranyl-succinic acid **85** (Scheme 20). Similarly, the dimethyl ester of 2-(*N*'-benzylidene-*N*-methylhydrazino)-but-2-enedioic acid **84** containing different substituents in the 4-position of phenyl, reacted with diborane to form β-aminoalkylboranes **86** – **88**.



86. R = Br, **87**. R = OMe, **88**. R = NO_2

Scheme 20

In cases when the crotyl or acrylic acids were used for reactions with diborane bis-(2-methoxyethyl)-ethers, were formed **89** and **90** from the corresponding esters respectively (Scheme 21).



Scheme 21

Hydroboration of trialkylamines

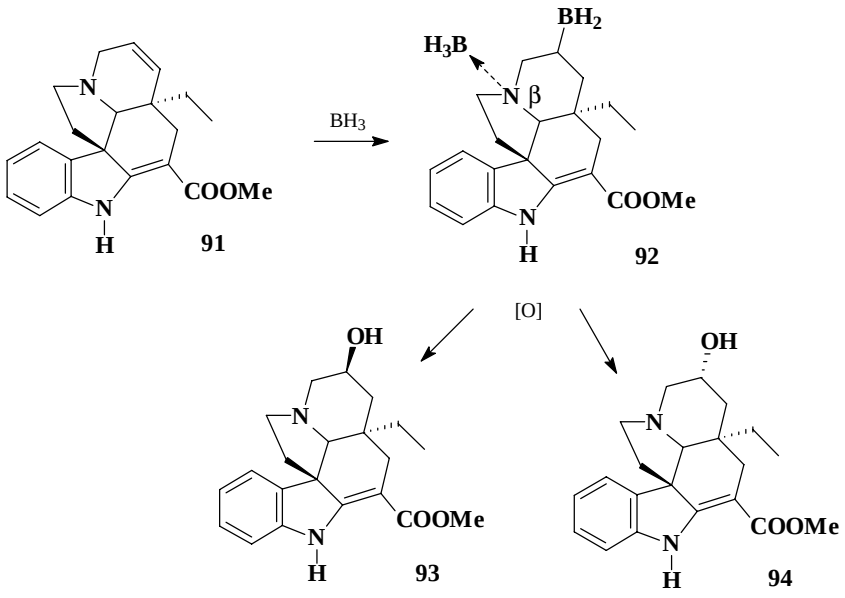
Amine groups complex strongly reacted with borane and β-hydroborate with formation of β-aminoalkylborane **92** [15,36], for instance of alkaloids **91** (Scheme 22), followed by oxidation to form two alcohol isomers **93** and **94**.

Complexation of amine groups with borane has also been found for some tetrafluoro derivatives **95** and **96** providing the corresponding alcohols **99** and **100** after oxidation. Intermediates were β-aminoalkylboranes **97** and **98** (Scheme 23) [15,36].

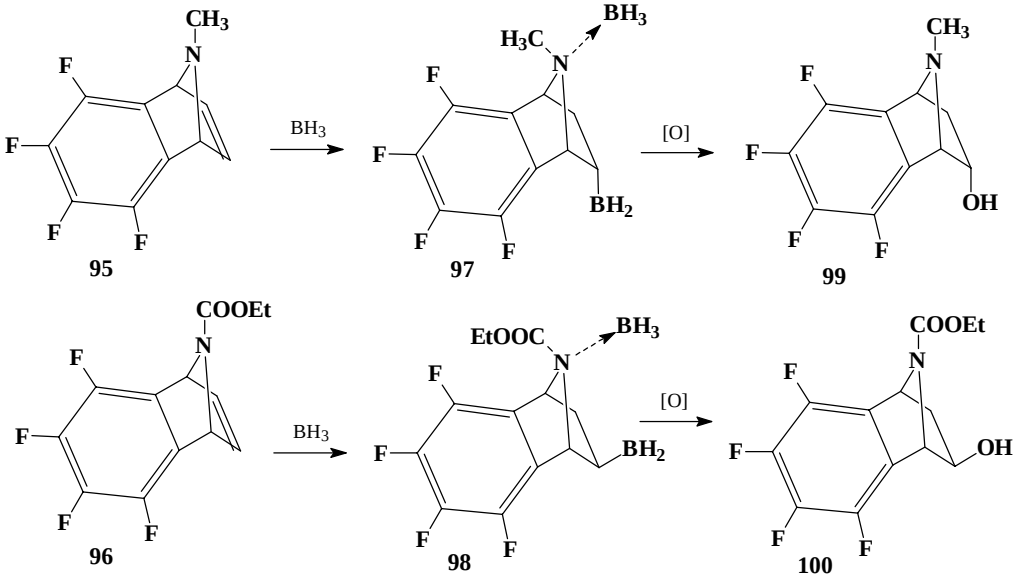
β-Sulfanylalkylboranes (B – C – C – SR)

