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# Boranes in Organic Chemistry
# 1. α-Carbonylalkyl- and β-Oxyalkylboranes 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

This review is devoted to the synthesis of α-carbonylalkyl- and β-hydroxy-alkyl boranes and their use in organic synthesis. α-Carbonyl-alkylboranes include several heteroatomic compounds, in particular, [1.2.3]-diazaborinines, uracyl boronic acids, and [1.2.3.4]diaza-diboretes. The latter type has been obtained by the ketene aminoborations. The reactions of halogenboranes with diazoesters and sulfur ylides resulting in formation of α-carbonyl alkylborates containing diazofunction or ylide structural fragment are described. Amino and halogen boration of acetylenic acid esters was also used for the synthesis of α-carbonyl alkyl boranes. Reactions involving Cr-carbene complexes and acetylenic borone esters were presented for the synthesis of naphthoquinone boronic acids. The formation of amidoboranes by boration of dichloroacetanilides was remined. Boration of 4,8-dimethoxy-2-quinolone with trimethylborates leading to 2-quinolone-3-boronic acid was described. The common synthetic method to α-carbonyl alkyl boranes based on the hydroboration of acrylic acid derivatives was discussed. The results of enhydrazones hydroboration, leading to stable cyclic complexes have been mentioned. The interaction of α-bromoketones with trialkyl or dialkylboranes represents as a general synthetic method to α-carbonyl alkyl boranes. Synthetic approaches to β-hydroxy alkyl boranes are performed. The wide spread hydroboration of vinyl and allyl esters received a well-described attention. The hydroboration of cyclanone enol acetates, 3-keto- and 17-keto-steroids and cyclic allyl alcohol acetates was discussed. The results of aliphatic and alicyclic vinyl esters (including dihydrofuran derivatives) boralylation leading to β-hydroxy alkyl boranes have been envisaged. The synthesis of optically active β-hydroxy alkyl boranes using chiral borane hydrides was discussed. The heterocyclic boran dihydrides are obtained by the hydroboration of dihydropyranes, chromenes and flavenes. Borosilylation of allyl allenylic esters was also been envisaged. The synthetic scheme to optically active boranes and further optically active alcohols were presented. The problems of selectivity regularities in hydroboration reaction by intermolecular complex formations have been discussed.

## Introduction

There are a lot of examples of the application of organoboron compounds as reactive intermediates and their role in modern organic synthesis has been reviewed [1-5]. Boron appears not only as an essential element in living organisms but also as a constituent of some antibiotics such as asplamomycin, boromycin, and borophycin [6]. For the last fifty years there have been many incentives to incorporate boron into different biologically active molecules [4], particularly for medicinal application as boron neutron capture therapy of brain tumors [6]. Other methods of synthesis and applications of boron-containing analogues of biomolecules or boron compounds having biological interest have been observed in some reviews [1,2,4,6].

α-Carbonylalkylboranes are oxygen containing compounds with general structure as B–C–C=O, which are mostly intermediates in some synthetic reactions. We found a few reactions where these compounds can be isolated.

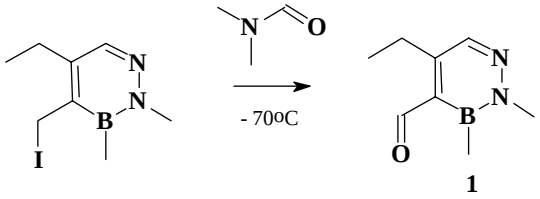
β-Oxyalkylboranes are also oxygen containing compounds with the corresponding structure B–C–C–OR. Both classes of these compounds classes have been only partially reviewed [1-6].

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

## α-Carbonylalkylboranes (B–C–C=O)

### *Synthesis of heteroaromatic boron compounds*

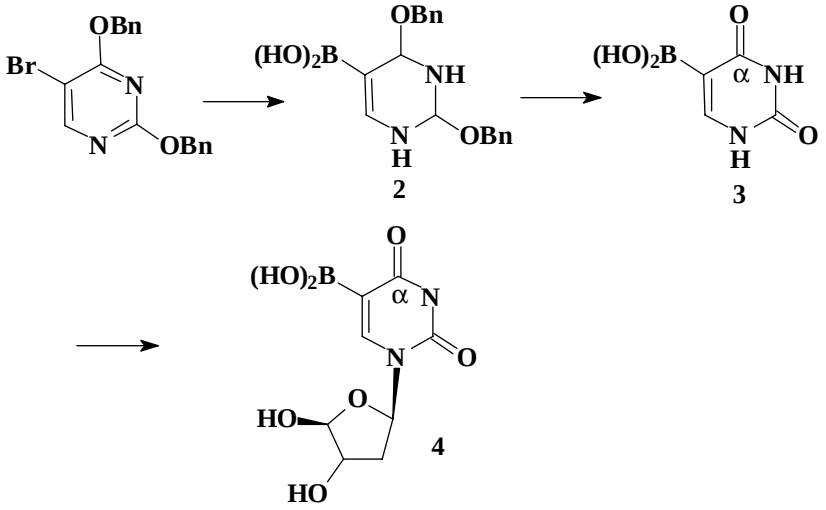
Gronowitz and Maltesson [7] found that 5-ethyl-4-iodo-2,3-dimethyl-2,3-dihydro-[1,2,3]diazaborinine reacted with *N*,*N*-dimethylformamide at - 70°C to form 5-ethyl-2,3-dimethyl-2,3-dihydro-[1,2,3]diazaborinine-4-carbaldehyde **1** (Scheme 1).




**1**

**Scheme 1**

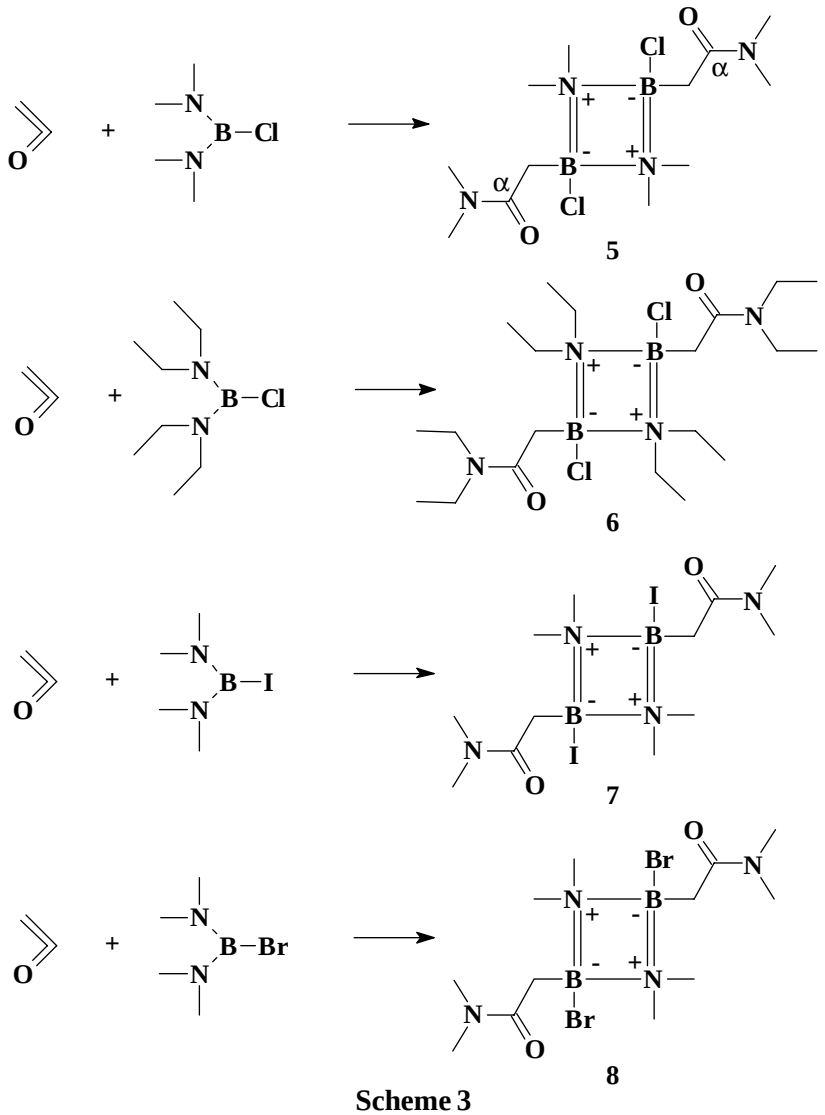
Liao et al. [8] first synthesized 5-dihydroxyboryluracil **3**, *via* a halogen-metal exchange reaction on 5-bromo-2,4-dibenzyloxypyrimidine by boration, however the product could not be isolated and it was converted directly to **3** by hydrogenation. Schinazi and Prusoff [9] resynthesized **3** by operating at – 95°C – 85°C (Scheme 2) *via* α-oxyalkylboranes **2** [1], and then used **3** for synthesis of boron nucleoside **4**.




**Scheme 2**

### *Boration reactions of ketene*

A series of products formed by aminoboration of ketene was observed by Paetzold and Kosma [10]. The aminoboration of ketene with $HalB(NR_2)_2$ leads to α-carbonylalkylboranes with the common structure $[(R_2N)HalB–CH_2–CONR_2]_2$. Thus, B-chloro-tetra-*N*-methylboranediamine reacted with ketene in pentane to form 2-(2,4-dichloro-4-dimethylcarbamoyl-methyl-1,1,3,3-tetramethyl-[1,3,2,4]di-azadiboret-2-yl)-*N*,*N*-dimethyl-acetamide **5** (Scheme 3) [11]. Also chloro-*bis*-diethyl-aminoborane reacted with ketene to form 2-(2,4-dichloro-4-diethylcarbamoylmethyl-1,1,3,3-tetraethyl[1,3,2,4]diazadiboret-2-yl)-*N*,*N*-diethyl-acetamide **6**. Reactions of bora-*bis*-(dimethylamino)-iodide and *bis*-dimethylaminoborabromide with ketene lead to the corresponding compounds such as 2-(4-dimethylcarbamoylmethyl-2,4-diiodo-1,1,3,3-tetramethyl-[1,3,2,4]diazadiboret-2-yl)-*N*,*N*-dimethyl-acetamide **7** and 2-(2,4-dibromo-4-dimethylcarbamoylmethyl-1,1,3,3-tetramethyl[1,3,2,4]diazadiboret-2-yl)-*N*,*N*-dimethyl-acetamide **8**.



**Scheme 3**

### *1,3-Boryl shifts at the C–C=O skeleton*

Paetzold and Biermann [12] studied the reactions of $Hg(CH_2C{=}O{-}OMe)_2$ with $X(Me_2N)BBr$ which yielded either (2-oxoethyl)boranes as α-carbonylalkylboranes **9**, **10** or **11** with the common structure $X(Me_2N)B{-}CH_2{-}CO{-}OMe$ or (vinyloxy)boranes $H_2C{=}C(OMe)_2{-}OBX(NMe)$. 1,3-Boryl shifts at the C–C=O skeleton was observed for $X(Me_2N)B{-}CH_2{-}CO{-}OMe$ which isomeriezed to the corresponding compounds $H_2C{=}C(OMe)_2{-}OBX(NMe)$. Under heating at 70-80°C the α-carbonylalkylboranes **9**, **10** and **11** were decomposed to give ketene and (dimethylamino)methoxyorganylborane (Scheme 4).

The (vinyloxy)boranes such as $H_2C = C(OMe)_2 - OBMe(NMe)$ underwent 1,3-boryl rearrangement to give **9** followed by polymerizations [12] (Scheme 5).

Paetzold and Kosma [10] also demonstrated that aminoboration of ketenes could form α-carbonylalkyl compound **12** followed by polymerization (Scheme 6).

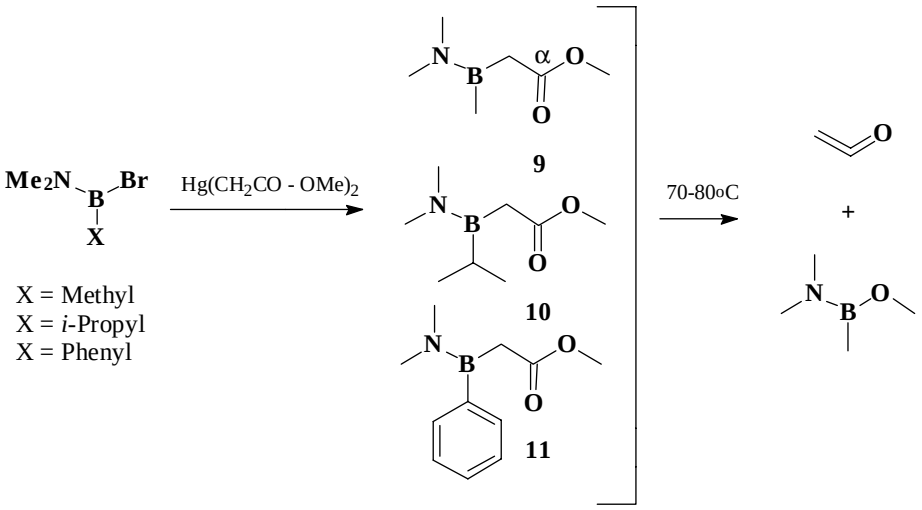
### *Reactions of diazo compounds*

Schöllkopf et al. [13] have been studied reactions of α-diazo-β-hydroxy-carboxylates and α-diazo-β-hydroxy-ketones with diazo compounds and their rearrangement into β-ketocarboxylates and β-diketones. 2-Chlorobenzo[1,3,2]-dioxaborole reacted at - 110°C in dichloromethane with stannum and/or silicon derivatives ethyl diazoacetate to form ethyl benzo[1,3,2]-dioxaborol-2-yl-diazo-acetate **13** (Scheme 7a).

