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

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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 borene 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 allenic 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].

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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-carboxaldehyde I (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.

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(NR2)2 leads to α-carbonylalkylboranes with the common structure [(R2N)HalB−CH2−CONR2]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-diethylacetamide 5 (Scheme 3) [11]. Also chloro- \textit{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-diethylacetamide 6. Reactions of bora- \textit{bis}-(dimethylamino)-iodide and \textit{bis}-dimethylaminoboramidobromide with ketene lead to the corresponding compounds such as 2-(4-dimethylcarbamoylmethyl-2,4-diodo-1,1,3,3-tetramethyl-[1,3,2,4]diazadiboret-2-yl)-N,N-diethylacetamide 7 and 2-(2,4-dibromo-4-dimethylcarbamoylmethyl-1,1,3,3-tetramethyl[1,3,2,4]diazadiboret-2-yl)-N,N-diethylacetamide 8.
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1,3-Boryl shifts at the C–C=O skeleton

Paetzold and Biermann [12] studied the reactions of Hg(CH₂C=O–OMe)₂ with X(Me₂N)BBr which yielded either (2-oxoethyl)boranes as α-carbonylalkylboranes 9, 10 or 11 with the common structure X(Me₂N)B–CH₂–CO–OMe or (vinylxylo)boranes H₂C=C(OMe)₂–OBX(NMe). 1,3-Boryl shifts at the C–C=O skeleton was observed for X(Me₂N)B–CH₂–CO–OMe which isomerized to the corresponding compounds H₂C=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 (vinylxylo)boranes such as H₂C=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

Scheme 7

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diethyl butynedioate at -78°C to form tris-(2-dimethylamino-1,2-dicarbethoxyethylenyl)boration 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≡COOEt₂ to form ethyl-2-bromo-1-(diphenylboryl)-1-methylene-acetate 16 (Scheme 9).

Reactions of trifluorovinyl-trifluoromethyl-boron derivatives

Pawelke et al. [18,19] have shown that dimethylamino-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-trifluorovinylborane gave (bis-trifluoromethylboryl)-oxo-acetic acid 18. If the reaction was carried out in CHCl₃ which has not been carefully dried, the carboxyborane 19 precipitated from the solution. The initially colourless mother liquid, which contained the trifluorooxiranylborane 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 of amidoboranes

N-Trimethylsilylamides reacted with bromodi-
Scheme 10

Scheme 11

Scheme 12
organylboranes quantitatively to form the correspond-
ing amidoboranes. In certain cases these were in equi-
librium with the dimeric forms [22]. Among these
reactions in one case the $\alpha$-carbonylalkylboranes
was formed (Scheme 13). Thus, $N$-phenyl-$N$-trimethyl-
silyl-dichloroacetamide reacted with bromodimethyl-
borane to form 23.

Hydroboration of functional derivatives of
alkenes

Hydroboration of enamines with five-membered
rings gives a stable $\alpha$-carbonylalkylboranes 24 [23]

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$_2$O and stirred for 0.5 h with 0.5 M Ce (IV) in 0.1 M aq. HNO$_3$.

Synthesis of novel alkaloids

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

Hydroboration of methyl 2-acetamidoacrylate

The heterocyclic borate complexes were obtained
by hydroboration of methyl 2-acetamidoacrylate, affor-
ding N-alkyl as well as and/or acylalaninates [27].
The authors synthesized five heterocyclic oxytri-
organoborates which were identified as $\alpha$-carbonyl-
alkylboranes 27-31 (Scheme 16).

Hydroboration of unsaturated esters

Hydroboration of unsaturated esters was observed
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 which followed by the rapid transfer of boron from carbon to the neighboring oxygen (Scheme 17).