Synthesis of boryl thioamino acid

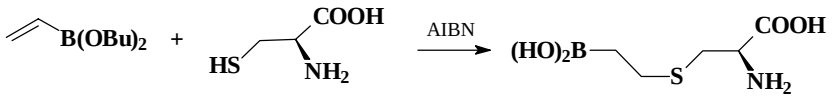
β-sulfanylalkylborane **101** was obtained by addition of cysteine to dibutyl vinylboronate (Scheme 24) [37].



Scheme 22



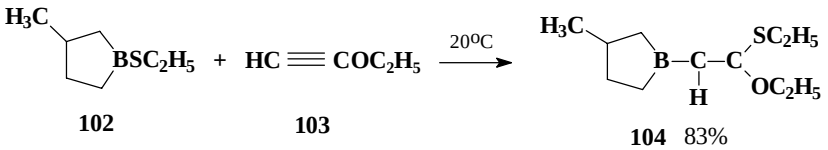
Scheme 23



Scheme 24

Thioboration of acetylenic compounds

3-Methyl-1-ethylthioboracyclopentane **102** reacted with ethoxyacetylene **103** to form stereospecifically *cis*-addition product β-boryl alkyl thioether **104** in good yield (83%) (Scheme 25) [38].

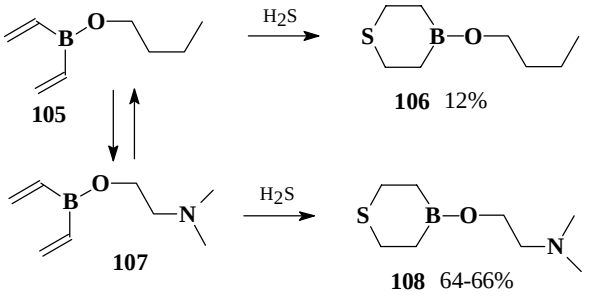


Scheme 25

Synthesis of heterocyclic compounds

Butyl divinylboronate **105** added to hydrogen sulfide in the presence of azobisisobutyronitrile to form 4-butoxy-1,4-thiaborinane **106**. Also divinylborinic acid 2-dimethylamino-ethyl ester **107** reacted with H_2S to form dimethyl-(2-[1,4]thiaborinan-4-yloxy-ethyl)-amine **108** (Scheme 26) [39].

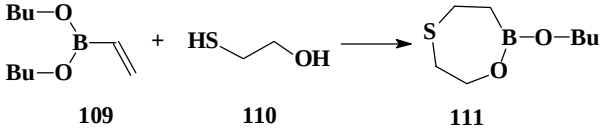
Dibutyl ester of vinylboronic acid **109** reacted with 2-mercaptoethanol **110** to form heterocyclic compound of 2-butoxy-[1,5,2]oxathiaborepane **111** (Scheme 27) [40].