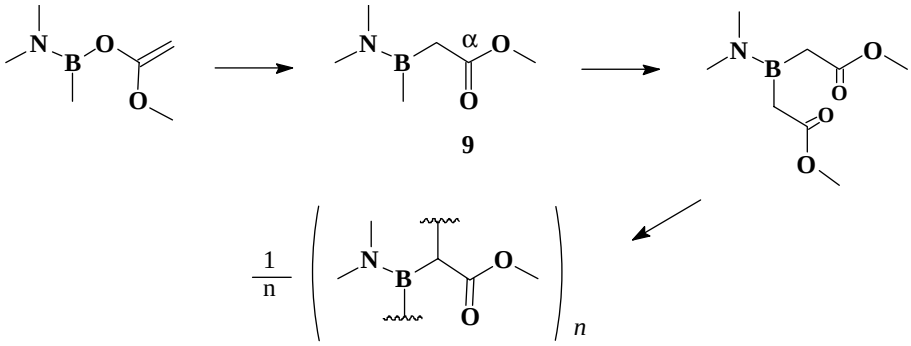
The same reaction was found for sulphur compounds [14,15] **14** (Scheme 7b).

### *Boration reactions with triple bond*

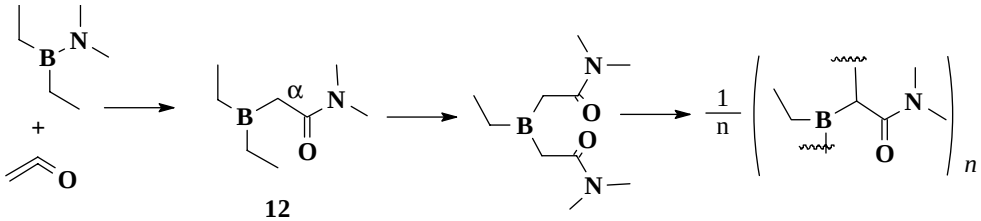
Hexa-*N*-methyl-boranetriamine easily reacted with




**Scheme 4**

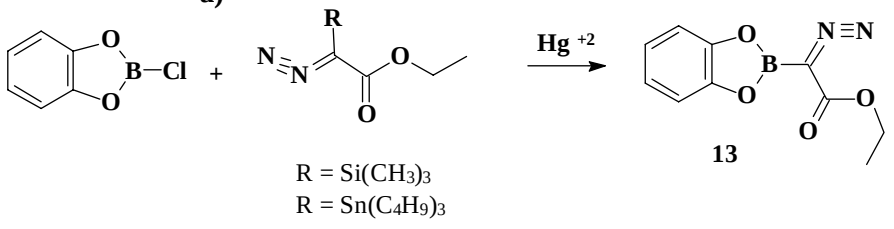



**Scheme 5**




**Scheme 6**

**a)**

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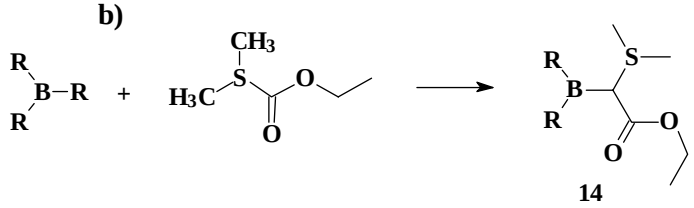
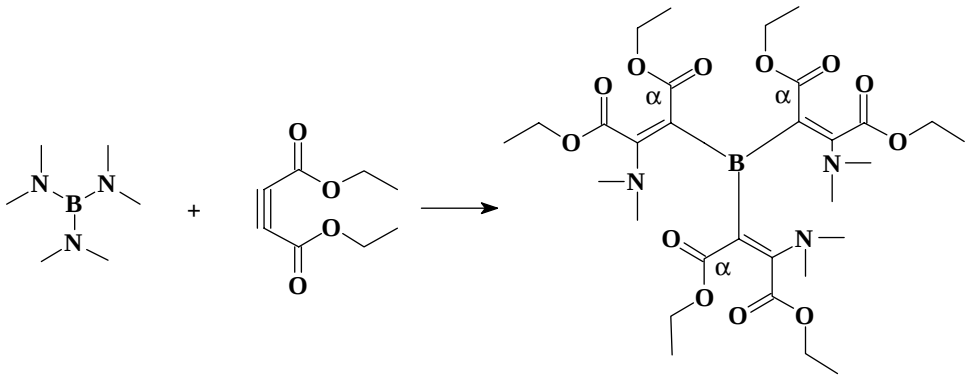



**Scheme 7**

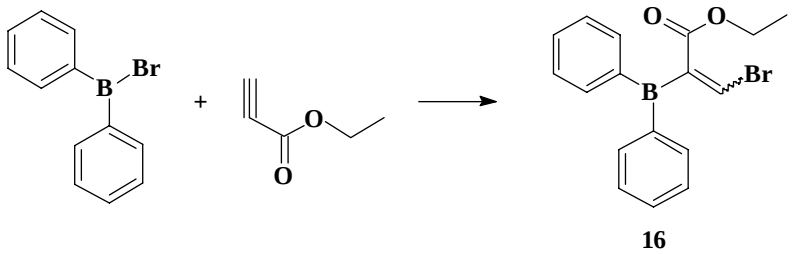
diethyl butynedioate at - 78°C to form *tris*-(2-dimethylamino-1,2-dicarbethoxyethylenyl)borane **15**, in 83% yield [16] (Scheme 8).

A series of reactions of halodiorganoboranes as well as dibenzylhaloboranes with triple bonds have been studied by Binnewirtz et al. [17]. According to experimental data dibenzylbromoborane reacted with $HC{\equiv}C{-}COOC_2H_5$ to form ethyl-2-bromo-1-(diphenylboryl)-1-methylene-acetate **16** (Scheme 9).



**15**

**Scheme 8**



**16**

**Scheme 9**

### *Reactions of trifluorovinyl-trifluoromethyl-boron derivatives*

Pawelke et al. [18,19] have shown that dimethyl-amino-*bis*(trifluoromethyl)-borane enters into numerous and novel reactions in which the boron atom increases its coordination number from three to four. Thus, ozonolysis of *bis*-trifluoromethyl-trifluorovinyl-borane gave (*bis*-trifluoromethylboranyl)-oxo-acetic acid **18**. If the reaction was carried out in $CHCl_3$ which has not been carefully dried, the carboxyborane **19** precipitated from the solution. The initially colourless mother liquid, which contained the trifluorooxiranyl-borane **17**, slowly turned yellow. This colour change resulted from the hydrolysis of **17** to form the yellow oxocarboxyborane **18** according to [19] (Scheme 10).

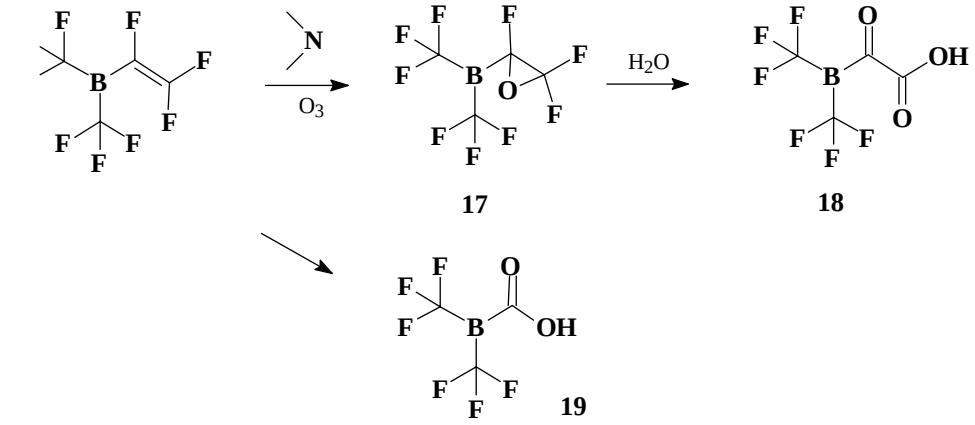
### *Formation the quinones of boronic esters*

Quinones represent a novel class of boronic acid esters and are a potentially valuable source of a range of quinone containing medicinally important agents [20]. Deives et al. [21] demonstrated a novel and highly regioselective Cr-mediated route to functionalized quinone boronic acid ester derivatives *via* α-carbonylalkylboranes. Oxidation of 2-butyl-4-methoxy-3-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-naphthalen-1-ol by cerium ammonium nitrate at 20°C for 30 min gave 2-butyl-3-(4,4,5,5-tetramethyl[1,3,2]-dioxaborolan-2-yl)-[1,4]naphthoquinone **16** (Scheme 11).

In general, direct oxidation of the crude reaction mixture after benzannulation provided a simple and routine method for the isolation of quinone boronic acid ester compounds **20** and **21** [21] (Scheme 12 and Table 1).

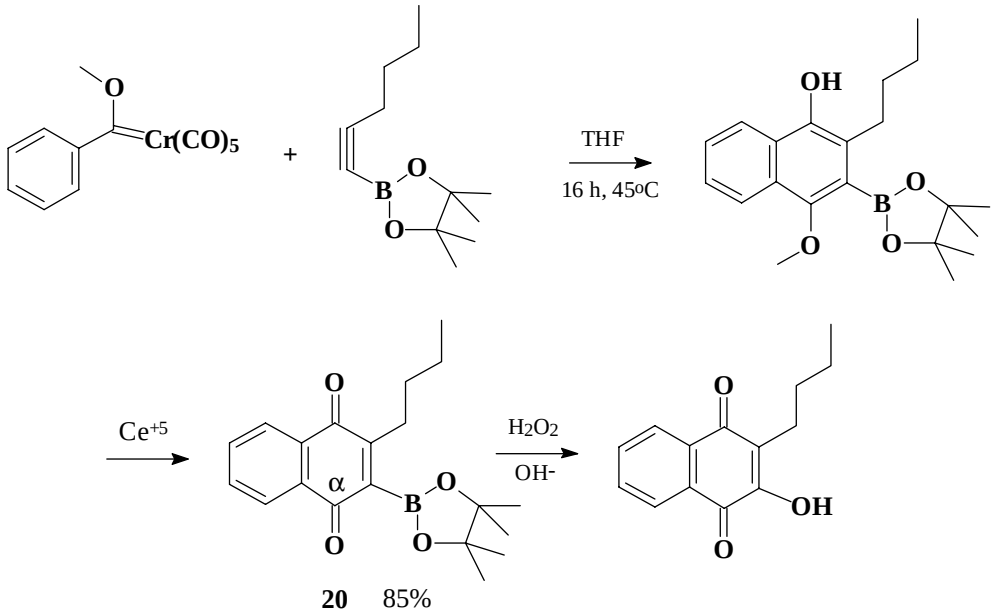
### *Formation of amidoboranes*

*N*-Trimethylsilylamides reacted with bromodi-



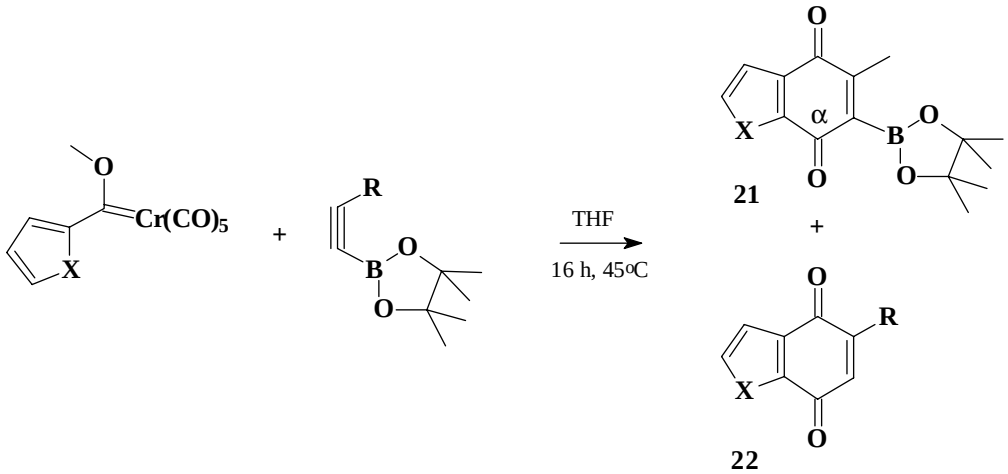
**17** **18** **19**

**Scheme 10**



**20** 85%

**Scheme 11**



**21** **22**

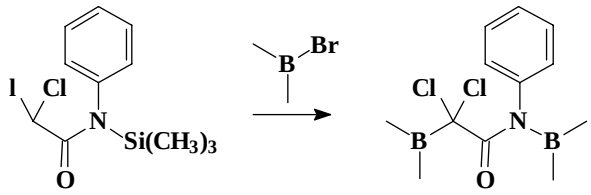
**Scheme 12**

**Table 1**
Benzannulation reaction of alkynylboronates and Fischer carbene complexes [21]

| Entry | X | R | Conditions[a] | Product Yield **21**, % | Product Yield **22**, % |
|---|---|---|---|---|---|
| 1 | CH=CH | Bu | THF, 45°C | 66 | 6 |
| 2 | CH=CH | Bu | Hexane, 45°C | 62 | 35 |
| 3 | CH=CH | Bu | $SiO_2$, 45°C | 0 | 84 |
| 4 | O | Bu | THF, 65°C | 47 | 30 |
| 5 | CH=CH | Ph | THF, 45°C | 57 | 12 |
| 6 | O | Ph | THF, 45°C | 35 | 42 |

[a] Reaction conditions: (1) 0.05 M solution of complex and 3 equiv of alkyne heated for 14–16 h under inert atmosphere. (2) Crude reaction mixture dissolved in $Et_2O$ and stirred for 0.5 h with 0.5 M Ce (IV) in 0.1 M aq. $HNO_3$.

organylboranes quantitatively to form the corresponding amidoboranes. In certain cases these were in equilibrium with the dimeric forms [22]. Among these reactions in one case the α-carbonylalkylboranes **23** was formed (Scheme 13). Thus, *N*-phenyl-*N*-trimethylsilyl-dichloroacetamide reacted with bromodimethylborane to form **23**.

