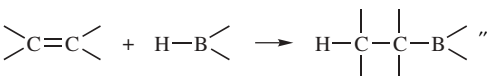
# HYDROBORATION

## 1. Introduction

Hydroboration is the addition of a boron–hydrogen bond across a double or triple carbon–carbon bond to give an organoborane:



(1)

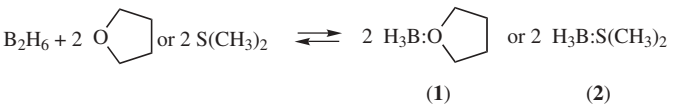
Other multiple bonds, eg, >C=O,–C≡N,–N=N–, also undergo the addition. However, those reactions not involving boron–carbon bond formation belong to reductions and are not described here. The boron atom in organoboranes can be replaced with other elements, usually with high stereoselectivity; many functional groups are tolerated. Consequently, organoboranes are among the most versatile synthetic intermediates, and their role in organic synthesis is constantly increasing.

One of the newer and more fruitful developments in this area is asymmetric hydroboration giving chiral organoboranes, which can be transformed into chiral carbon compounds of high optical purity. Other new directions focus on catalytic hydroboration, asymmetric allylboration, cross-coupling reactions, enolboration–aldolization, and applications in biomedical research. This article gives an account of the most important aspects of the hydroboration reaction and transformations of its products. For more detail, monographs and reviews are available (1–13).

## 2. The Hydroboration Reaction

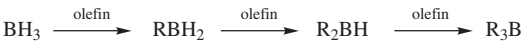
Diborane [19287-45-7], the first hydroborating agent studied, reacts sluggishly with olefins in the gas phase (14). In the presence of weak Lewis bases, eg, ethers and sulfides, it undergoes rapid reaction at room temperature or even $<0^{\circ}C$ (15). The catalytic effect of these compounds on the hydroboration reaction is attributed to the formation of monomeric borane complexes from the borane dimer, eg, borane–tetrahydrofuran (borane–THF, $BH_3$/THF) [14044-65-6] (**1**) or borane–dimethyl sulfide (BMS) [13292-87-0] (**2**) (16–17). Note that the borane–THF complex exists only in solution and has not been isolated. A wide variety of borane adducts with amines is available and certain of these are applicable for hydroboration (18–19).

Borane adducts with phosphines are still stronger and find other important applications (19).



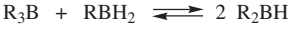

(**1**) (**2**) (2)

Mono-, di-, and trialkylboranes may be obtained from olefins and the trifunctional borane molecule. Simple unhindered alkenes yield trialkylboranes, and it is not possible to halt the reaction at the mono- or dialkylborane stage. With more hindered and trisubstituted alkenes the reaction can be controlled to stop at the dialkylborane stage.




(3)

Tetrasubstituted and some hindered trisubstituted alkenes react rapidly only to the monoalkylborane stage. Rarely, when the tetrasubstituted double bond is incorporated in a cyclic structure, does hydroboration fail under normal conditions (20). However, such double bonds may react under conditions of greater force (20–22). Generally, trialkylboranes are stable at normal temperatures, undergoing thermal dissociation at temperatures $>100^{\circ}C$ (23,24). In the presence of B–H bonds, trialkylboranes undergo a redistribution reaction (13,25).

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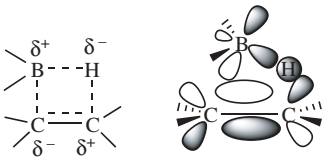



(a) (b)

**Fig. 1.** Four-center transition-state model of hydroboration.

Mono- and dialkylboranes usually exist as bridged dimers, sym-dialkyldiboranes and sym-tetraalkyldiboranes. Only very hindered alkylboranes, eg, bis(2,3-dimethyl-2-butyl)borane (26), are monomeric. However, for convenience of presentation, monomers are shown in the equations.

**2.1. Mechanism.** The characteristic features of hydroboration were originally accounted for in terms of a simple four-center transition-state model (Fig. 1**a**), serving as a useful working hypothesis (1, 27). Participation of the π orbital of boron removes symmetry restrictions for the $2\pi_s + 2\sigma_s$ addition (28). The electron donation from the π orbital of an olefin to the π orbital of boron and back-donation from the boron–hydrogen bond to the π* orbital would account for a concerted reaction involving the transition state shown in Figure 1**b**.