Scheme 26

Synthesis and stereochemistry β-S-substituted olefins

Pasto and Snyder [41] prepared β-substituted



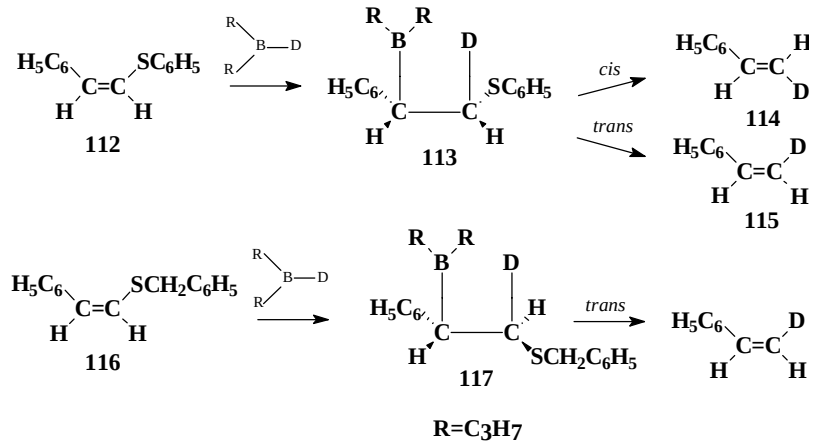
Scheme 27

organoboranes by deuteroboration. Addition of deuteroborane $(n\text{-Pr})_2$BD to *cis*-β-phenylmercaptosterene **112** and *trans*-β-benzylmercaptostyrene **116** produced the corresponding *cis*- and *trans*- β-sulfanylalkyl- boranes **113** and **117**. The interaction between the boron and sulfur was not sufficient to lead to *cis* elimination **114**. The inability to affect an acid catalyzed elimination with was also probably due to too weak interactions between the sulfur and BF_3. β-Boryl alkyl thioether intermediate **113** underwent a facile *trans* elimination in the presence of *n*-butyllithium **115** and **118**. Deuterioboration of **116** gave also β-boryl alkyl thioether as intermediate **117** which did not undergo an uncatalized elimination. Treatment **117** with BF_3 produced *trans*-β-deuteriostyrene *via* a *trans* elimination. The difference in the reactivity **113** and **117** must be due to the difference in the electronic effects of the groups bonded to the sulfur atom, the phenyl group being strongly electron withdrawing, and hence reducing the electron density on the sulfur (Scheme 28) [41,42].

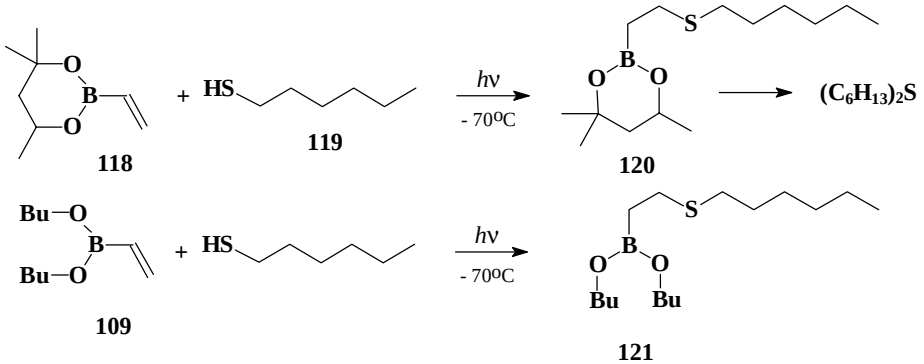
Reactions of thiols with ethylene boron compounds

Woods and Bengelsdorf [43] obtained β-sulfanylalkylborane **120** by addition of 1-hexanethiol **119** to 2-vinyl-4,4,6-trimethyl-1,3,2-dioxaborinane **118** (Scheme 29). The lower reactivity of **118** in this reaction indicated a reduced stability of intermediate **120** compared with di-*n*-butyl ethyleneboranate **109** which reacted also with 1-hexanethiol to give dibutoxy-(2-hexylmercaptoethyl)borane **121**. This compound has also been obtained by other researchers [44,45].

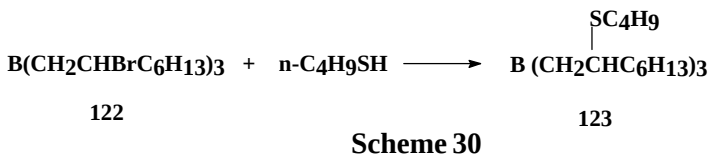
Mikhailov and Nikolaeva [46] reported that *tris*-(2-brom-octyl)boran **122** reacted with butane-1-thiol to form the butyl ester of *bis*-(2-butylmercapto-octyl)borin **123** (Scheme 30).