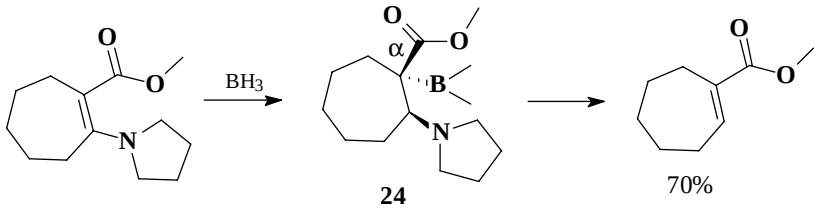



**23**

**Scheme 13**

### *Hydroboration of functional derivatives of alkenes*

Hydroboration of enamines with five-membered rings gives a stable α-carbonylalkylboranes **24** [23] (Scheme 14). Oxidation of these compounds with hydrogen peroxide in alcohol formed the corresponding carboxylic acids.




**24** 70%

**Scheme 14**

### *Synthesis of novel alkaloids*

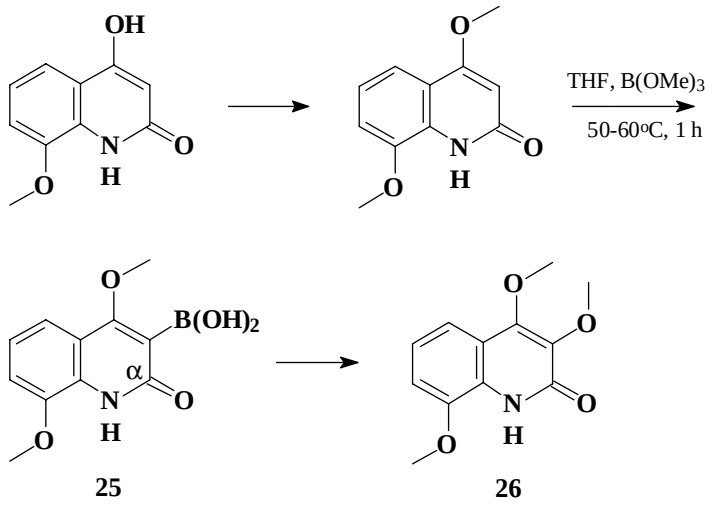
Novel alkaloids of 4,8-dimethoxy-2(1*H*)-quinolone derivatives with a functional group at 3-position have been isolated from *Eriostemon gardneri* [24,25]. Synthesis of 3,4,8-trimethoxy-2(1*H*)-quinolone **26** was reported by Tagawa et al. *via* α-carbonylalkylboranes **25** [26] (Scheme 15).

### *Hydroboration of methyl 2-acetamidoacrylate*

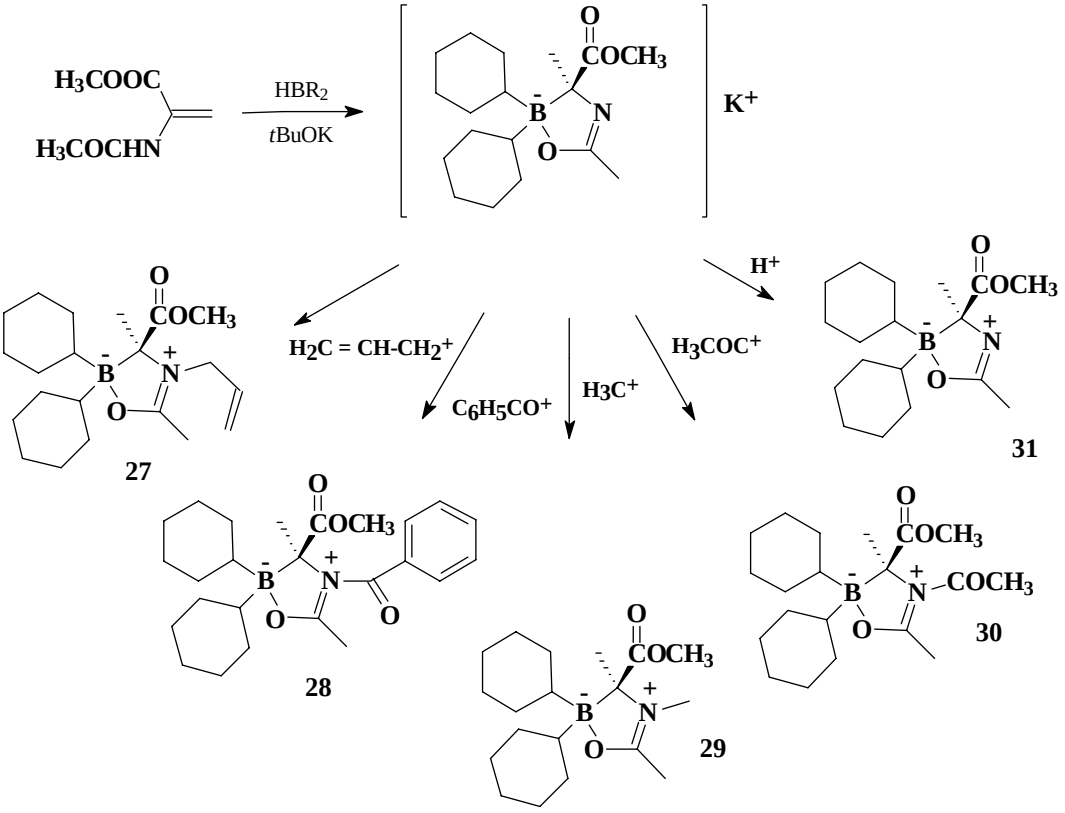
The heterocyclic borate complexes were obtained by hydroboration of methyl 2-acetamidoacrylate, affording N-alkyl as well as and/or acylalaninates [27]. The authors synthesized five heterocyclic oxytriorganoborates which were identified as α-carbonylalkylboranes **27**-**31** (Scheme 16).

### *Hydroboration of unsaturated esters*

Hydroboration of unsaturated esters was observed




**Scheme 15**

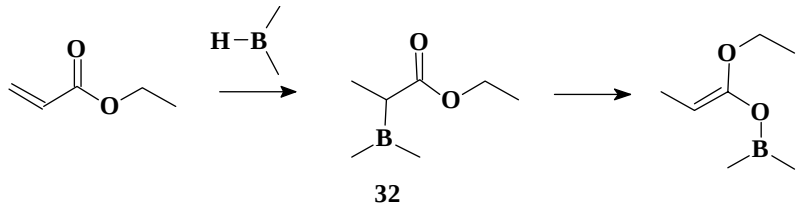



**Scheme 16**

by Brown and Keblys [28]. The authors found that the unusual reactivity of ethyl acrylate, suggesting that the hydroboration-reduction of this ester must proceed at very different rates. The first step might involve 1,2-addition with formation of the unstable α–carbonylalkylboranes **32** which followed by the rapid transfer of boron from carbon to the neighboring oxygen (Scheme 17).

### *Reactions of enehydrazones*

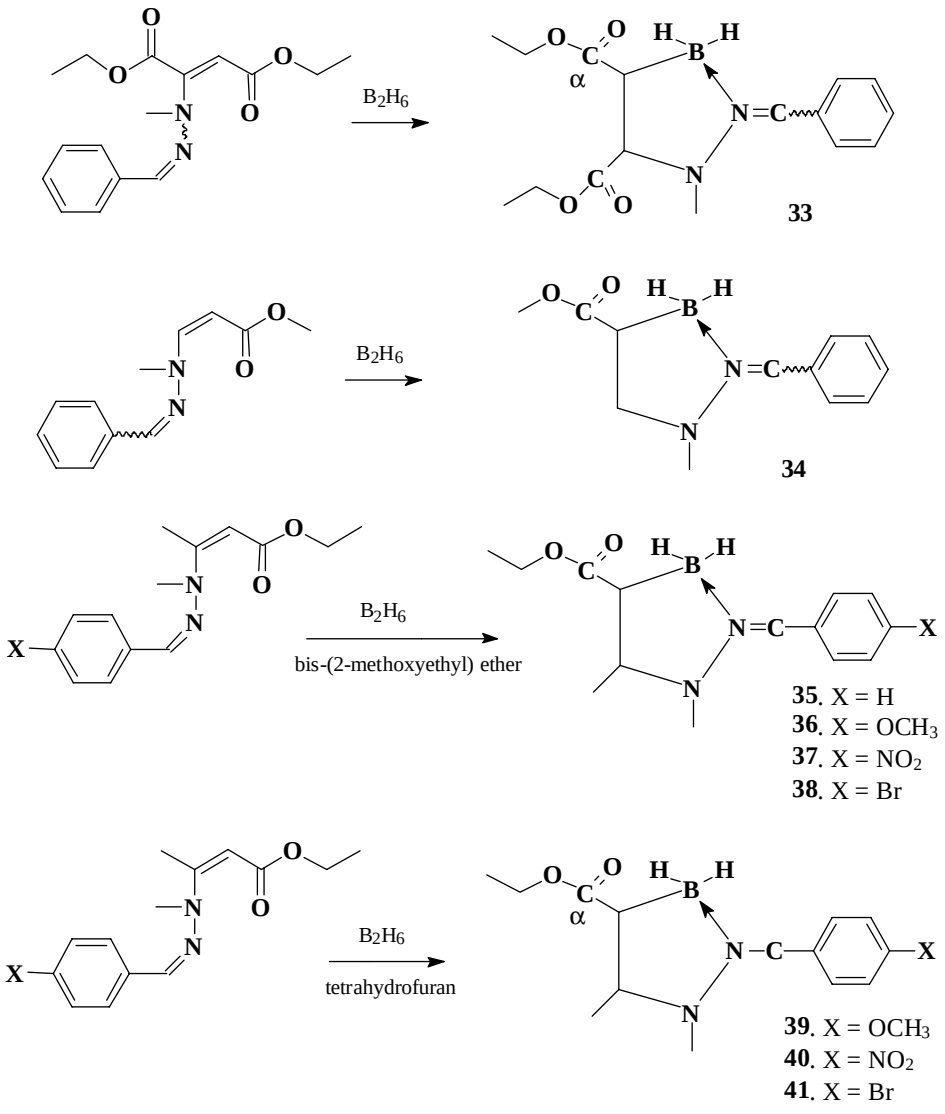
According to Sucrow et al. [29] the hydroboration of the enehydrazones and their derivatives leads to the stable boranes which are α-carbonylalkylboranes **33** – **41** (Scheme 18). Hydroboration in different ethereal solvents was studied. Thus, the dimethyl-2-(*N*'-benzylidene-*N*-methyl-hydrazino)-but-2-enedi-