The gas-phase reaction of ethylene with the borane monomer proceeds with small, ∼8.4 kJ/mol, activation energy (29). Calculations suggest the formation of a loose π-complex reorganizing to a four-center transition state having little or no activation energy. The experimental results obtained for solution reactions establish the dissociation to the free monomer and its reaction with an olefin as a general mechanism for all hydroborations with borane–electron donor base complexes as well as dialkylborane dimers (17). Thus, the borane–dimethyl sulfide complex reacts with 2,3-dimethyl-2-butene in toluene by a two-step dissociation mechanism. The complex first liberates borane in an equilibrium and then the free borane reacts with the alkene to give 2,3-dimethyl-2-butylborane (**3**).

$$H_3B{:}S(CH_3)_2 \longrightarrow BH_3 + S(CH_3)_2$$

$$BH_3 + \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C{=}C\!<\!\begin{matrix} CH_3 \\ CH_3 \end{matrix} \longrightarrow H{-}\overset{\displaystyle CH_3\ CH_3}{\overset{|\quad\ |}{C{-}C}}{-}BH_2 \qquad (6)$$

(3)

Retardation of the reaction rate by the addition of dimethyl sulfide is in accord with this mechanism. Borane–amine complexes and the dibromoborane–dimethyl sulfide complex react similarly (30). Dimeric dialkylboranes initially dissociate (at rate $k_1$) to the monomers subsequently reacting with an olefin at rate $k_2$ (31). For highly reactive olefins $k_2 > k_{-1}$ (recombination) and the reaction is first order in the dimer. For slowly reacting olefins $k_{-1} > k_2$ and the reaction shows 0.5 order in the dimer.

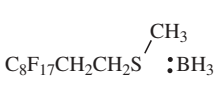
**2.2. Hydroborating Agents.** Mono- and dialkylboranes obtained by controlled hydroboration of hindered olefins and by other methods can serve as

valuable hydroborating agents for more reactive olefins. Heterosubstituted boranes are also available and used for this purpose. These borane derivatives show differences in reactivity and selectivity.

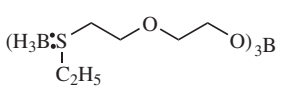
*Borane Complexes.* Borane solutions in THF are commercially available or can be prepared by absorbing gaseous diborane in THF. Diborane can be conveniently generated from the reaction of sodium borohydride with boron trifluoride etherate (3), and recently, improved procedures were reported (32). Several other methods for its preparation or generation and use *in situ* are known (for example Refs. (33–36)). Although $BH_3$/THF is a useful reagent (37), it must be stabilized with small amounts of sodium borohydride for longer storage at 0°C. The choice of solvent is limited to THF, and concentration does not exceed 2 *M* in $BH_3$.

Borane–dimethyl sulfide complex (**2**) is free of these inconveniences and is widely used in laboratory practice (37). The complex is a pure 1: 1 adduct, ~10 *M* in $BH_3$, stable indefinitely at room temperature and soluble in ethers, dichloromethane, benzene, and other solvents (38). Its disadvantage is the unpleasant smell of dimethyl sulfide, which is volatile and water insoluble. These inconveniences can be circumvented using borane complexes with less volatile sulfides such as 1,4-oxathiane (38,39) diisoamyl sulfide (40), bis-(sulfides) (41), 2-(perfluorooctyl)ethyl methyl sulfide (**4**) (42), and borate esters of hydroxydialkyl sulfides, eg, (**5**), which are completely miscible with water (43).

A wide variety of borane adducts with amines and phosphines is also available (19). Borane adducts with simple unhindered amines are strongly bonded and they require somewhat elevated temperature to achieve hydroboration. Borane–triethylamine complex is used when slow liberation of borane at elevated temperatures is advantageous, eg, in the cyclic hydroboration of trienes to avoid the formation of polymers (44). However, some of the organoboranes are labile and should be protected from such temperatures. Fortunately, recent studies revealed a range of tertiary amines and silylamines of intermediate steric requirements, strong enough to form a 1:1 adduct with borane, but weak enough to supply borane to an olefin at room temperature (18,43,45–48), eg, (**6**) (45), (**7**) (46), (**8**) (47), (**9**) (48). The possibility of recovering the carrier amine from the hydroboration or reduction products makes these new borane–amine adducts highly promising and environmentally benign reagents.




(**4**)

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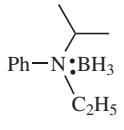


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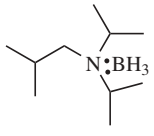


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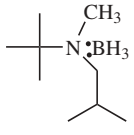


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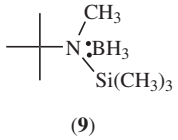
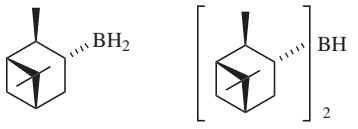


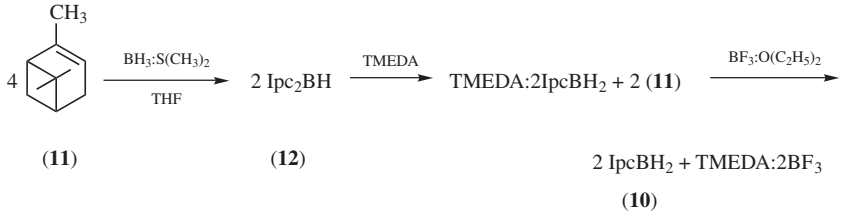

(**9**)

*Monosubstituted Boranes.* Only a few monoalkylboranes are directly available by hydroboration. 2,3-Dimethyl-2-butylborane [3688-24-2] (thexylborane, $ThxBH_2$) (**3**), easily prepared from 2,3-dimethyl-2-butene, is best studied (3,49). It should be used at 0°C, freshly prepared, to avoid isomerization at ambient temperatures. Its complex with *N,N*-diethylaniline is significantly more stable, fortunately retaining the reactivity (50). Thexylborane is a selective hydroborating agent useful for stepwise hydroboration of olefins, selective and cyclic hydroboration of dienes and functional derivatives (4,37,51).