Scheme 28

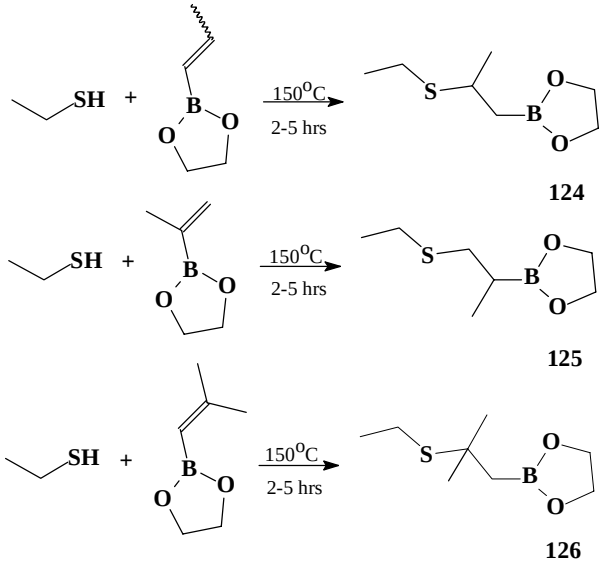


Scheme 29



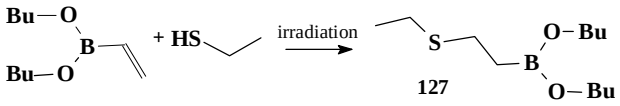
Scheme 30

Reactions of ethanethiol with dioxaborolanes have been studied by Braun [47] and obtained some β-sulfur derivatives **124 - 126**. The author showed that 2-propenyl-[1,3,2]dioxaborolane reacted with ethanethiol to give 2-(2-ethylsulfanyl-propyl)-[1,3,2]dioxaborolane **124**. Also 2-isopropenyl-[1,3,2]dioxaborolane reacted with ethanethiol to form 2-(2-ethylsulfanyl-1-methyl-ethyl)-[1,3,2]dioxaborolane **125**, and 2-(2-methyl-propenyl)-[1,3,2]dioxaborolane reacted with ethanethiol to form 2-(2-ethylsulfanyl-2-methyl-propyl)-[1,3,2]dioxaborolane **126** (Scheme 31).



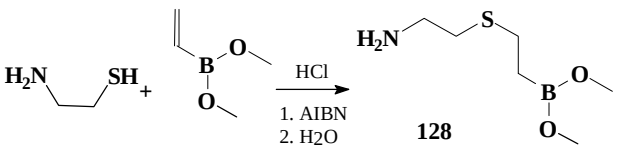
Scheme 31

Reaction between the dibutyl ester of vinylboronic acid with ethanethiol formed dibutyl-(2-ethylmercapto-ethylboronate) **127** (Scheme 32) [39].



Scheme 32

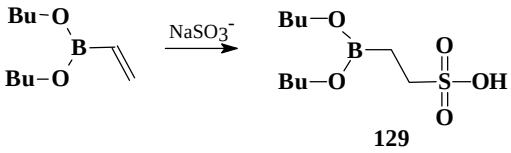
Also β-sulfanylalkylboranes **128** could be obtained in the reaction of 2-amino-ethanethiol with the dibutyl ester of vinylboronic acid (Scheme 33) [40].



Scheme 33

Reaction of boronic acid with $NaSO_3^-$

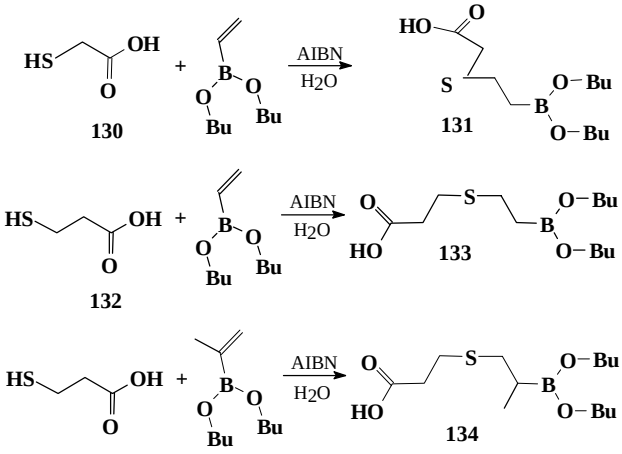
According to Matteson et al. [40] the dibutyl ester of vinylboronic acid reacted with $NaSO_3^-$ on an ion-exchange resin (H^+ form) to give 2-boronoethane-sulfuric acid **129** (Scheme 34).