**32**

**Scheme 17**

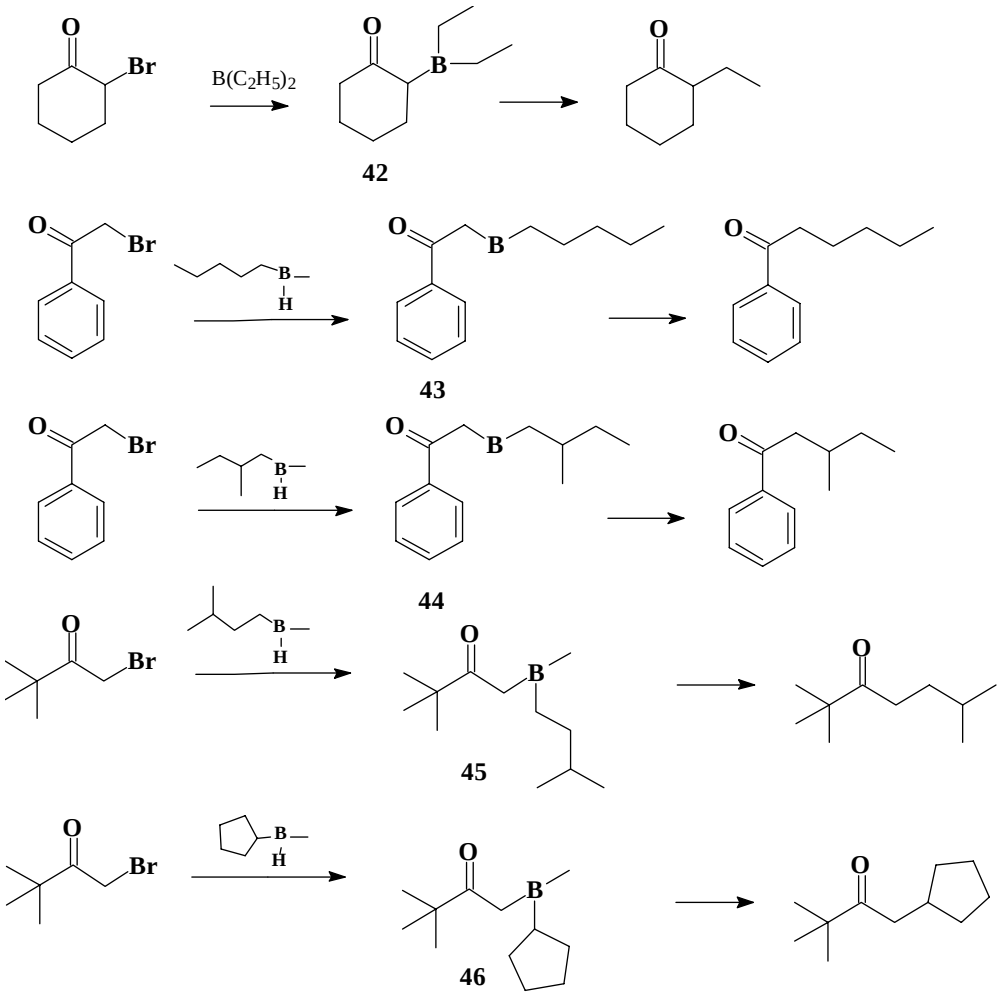
oate reacted with diborane in *bis*-(2-methoxy-ethyl)ether to form the dimethyl-2-(*N*'-benzylidene-*N*-methyl-hydrazino)-3-boranyl-succinate **33**. The methyl-3-(*N*'-benzylidene-*N*-methyl-hydrazino)-acrylate reacted in *bis*-(2-methoxy-ethyl)ether to form the methyl-3-(*N*'-benzylidene-*N*-methyl-hydrazino)-2-boranyl-propionate **34**. Ethyl-(2*E*)-3-(2-benzylidene-1-methylhydrazino)crotonate reacted with diborane also in *bis*-(2-methoxy-ethyl)ether to form the ethyl-3-(*N*'-benzyl-*N*-methylhydrazino)-2-boranyl-butyrate **35**. The ethyl-(2*E*)-3-[2-(4-methoxy-benzylidene)-1-methylhydrazino]crotonate reacted with diborane in tetrahydrofuran to form the ethyl-2-boranyl-3-[*N*'-(4-methoxy-benzyl)-*N*-methylhydrazino]butyrate **39**. In another reactants it was found that the corresponding α-carbonylalkylboranes have been formed.




**Scheme 18**

### *Reactions with α-bromo ketones*

Brown et al. [30] have shown that α-bromo ketones reacted with triethylboranes to form α-carbonylalkylboranes **42-46** as intermediates which under the influence of potasium *t*-butoxide in tetrahydrofuran lead to the corresponding α–carbonylalkyboranes (Scheme 19).




**Scheme 19**

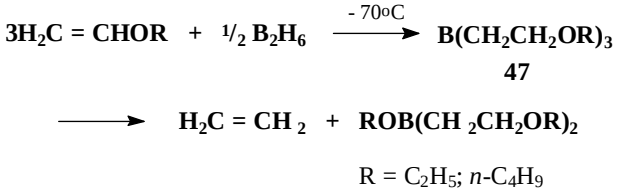
## β-Oxyalkylboranes (B–C–C–OR)

### *Hydroboration of vinyl and allyl ethers*

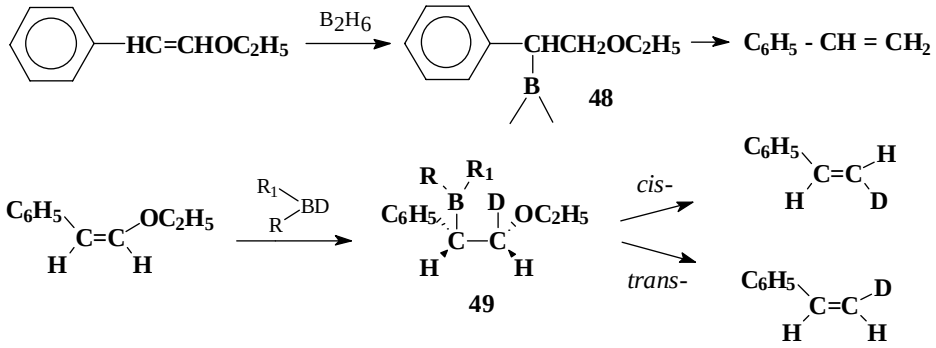
According to Mikhailov et al. [31,32] the reaction of diborane and vinyl ethyl or vinyl butyl ether in ethereal solutions at – 70°C followed by slow heating to room temperature, leads to thermally unstable boranes **47** [33] (Scheme 20).

The hydroboration of β-ethoxystyrene with diborane in tetrahydrofuran produced β-oxyalkylboranes **48** and **49** [34] and formation of the latter two alcohols was explained by the hydroboration-oxidation of styrene. Interestingly, in a study of the deuteroboration of *cis*-β-ethoxystyrene by Pasto and Snyder [35] *cis*-β-ethoxystyrene spontaneously underwent *cis*-elimination to form *trans*-β-deuterostyrene *via* β-borylethers. In the presence of a basic ($C_4H_9Li$) or acid catalyst ($BF_3$), a *trans*-elimination with the formation of *cis*-β-deuterostyrene was observed (Scheme 21).

Hydroboration-oxidation of 1-ethoxycyclohexene in tetrahydrofuran to form *trans*-2-ethoxycyclohexanol, indicated that the addition of boron occurred at the β-position according to the relative thermal stability of the β-oxyalkylborane **50** than α-oxyalkyl-




**Scheme 20**



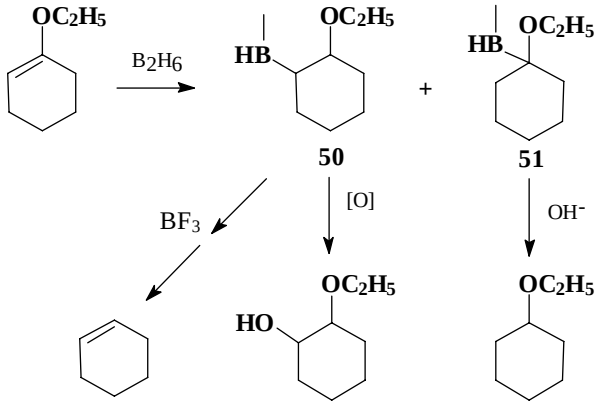

**Scheme 21**

borane **51** [34] (Scheme 22). The addition of boron trifluoride to the hydroboration products caused decomposition of the β-boryl alkyl ethers.

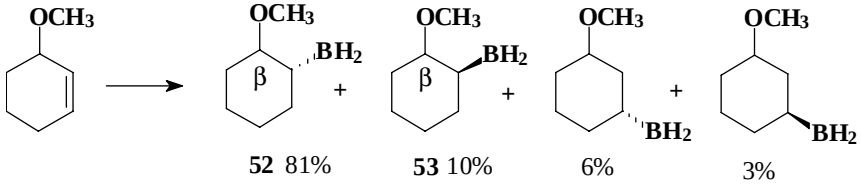
Pasto and Hickman [36] established that 3-methoxycyclohexene underwent hydroboration to form two 1,2-isomers **52** (81%) and **53** (10%), whereas only 9% occurred at the 1,3-position (Scheme 23).

Cyclohexyl acetate underwent hydroboration with diborane in tetrahydrofuran to form intermediate **54**, which was oxidized to *trans*-cyclohexane-1,2-diol and cyclohexanol [37,38] (Scheme 24).

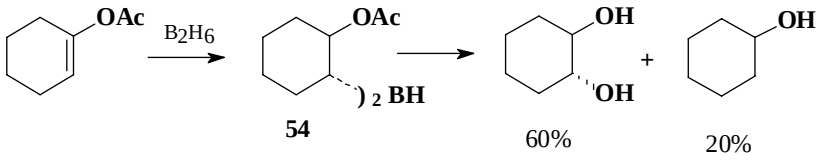
Lewis and Pearce [39] also studied the hydroboration of 2- and 6-methyl-cyclohex-1-enyl acetates with




**Scheme 22**

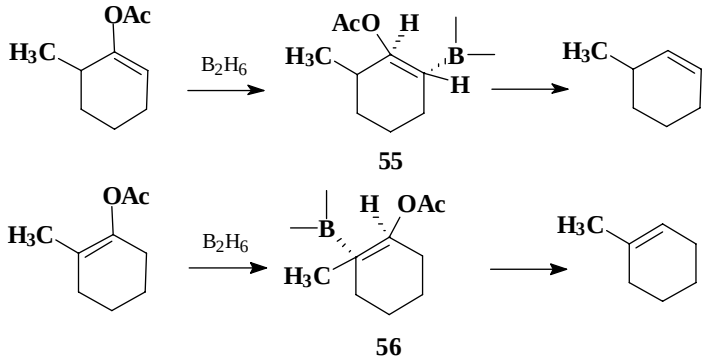



**Scheme 23**



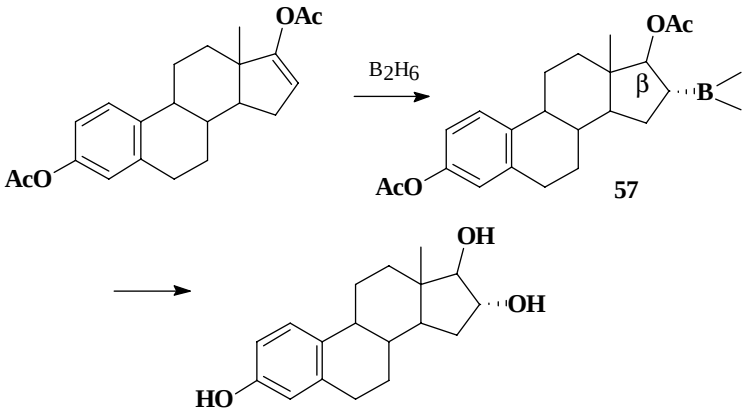

**Scheme 24**

diborane. Both compounds gave β-oxyalkylboranes (**55** and **56**) (Scheme 25). A similar mechanism where hydroboration was electronically controlled by the acetoxy group was suggested.




**Scheme 25**

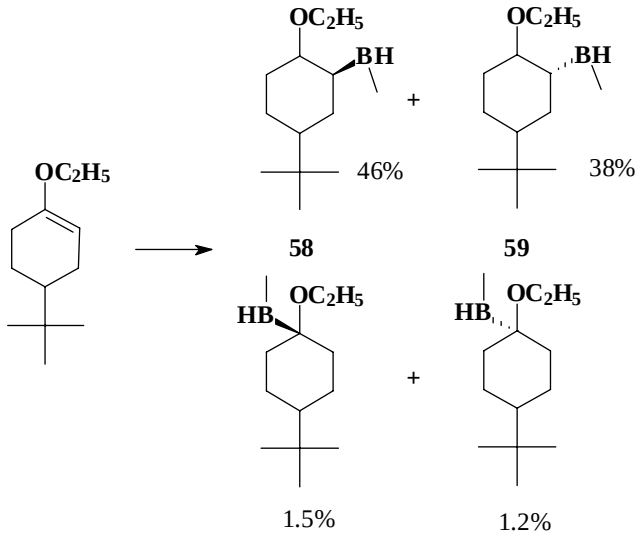
Similar results were obtained with 1,3,5,16-estratetraene-3,17-diol diacetate which was converted to estriol by hydroboration-oxidation *via* β-oxyalkylborane **57** [40] (Scheme 26).



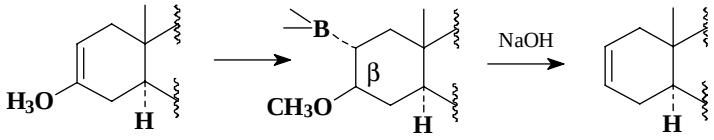

**Scheme 26**

Diborane reacted with 4-*tert*-butyl-1-ethoxycyclohexene to form four isomers in this reaction where the boron atom predominantly attached to C2- in the *cis*- and *trans*-position (**58** and **59**) with respect to the *tert*-butyl group [34,41] (Scheme 27). Addition of the boron to C1 in the *cis*- and *trans*-position occurred in a negligible amount.