Reactions of eneydrazones

According to Sucrow et al. [29] the hydroboration of the eneydrazones and their derivatives leads to the stable boranes which are α-carbonylalkylboranes (Scheme 18). Hydroboration in different ethereal solvents was studied. Thus, the dimethyl-2-(N'-benzyldene-N-methyl-hydrazino)-but-2-enedi-
oate reacted with diborane in bis-(2-methoxy-ethyl)ether to form the dimethyl-2-(N'-benzylidene-N-methyl-hydrazino)-3-boranylic 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-(2E)-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-boranylic butyrate 35. The ethyl-(2E)-3-[2-(4-methoxy-benzylidene)-1-methylhydrazino]crotonate reacted with diborane in tetrahydrofuran to form the ethyl-2-boranylic-3-[N'(4-methoxy-benzyl)-N-methylhydrazino]butyrate 39. In another reactants it was found that the corresponding α-carbonylalkylboranes have been formed.
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 potassium t-butoxide in tetrahydrofuran lead to the corresponding α-carbonylalkyboranes (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-ethoxy styrene 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-deutero styrene via β-borylethers. In the presence of a basic (C₆H₅Li) or acid catalyst (BF₃), a trans-elimination with the formation of cis-β-deutero styrene 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-
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...
diborane. Both compounds gave $\beta$-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 $via$ $\beta$-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-5$\alpha$-cholest-2-ene, boron also predominantly attached to C2 as in 60, which was converted to 5$\alpha$-cholest-2-ene by treatment with NaOH [42] (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).

Allylboranones may react with compounds containing an activated double bond [44,45]. For example, heating triallylborne with vinyl n-butyl ether leads to penta-1,4-diene via β-boryl alkyl ether as intermediate 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 \( \beta \)-oxyalkylborane 63 [46] (Scheme 31).

\[
\text{(C}_3\text{H}_5)_3\text{B} + \text{CH}_3\text{O}_\text{H} \rightarrow \text{CH}_3\text{O}_\text{H} - \text{H}_3\text{C} + \text{H}_3\text{C} - \text{OH}\]

Scheme 31

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

\[
\text{OAc} \quad \text{OAc} \quad \text{OH} \quad \text{OH} \quad \text{OH}
\]

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 \( \beta \)-oxyalkylboranes 66, according to Scheme 33:

\[
\text{RO} \quad \text{R}_1 \quad \text{C} = \text{CH} \quad \text{R}_2 \quad \text{B}_{\text{ipc}2} \quad \text{RO} \quad \text{R}_1 \quad \text{C} = \text{CH} \quad \text{R}_2 \quad \text{B}_{\text{ipc}2} \quad \text{(H)RO} \quad \text{R}_1 \quad \text{C} = \text{CH} \quad \text{R}_2 \quad \text{B}_{\text{ipc}2}\]

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 \( \beta \)-oxyalkylboranes (compounds 72 and 74) (Scheme 34). Experimental details are shown in Table 2.
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).

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

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

Scheme 34

Table 2

Hydroboration of enol derivatives 67 - 71 and 73 with Ipc₂BH

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).

Scheme 36

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crystalline solid formed which was shown to be 1-t-butyl-1-bora-4-oxacyclohexane 80 (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-ethoxy styrene 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).
**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-dihydropyran [37].

![Scheme 40](image)

Hydroboration of 3-chromene 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](image)
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-dihydro-pyran 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].

Reactions of borylsilane

2-(Dimethylphenylsilanyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane regioselectively 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].

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 [C5Me5Re(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 BEt3 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
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 tetra- hydrofuran 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-bora-bicyclo[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-
D-glucopyranose with 10-hexyl-9-oxa-10-borabicyclo[3.3.2]decan 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]decan 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)-
Asymmetric hydroboration

Purified (-)-diisopinocamphylborane 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 (-)-diisopinocamphylborane 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-hydroxytetrahydrofuran 113 (Scheme 52). In a similar manner 3,4-dihydropyran was converted to (R)-3-hydroxytetrahydrofuran via β-boryl alkyl ether 114 and 115. Similar transformations yielded (1R,2S,4R)-1,4-epoxy-2-hydroxy-1,2,3,4-tetrahydro-naphtalene 118 via the corresponding β-oxyalkylborane 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

Scheme 51

Scheme 52

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

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.

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

**Hydroboration of unsaturated epoxides**

Zaidlewicz and Uzarewicz [83, 84] found that cyclic unsaturated epoxides \( \text{134} \) were converted by the action of diborane to \( \alpha,\beta \)-unsaturated alcohols \( \text{136} \) via \( \beta \)-oxyalkyl borane \( \text{135} \) (Scheme 58).

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