Scheme 34

Reactions of thiocarboxylic acids

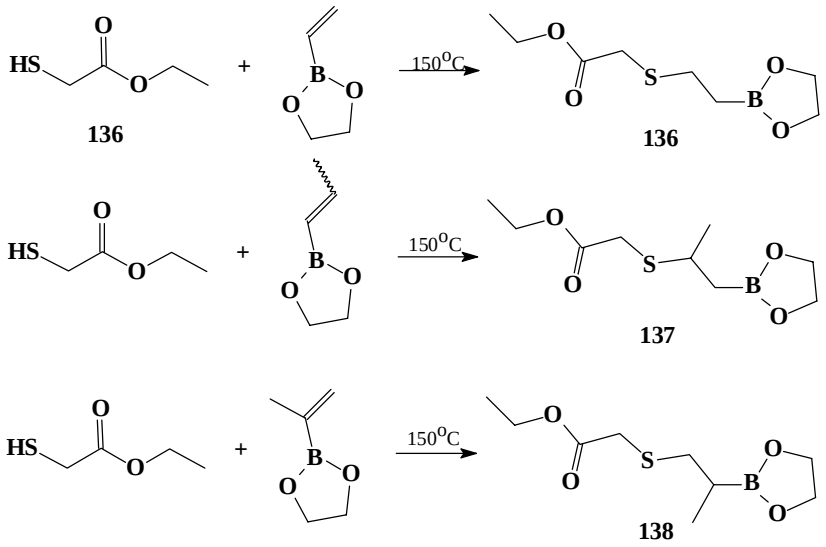
The thioacetic acid **130** reacted with dibutyl ester of vinylboronic acid to form dibutyl-2-acetylthio-ethaneboronate **131**. Similarly 3-mercaptopropionic acid **132** reacted with the dibutyl ester of vinylboronic acid to form 3-(2-boronethylthio)-propionic acid **133** (Scheme 35). Also the dibutyl ester of isopropenyl-boronic acid reacted with 3-mercaptopropionic acid **132** to form 3-(2-boron-1-propylthio)propionic acid **134** [40].



Scheme 35

Braun and coworkers [47] have also been studied reactions of the ethyl ester of mercaptoacetic acid **135** with different dioxaborolanes **136 - 138**. Thus, 2-vinyl-[1,3,2]dioxaborolane reacted with mercaptoacetic acid ethyl ester to form the ethyl ester of (2-[1,3,2]dioxaborolan-2-yl-ethylsulfanyl)-acetic acid **136**, and 2-propenyl-[1,3,2] dioxaborolane reacted with ethyl ester of mercaptoacetic acid to form the ethyl ester of (2-[1,3,2]dioxaborolan-2-yl-1-methyl-ethylsulfanyl)-

acetic acid **137**. 2-Isopropenyl-[1,3,2]dioxaborolane reacted with the ethyl ester of mercaptoacetic acid to give the ethyl ester of (2-[1,3,2]dioxaborolan-2-yl-propylsulfanyl)-acetic acid **138** (Scheme 36).



Scheme 36

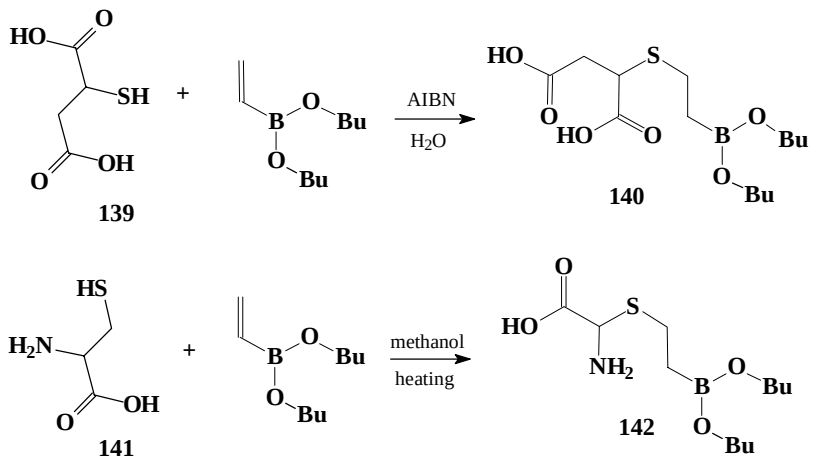
Matteson et al. [40] have also been studied the reactions of vinylboronic acids with thiodicaboxylic and thioamino acids. Thus, mercaptosuccinic acid **139** reacted with the dibutyl ester of vinylboronic acid to give (2-boron-ethylthio)bernstein acid **140**. And cysteine **141** reacted with the dibutyl ester of vinylboronic acid to form S-(2-boron-ethylthio)cysteine **142** (Scheme 37).