In the case of methoxy group, for example, in 3-methoxy-5α-cholest-2-ene, boron also predominantly attached to C2 as in **60**, which was converted to 5α-cholest-2-ene by treatment with NaOH [42] (Scheme 28).




**Scheme 27**

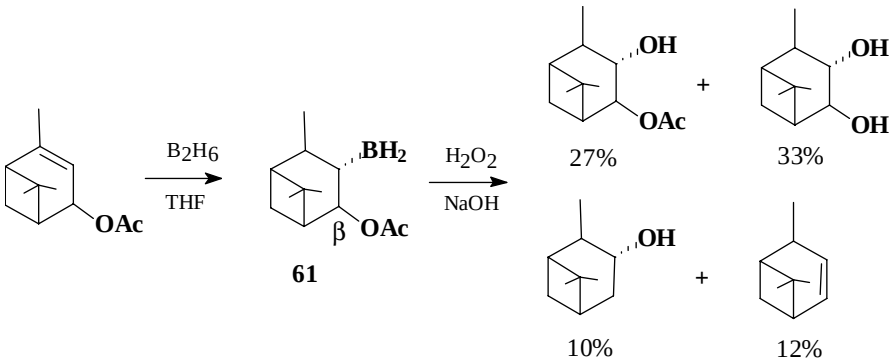



**60**

**Scheme 28**

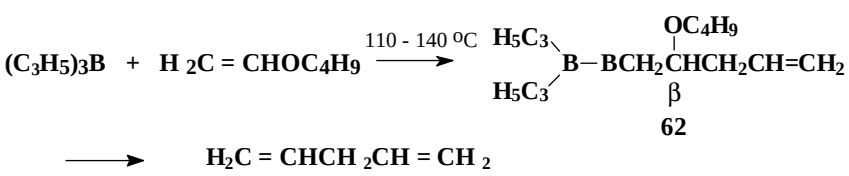
The hydroboration of *cis*-verbenyl acetate proceeded from the side opposite to the *gem*-dimethyl group at β-position **61** with respect to the acetoxy group [43]. Oxidation resulted in a mixture of four compounds (Scheme 29).

Allylboranes may react with compounds containing an activated double bond [44,45]. For example, heating triallylborane with vinyl *n*-butyl ether leads to penta-1,4-diene *via* β-boryl alkyl ether as intermediate **62** (Scheme 30).




**61**

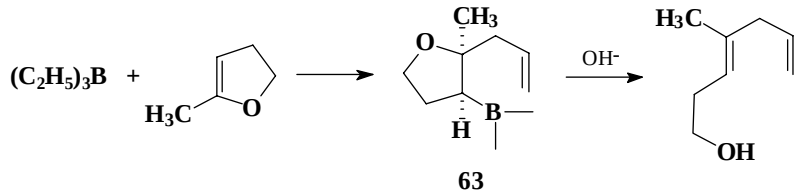
**Scheme 29**




**62**

**Scheme 30**

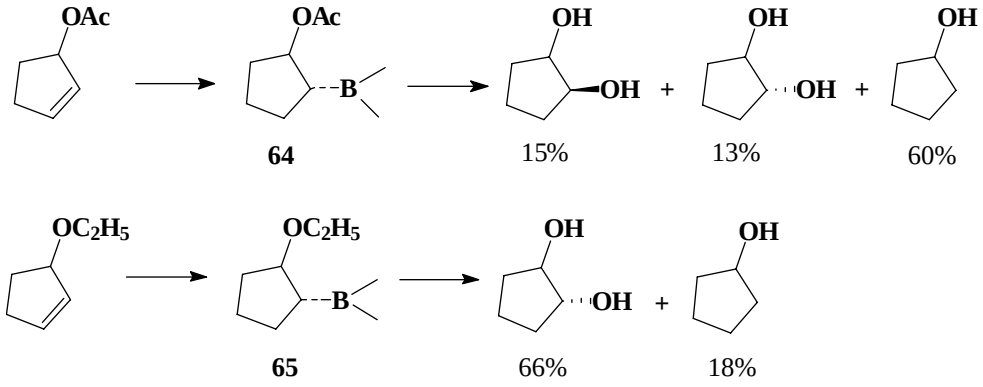
Hydroboration of cyclic vinyl ethers is a convenient preparative procedure for the synthesis of novel 1,4-dienoic hydrocarbons and their substituted derivatives *via* β-oxyalkylborane **63** [46] (Scheme 31).




**63**

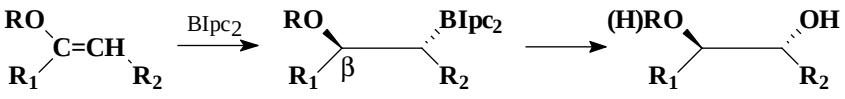
**Scheme 31**

A series of representative 3-substituted cyclopentenes was hydroborated with diborane [47]. The intermediates were β-boryl alkyl ethers **64** and **65**. 3-Acetoxycyclopentene formed *cis*-1,2-cyclopentanes without any 1,3-cyclopentane derivatives. It was shown that no *cis*-1,2-diol products were formed from 3-ethoxy-cyclopentene. The predominant product (66%) was *trans*-2-ethoxycyclopentanol (Scheme 32).




**Scheme 32**

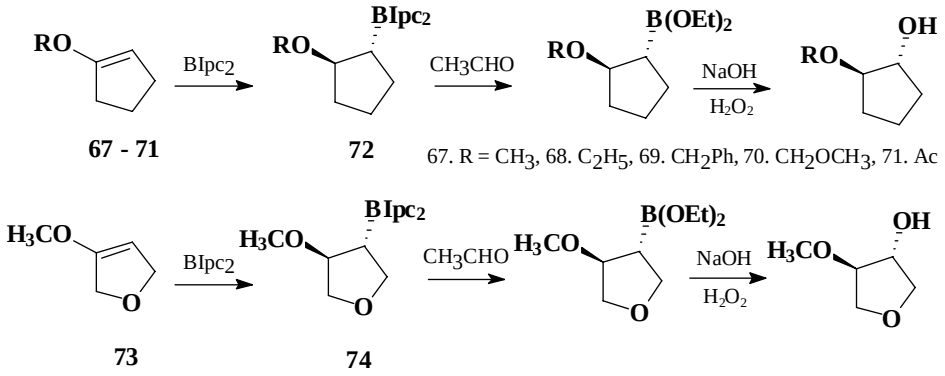
Achiral hydroboration of oxysubstituted alkenes such as enol ethers, [34,35,48-50] enol acetates [38,39] and enolates [51] were reported previously. Optically active 1,2-diol derivatives were obtained *via* the formation of β-oxyalkylboranes **66**, according to Scheme 33:




**66**

**Scheme 33**

Asymmetric hydroboration of 1-cyclopentenol derivatives (**67-71**, **73**) was studied recently by Brown et al. [52]. Boron attached predominately to C2-position to form β-oxyalkylboranes (compounds **72** and **74**) (Scheme 34). Experimental details are shown in Table 2.




**Scheme 34**

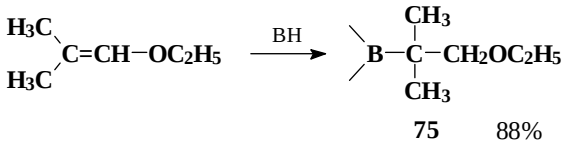
**Table 2**
Hydroboration of enol derivatives **67** - **71** and **73** with $Ipc_2BH$

| Substrate | Hydroboration | | Oxidation product | Yield, % | Ref. |
|---|---|---|---|---|---|
| | Temp, °C | Time, h | | | |
| **67** | - 25 | 76 | (1*R*,2*R*)-(-)-2-methoxy-cyclopentanol | 93 | 53 |
| **68** | - 25 | 80 | (1*R*,2*R*)-(-)-2-ethoxy-cyclopentanol | 95 | 54 |
| **69** | - 15 | 120 | (1*R*,2*R*)-(-)-2-benzyloxy-cyclopentanol | 75 | 55 |
| **70** | - 15 | 120 | (1*R*,2*R*)-(-)-2-(methoxy-methoxy)-cyclopentanol | 77 | 52 |
| **71** | - 10 | 72 | (1*R*,2*R*)-(-)-cyclopentane-1,2-diol | 40 | 56,57 |
| **73** | - 25 | 30 | (1*R*,2*R*)-(+)-4-methoxy-tetrahydrofuran-3-ol | 70 | 58 |

### *Synthesis of β -oxyalkylboranes from butenyl derivatives*

Isobutenyl ethyl ether reacted with borane to give β-oxyalkylborane **75** as the final compound [50] (Scheme 35). The ethoxy group caused the olefin to be highly reactive and, further, reversed the addition pattern of the isobutylene system. A trace amount of *iso*-butyraldehyde was found among products in this reaction.

The directive influence of the 1-butenyl moiety is considerably lower than of the isobutenyl moiety. Thus, both *cis*- and *trans*-1-ethoxy-1-butenes rapidly consumed only one equiv of hydride [50]. Also both crotyl ethyl ether and 1-butenyl ethyl ether yielded the same β-boryl alkyl ether **30** (Scheme 36).

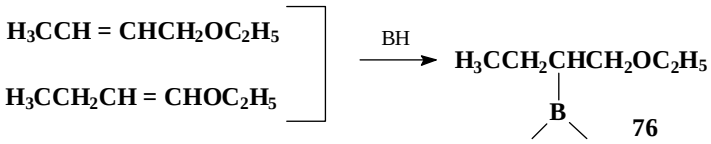



**Scheme 35**

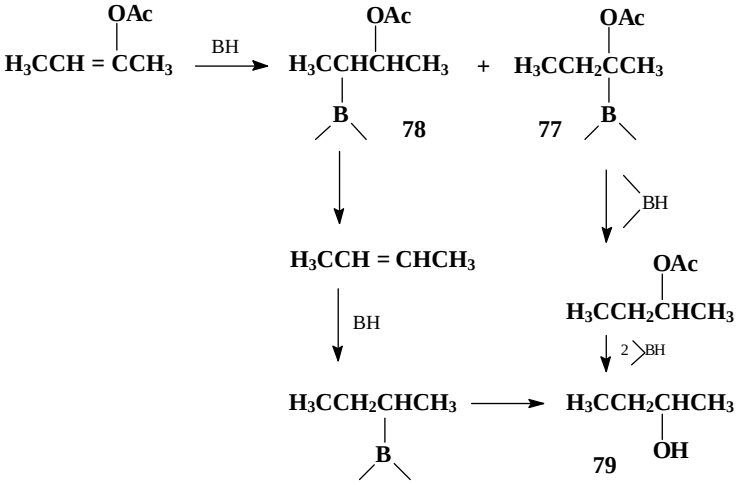
In the case of 2-butenyl-2 derivatives both α- **77** and β-oxyalkylboranes **78** [50] were obtained which in the process of hydroboration-oxidation produced the same compound **79** (Scheme 37).

### *Synthesis of heterocyclic compounds*

Divinyl ether and trimethylamine *t*-butylborane reacted without solvent under atmospheric pressure at -70°C [42]. As the reaction proceeded, a volatile

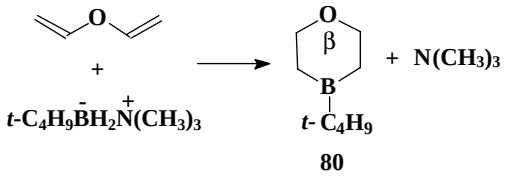



**Scheme 36**



**Scheme 37**

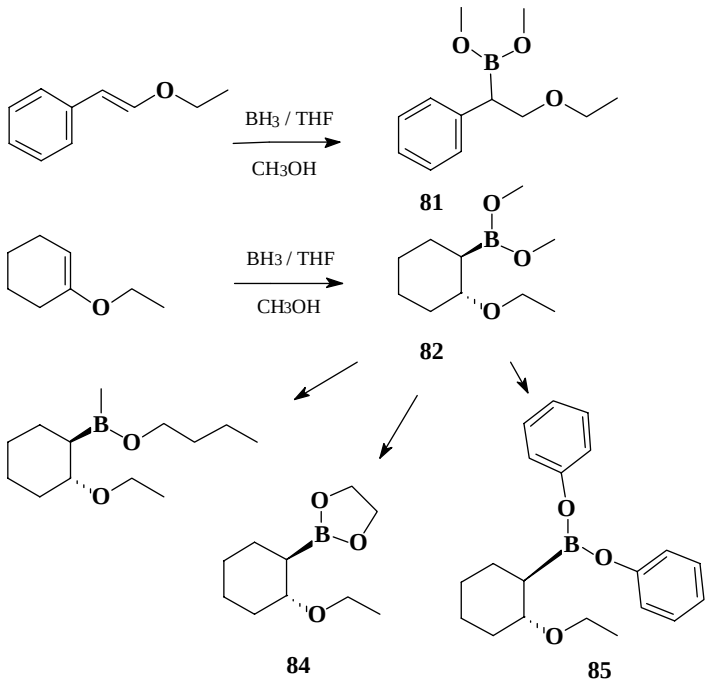
crystalline solid formed which was shown to be 1-*t*-butyl-1-bora-4-oxacyclohexane **80** (Scheme 38).



**Scheme 38**

### *Transfer reactions*

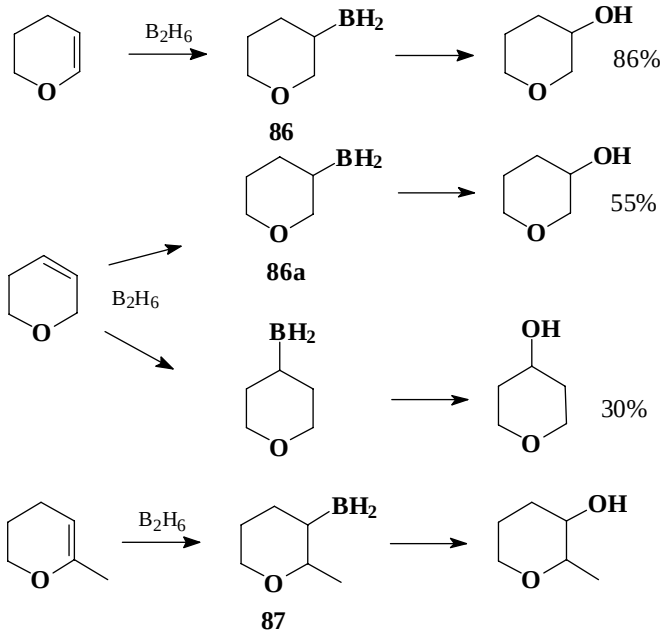
The kinetics of the Lewis acid-catalyzed dealkoxyboronation of esters of trans-2-ethoxycyclohexaneboronic acid in a variety of donor solvents and with a variety of Lewis acids have been studied by Pasto and Timony [59]. β-Oxyalkylboranes **81-85** were obtained. Preparation of dimethyl 2-ethoxy-1-phenyl-1-ethaneboronate **81** by hydroboration of β-ethoxystyrene in tetrahydrofuran followed by methanolysis was reported. The borinate **83** was prepared by reaction of **82** with methyl-magnesium iodide in ether at –78°C followed by hydrolysis and extraction with 1-butanol. The boronates of **84** and **85** were prepared by treatment of **36** with excess ethylene glycol and phenol respectively (Scheme 39).



**Scheme 39**

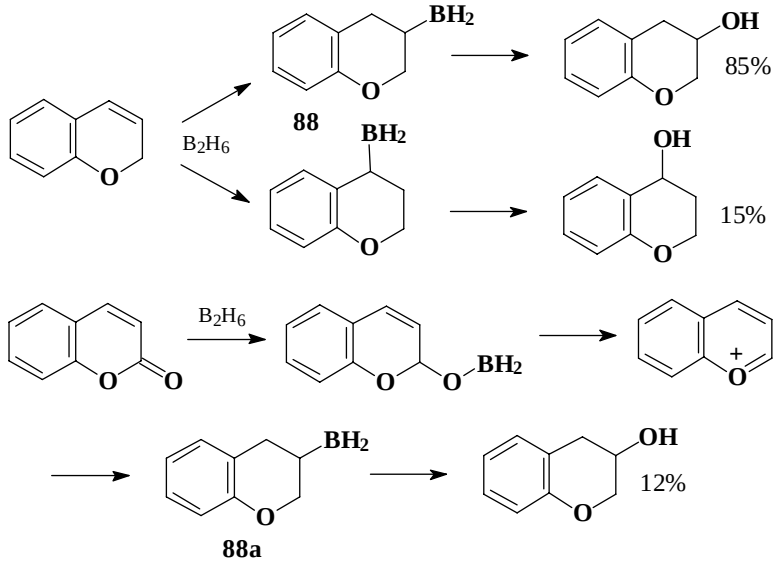
### *Hydroboration of dihydropyran derivatives*

Hydroboration of dihydropyran and derivatives has been reported [60-63]. Thus, 2-dihydropyran could be converted to tetrahydro-3-pyranol *via* β-oxyalkylborane **86** (Scheme 40) [60-62] while 3-dihydropyran formed a mixture of tetrahydro-3- (55%) and tetrahydro-4-pyranol (30%), of which **86a** is β-boryl alkyl ether [61,62]. Also β-boryl alkyl ether **87** could be formed during hydroboration of 2-methyl-dihyropyran [37].




**Scheme 40**

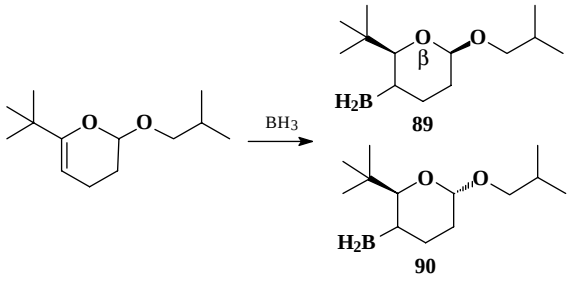
Hydroboration of 3-chromeme to form a mixture of 3- and 4-chromanols has been described [64,65]. 3-Chromanol was formed *via* the β-oxyalkylborane **88** (Scheme 41). In the hydroboration of coumarin 3-chromanol was formed *via* β-boryl alkyl ether **88a** according to Scheme 41 [62,66].



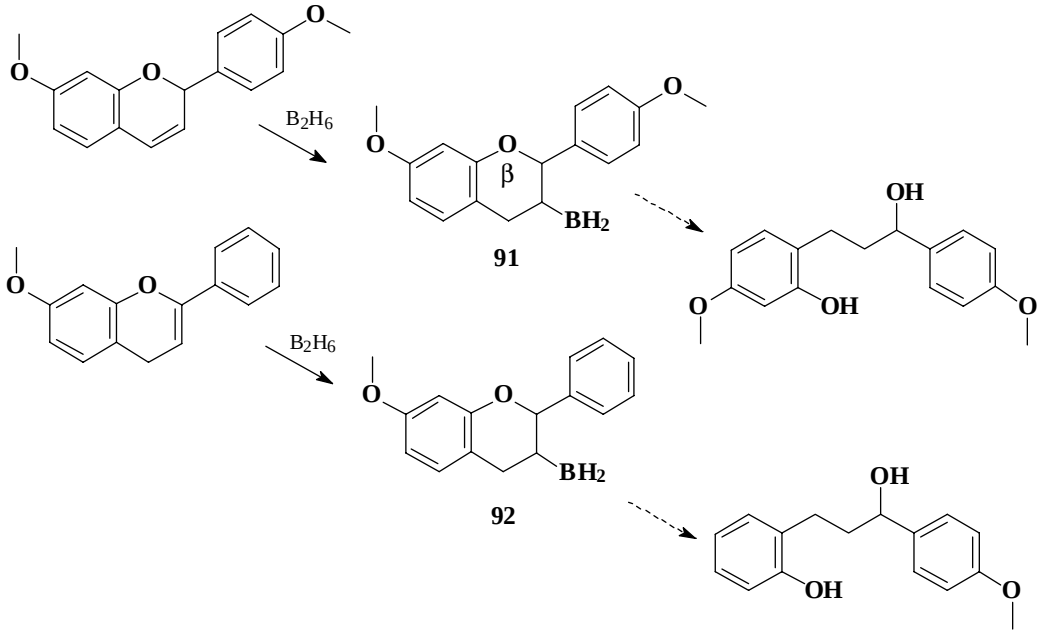

**Scheme 41**

Two isomers of 2-*tert*-butyl-6-isobutoxy-tetrahydro-pyran-3-yl-borane **89** and **90** were obtained in the reaction of 2-isobutoxy-6-*tert*-butyl-2H-dihydropyran with boron hydride in tetrahydrofuran (Scheme 42) [67].

Hydroboration of 4',7-dimethoxy-3-flavene and 4'-methoxy-2-flavene leads to 1,3-diaryl-1-propanols *via* the corresponding intermediates **91** and **92**, respectively (Scheme 43) [65,68].



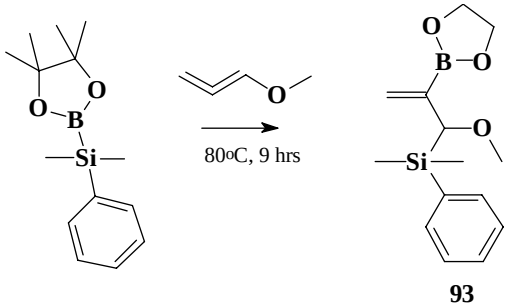

**Scheme 42**




**Scheme 43**

### *Reactions of borylsilane*

2-(Dimethylphenylsilanyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane regioselec-tively reacted with methoxypropadiene in the presence of palladium complexes in tetrahydrofuran to form in high yields 2-{1-[(dimethylphenylsilanyl)methoxy-methyl]-vinyl}-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane **49** having allylsilane moieties (Scheme 44) [69].



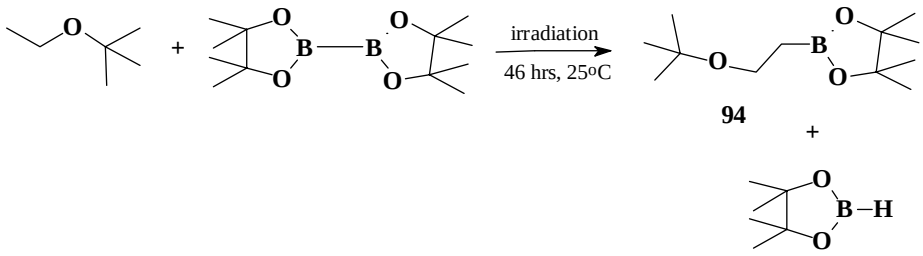

**Scheme 44**

### *Rhenium catalyzed borylation*

4,4,5,5,4',4',5',5'-Octamethyl-[2,2']bis[[1,3,2]dioxaborolanyl] reacted with 2-ethoxy-2-methyl-propane at 25°C in pentane in the presence of catalyst $[C_5Me_5Re(CO)_3]$ for 46 hrs under photochemical conditions to give 2-(2-*tert*-butoxy-ethyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane **70** (yield 26%), and also 4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (Scheme 45) [70].

### *Synthesis of glycosyl boranes and borinates*

Vasella et al. [71-73] showed that the insertion of glycosylidene carbenes into a boron-carbon bond of $BEt_3$ led to unstable glycosyl boranes, while insertion into a boron-carbon bond of boronic esters yielded stable anomeric glycosyl borinates. The glycosylidene carbenes were generated by thermolysis or photolysis of glycosylidene diazirines. Thus, 1-azi-2,3,4,6-tetra-O-benzyl-1-deoxy-D-glucopyranose **95** reacted