Synthesis of borazin derivatives

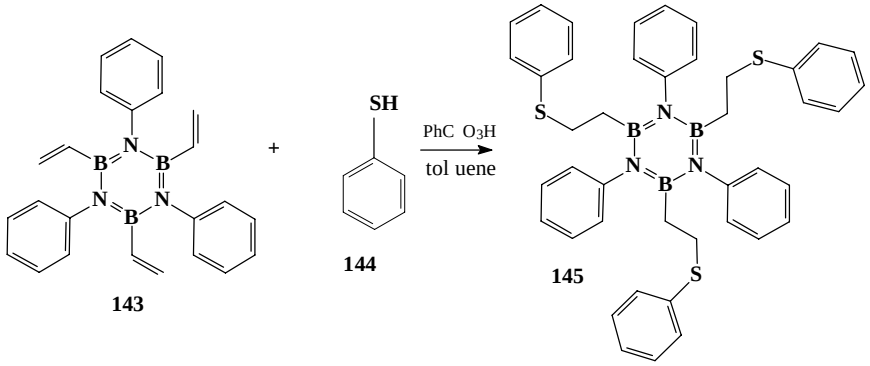
B,B,B-Trivinyl-*N*,*N*,*N*-triphenylborazine **143** reacted with benzenethiol **144** in toluene to form B-*tris*-(phenylmercaptoethyl)-*N*-triphenylborazine **145** (Scheme 38) [48].

Asymmetric hydroboration

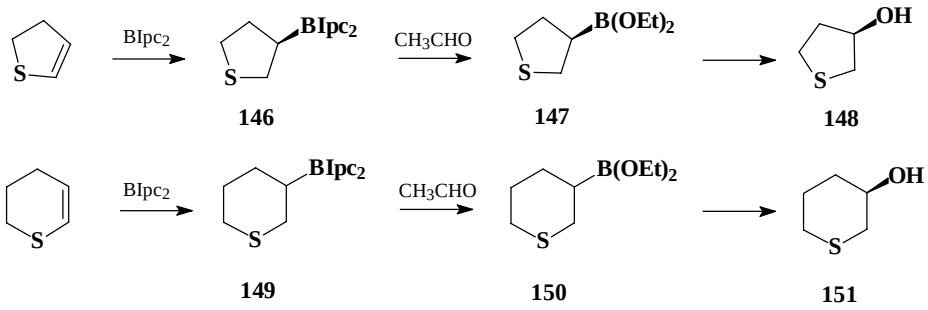
Brown and Vara Prasad [49] studied hydroboration of 2,3-dihydrothiophene with diisopinocampheylborane. The authors showed that β-boryl alkyl thioethers **146** and **147** were intermediates. **147** was converted to (+)-(*R*)-3-hydroxytetrahydro-thiophene **148** (Scheme 39). In a similar fashion 3,4-dihydrothiapyran was transformed to (*R*)-3-hydroxytetrahydrothiapyran **151** *via* β-sulfanylalkylboranes **149** and **150**.



Scheme 37



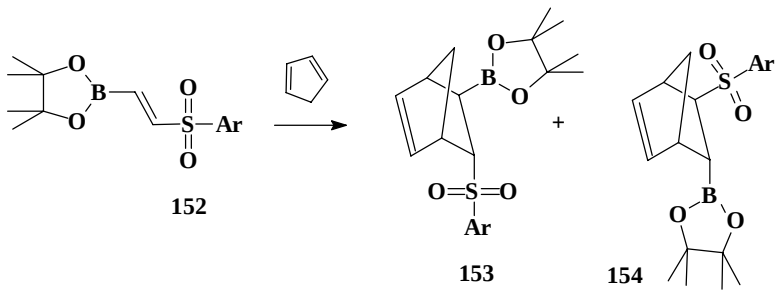
Scheme 38



Scheme 39

Diels-Alder reactions

Boronic esters such as the sulfone **152** were found to be good dienophiles that reacted with cyclopentadiene to form β-sulfanylalkylboranes **153** and **154** [50,51] (Scheme 40).



Scheme 40

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