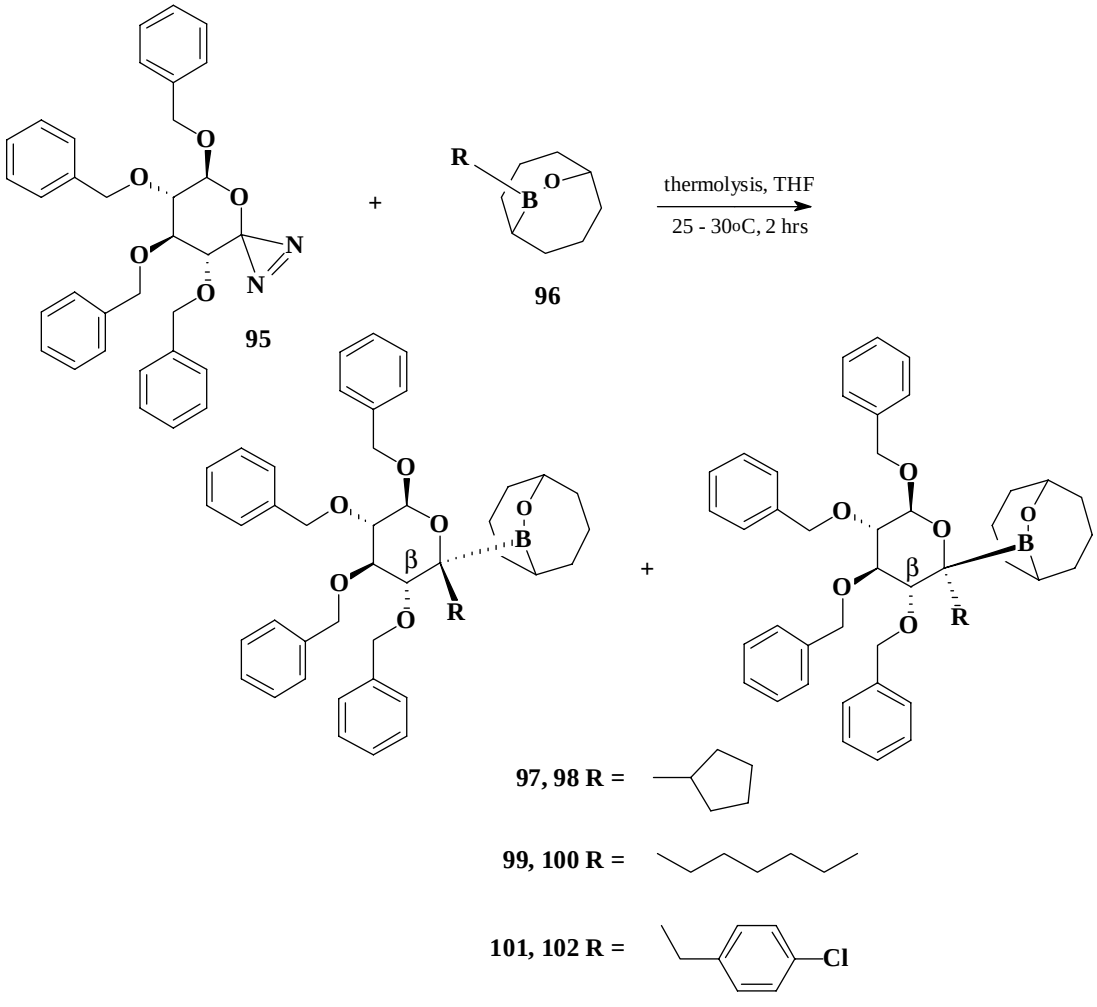



**Scheme 45**

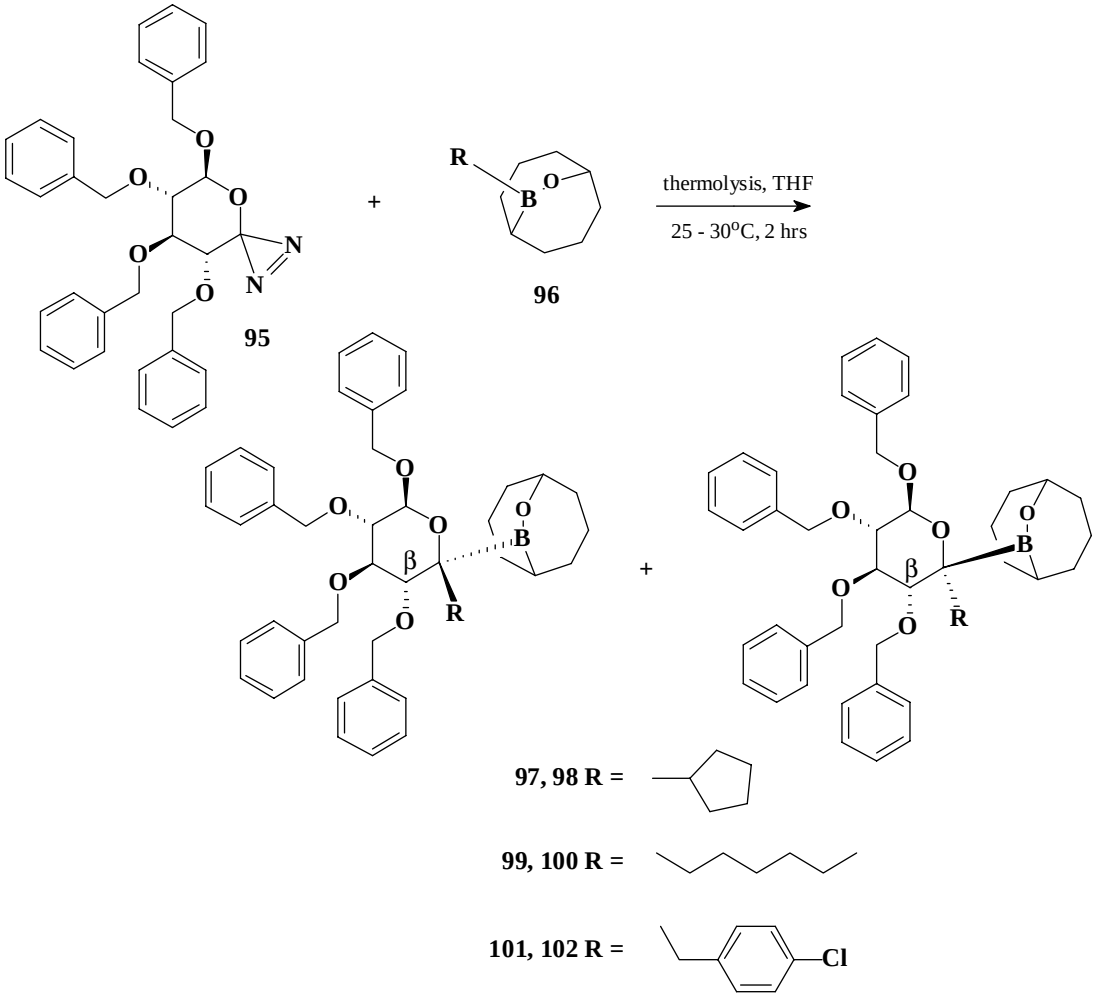
with 10-cyclopentyl-9-oxa-10-bora-bicyclo[3.3.2]-decane **96**, 10-hexyl-9-oxa-10-bora-bicyclo-[3.3.2]-decane and 10-[2-(4-chloro-phenyl)-ethyl]-9-oxa-10-bora-bicyclo[3.3.2]- decane at 25 - 30°C, in tetrahydrofuran for 2 hrs under thermolysis conditions to form two isomers of 10-(3,4,5-tris-benzyloxy-6-benzyloxymethyl-2-cyclopentyl-tetrahydro-pyran-2-yl)-9-oxa-10-bora-bicyclo[3.3.2]-decane **97** and **98**, 10-(3,4,5-tris-benzyloxy-6-benzyloxymethyl-2-hexyl-tetrahydro-pyran-2-yl)-9-oxa-10-bora-bicyclo [3.3.2]decane **99** and **100**, and 10-{3,4,5-tris-benzyloxy-6-benzyloxymethyl-2-[2-(4-chloro-phenyl)-ethyl]-tetrahydro-pyran-2-yl}-9-oxa-10-borabicyclo[3.3.2]decane **101** and **102**, respectively (Scheme 46).

1-Azi-2,3,4,6-tetra-O-benzyl-1-deoxy-D-glucopyranose reacted with triethylborane to form 3',7-anhydro-4,5,6,8-tetra-O-benzyl-3-C-ethyl-3-C-(ethylhydroxyboryl)-1,2,3-tri-deoxy-D-gluco-octitol **103** (Scheme 47) [72].

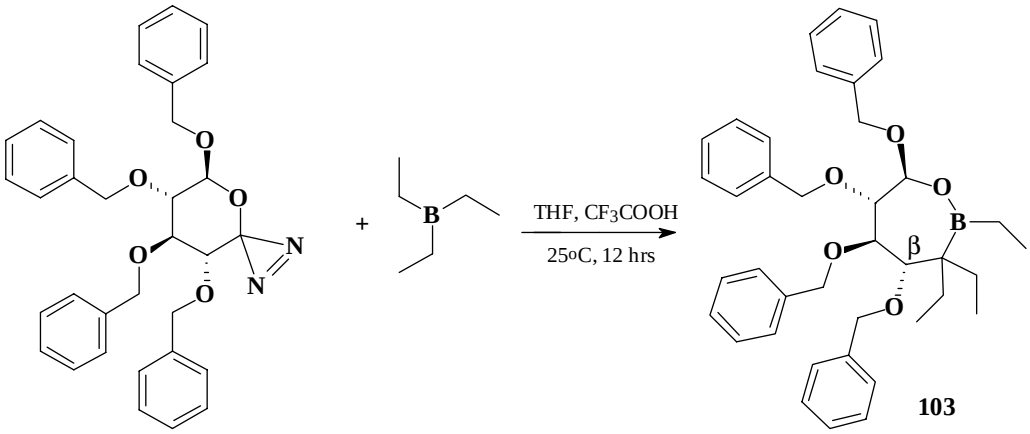
Reaction of 1-azi-2,3,4,6-tetra-O-benzyl-1-deoxy-




**Scheme 45**



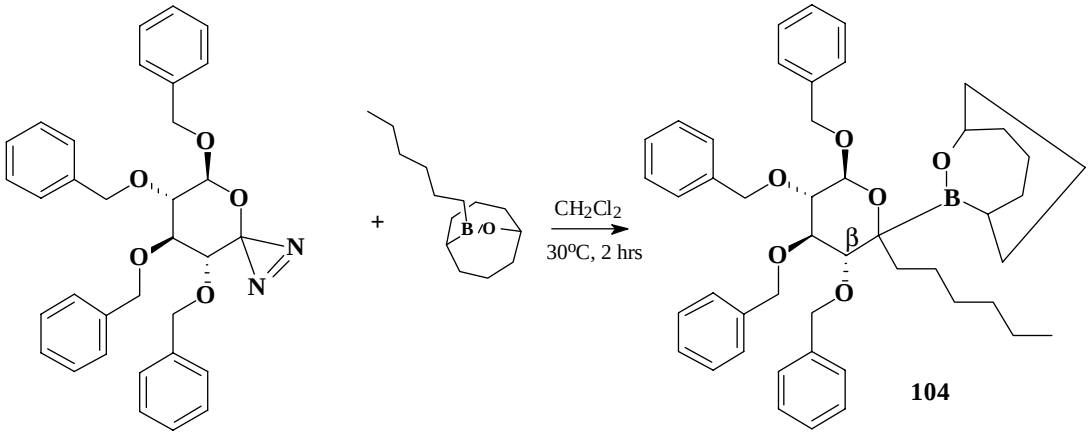

**Scheme 46**




**Scheme 47**

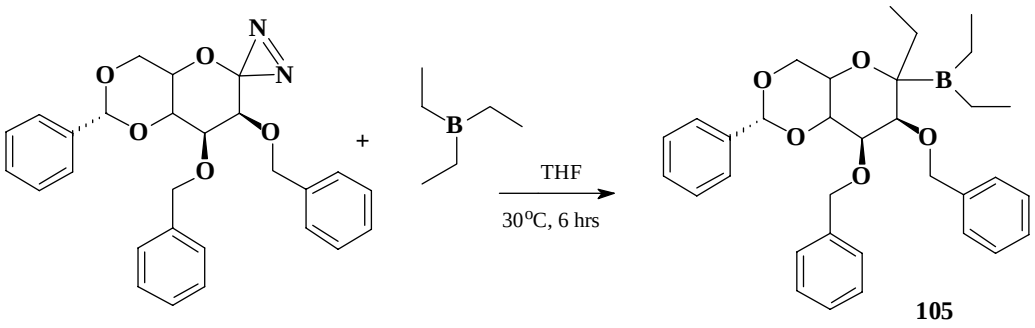
D-glucopyranose with 10-hexyl-9-oxa-10-borabicyclo[3.3.2]decane in dichloromethane at 30°C under thermolysis condition formed 10-(8,9,10,12-tetra-O-benzyl-1,2,3,4,5,6-hexadeoxy-D-gluco-dodec-7,11-pyranosyl)-9-oxa-10-borabicyclo[3.3.2]decane **104** (Scheme 48) [72].

In the reaction between 1,5-anhydro-1-azi-2,3-di-O-benzyl-4,6-O-benzylidene-D-mannitol and triethylborane in tetrahydrofuran (7,8-bis-benzyloxy-6-ethyl-2-phenyl-hexahydro-pyrano[3,2-d][1,3]dioxin-6-yl)-




**Scheme 48**

diethyl-borane **105** were obtained (Scheme 49) [72].




**Scheme 49**

In the reaction of 1,5-anhydro-1-azi-2,3-di-O-benzyl-4,6-O-benzylidene-D-mannitol and/or 10-hexyl-9-oxa-10-bora-bicyclo[3.3.2]decane and 10-[2-(4-chloro-phenyl)-ethyl]-9-oxa-10-bora-bicyclo[3.3.2]-decane in dichloromethane under thermolysis conditions two isomers of 10-(8,9-di-O-benzyl-10,12-O-benzylidene-1,2,3,4,5,6-hexadeoxy-β-D-manno-dodec-7-ulo-7,11-pyranosyl)-9-oxa-10-borabicyclo-[3.3.2] decane **106** and **107**, and 10-[4,5-di-O-benzyl-6,8-O-benzylidene-1-C-(4-chloro-phenyl)-1,2-dideoxy-β-D-manno-oct-3-ulo-3,7-pyranosyl]-9-oxa-10-borabicyclo- [3.3.2]decane **108** and **109** respectively were formed (Scheme 50) [72].

### *Oxidation of fluorovinylboranes*

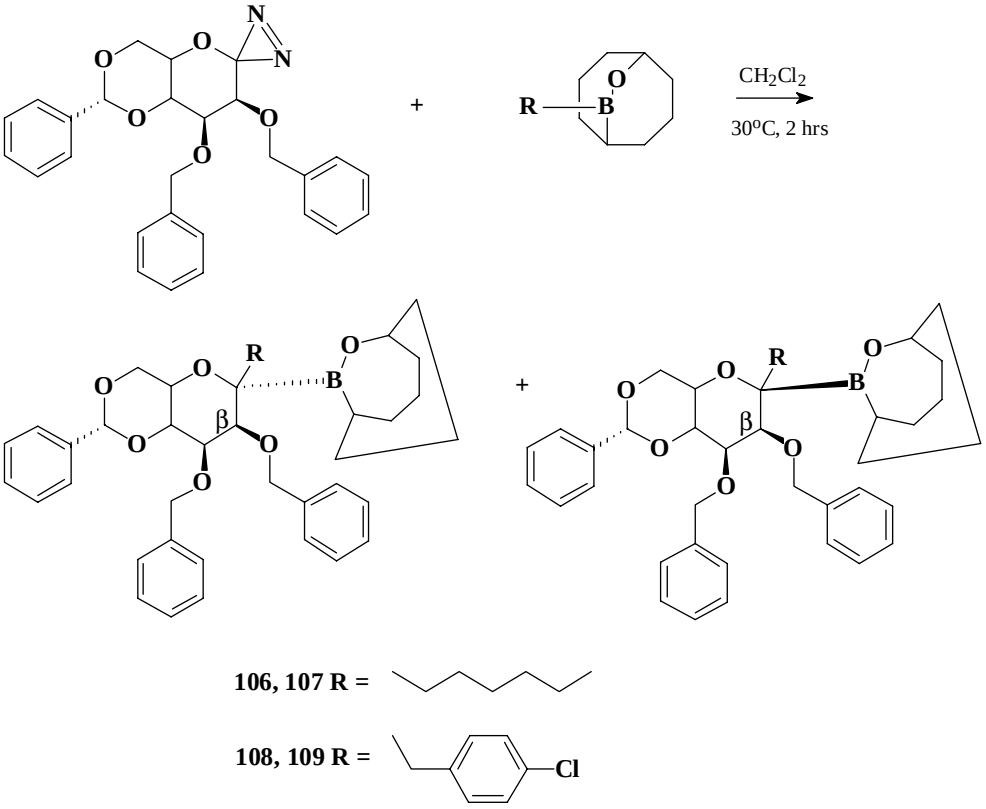
Ozonolysis of *bis*-trifluoromethyl-trifluorovinyl-borane with dimethylamine resulted in the unseparable two compounds of *bis*-trifluoromethyl-(2,3,3-trifluoro-oxiranyl)borane and β-oxyalkylborane **110** (Scheme 51) [74].

### *Asymmetric hydroboration*

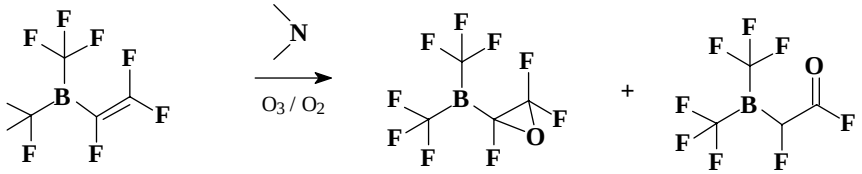
Purified (-)-diisopinocampheylborane is an effective reagent for the asymmetric hydroboration of acyclic olefins leading to enantiomerically pure products [75]. For example, treatment of 2,3-dihydrofuran with (-)-diisopinocampheylborane led to intermediates such as β-oxyalkylborane **111**, which was liberated with acetaldehydes to be (+)-a-pinene, and diethyl (*R*)-(3-tetrahydrofuranyl)borane **112**, which was converted in alkaline hydrogen peroxide to (-)-(*R*)-3-hydroxy-tetrahydrofuran **113** (Scheme 52). In a similar manner 3,4-dihydropyran was converted to (*R*)-3-hydroxytetrahydropyran *via* β-boryl alkyl ether **114** and **115**. Similar transformations yielded (1*R*,2*S*,4*R*)-1,4-epoxy-2-hydroxy-1,2,3,4-tetrahydro-naphtalene **118** *via* the corresponding β-oxyalkylboranes derivatives **116** and **117**.

Hydroboration of 2,3- and 3,4-dihydrofurans gave also β-oxyalkylborane **119** [2,6] (Scheme 53).

High diastereoselectivity was found for allylic tin compound **120** that was converted to diol **121** *via* β-

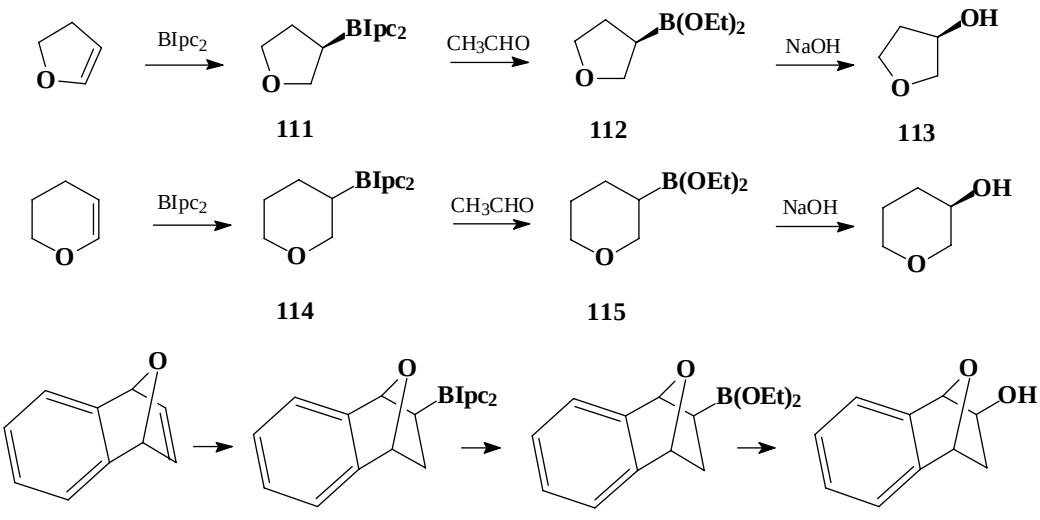



**Scheme 50**

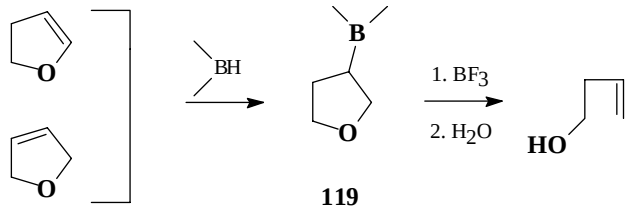



**110**

**Scheme 51**



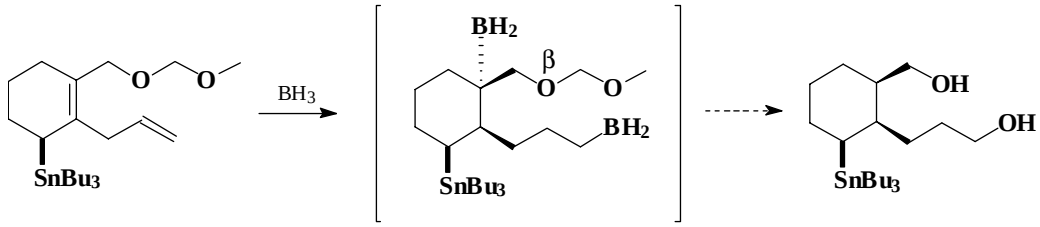

**Scheme 52**




**119**

**Scheme 53**

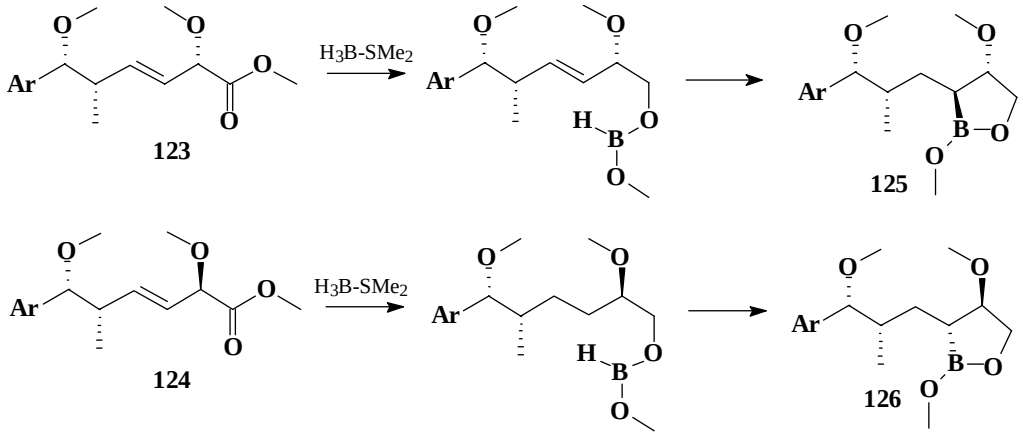
boryl alkyl ether **122** (Scheme 54) [50].




**120** **121** **122**

**Scheme 54**

α-Alkoxy carboxylic esters reacted with borane dimethyl sulfide to form five-membered heterocyclic compounds **125** and **126** (Scheme 55) [77]. α-Methoxy ester **123** was converted mainly to borolane **125**, and the diastereomeric α-methoxy ester **124** yielded mostly **126**.




**123** **124**

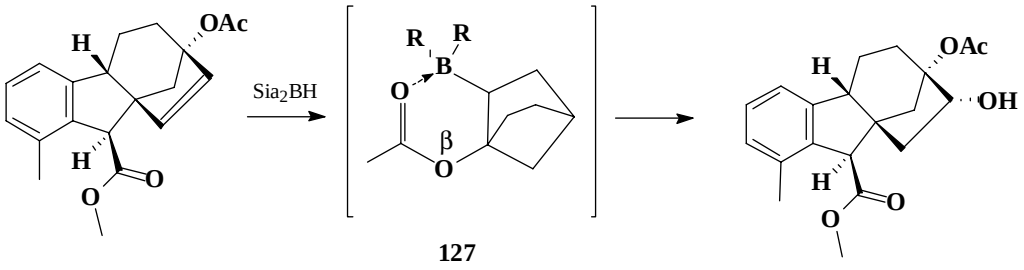
**Scheme 55**

### *Hydroboration of the functional derivatives of alkenes*

An hydroxy group in some cases may direct attack from the same side *via* intermediate β-oxyalkylborane **127** (Scheme 56) [78].

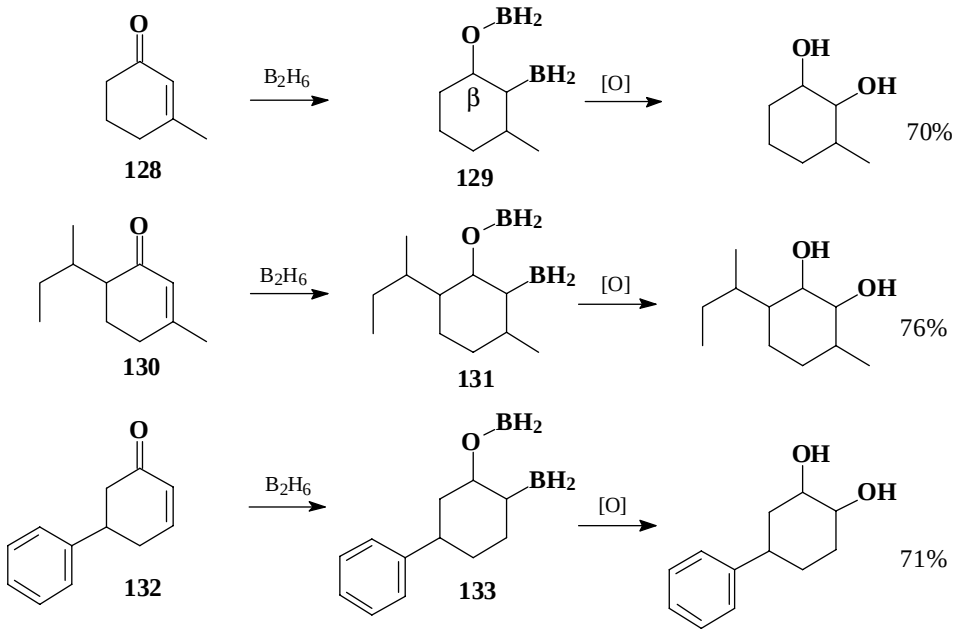
### *Hydroboration of cyclohexenone derivatives*

Hydroboration of cyclohexenone derivatives usually forms β-boryl alkyl ethers as intermediates. Thus, 3-methyl-2-cyclohexenone **128** formed 70% of diol *via* β-oxyalkylborane **129** (Scheme 57) [79-82]. Piperitone **130** formed a mixture of *trans*-diequatorial diols in equal quantities also *via* β-oxyalkylborane **131** [72]. The same reaction was found for 5-phenyl-2-cyclohexenone **132** which was transformed to the corresponding diols *via* β-boryl alkyl ether **133** [81].




**127**

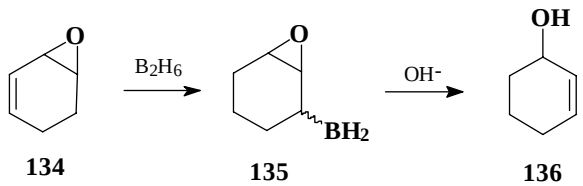
**Scheme 56**




**Scheme 57**

### *Hydroboration of unsaturated epoxides*

Zaidlewicz and Uzarewicz [83,84] found that cyclic unsaturated epoxides **134** were converted by the action of diborane to α,β-unsaturated alcohols **136** *via* β-oxyalkyl borane **135** (Scheme 58).




**134** **135** **136**

**Scheme 58**

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