(**10**) (**12**)

Monoisopinocampheylborane [64234-27-1], $IpcBH_2$ (**10**) is an important asymmetric hydroborating agent. It is prepared from α-pinene (**11**) [80-56-8] either directly or better by indirect methods. The product obtained directly by hydroboration of α-pinene is an equilibrium mixture. Optically pure monoisopinocampheylborane is best prepared from α-pinene via diisopinocampheylborane [1091-56-1], $Ipc_2BH$ (**12**) (4,52). Both enantiomers are readily available.




(**11**) (**12**) (**10**) (7)

The method does not require optically pure α-pinene because >99% enantiomeric excess (ee) is achieved by crystallization of the intermediate $TMEDA{:}2IpcBH_2$ adduct, where $TMEDA = (CH_3)_2NCH_2CH_2N(CH_3)_2$ (tetramethylethylenediamine). Other chiral monoalkylboranes derived from 2-alkyl- and 2-phenylapopinene are slightly more selective reagents as compared to monoisopinocampheyl-borane (4,53).

A number of less hindered monoalkylboranes is available by indirect methods, eg, by treatment of a thexylborane–amine complex with an olefin (54), the reduction of monohalogenoboranes or esters of boronic acids with metal hydrides (54), the redistribution of dialkylboranes with borane (52), or the displacement of an alkene from a dialkylborane by the addition of a tertiary amine (55). To avoid redistribution, monoalkylboranes are best used *in situ* or freshly prepared. However, they can be stored as monoalkylborohydrides or complexes with tertiary amines. The free monoalkylboranes can be liberated from these derivatives when required (54,56). Methylborane, a remarkably unhindered monoalkylborane, exhibits extraordinary hydroboration characteristics. It hydroborates hindered and even unhindered olefins to give sequentially alkylmethyl- and dialkylmethylboranes (57).

Monohalogenoboranes are conveniently prepared from BMS and boron trihalides ($BX_3$ where X = Cl, Br, I) by the redistribution reaction, eg, for monochloroborane–dimethyl sulfide [63348-81-2] (**13**) (58–60). Other methods are also known (61,62).

$$2\ BH_3{:}S(CH_3)_2 + BCl_3{:}S(CH_3)_2 \longrightarrow \underset{(\mathbf{13})}{3\ H_2BCl{:}S(CH_3)_2} \quad (8)$$

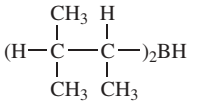
The products are liquids, soluble in various solvents and stable over prolonged periods. Monochloroborane is an equilibrium mixture containing small amounts of borane and dichloroborane complexes with dimethyl sulfide (58). Monobromoborane–dimethyl sulfide complex shows high purity (59, 60). Solutions of monochloroborane in THF and diethyl ether can also be prepared. Strong complexation renders hydroboration with monochloroborane in THF sluggish and inconvenient. Monochloroborane solutions in less complexing diethyl ether, an equilibrium with small amounts of borane and dichloroborane (62), show excellent reactivity (62,63), and the etherate [36594-41-9] may be represented as $H_2BCl{:}O(C_2H_5)_2$. 1,4-Dioxane forms stable and reactive adduct with monochloroborane, which is a superior reagent for the selective hydroboration of terminal alkenes (64).

*Disubstituted Boranes.* Even slight differences in steric or electronic effects of substituents may have an effect on the hydroboration reaction course. These effects are well demonstrated in disubstituted boranes, and consequently a range of synthetically useful reagents has been developed.

Primary dialkylboranes react readily with most alkenes at ambient temperatures and dihydroborate terminal acetylenes. However, these unhindered dialkylboranes exist in equilibrium with mono- and trialkylboranes and cannot be prepared in a state of high purity by the reaction of 2 equiv of an alkene with borane (13,25,26). Nevertheless, such mixtures can be used for hydroboration if the products are acceptable for further transformations (65). When pure primary dialkylboranes are required they are best prepared by the reduction of dialkylhalogenoboranes with metal hydrides (66). To avoid redistribution they must be used immediately or be stabilized as amine complexes or converted into dialkylborohydrides. Diethylborane is used for hydroboration transmetalation leading to organozinc compounds, highly versatile synthetic reagents (67,68).

In contrast to simple unhindered dialkylboranes, borinanes and borepanes do not redistribute readily. These boraheterocyclic reagents can be prepared by hydroboration of the corresponding dienes with borane, 9-borabicyclo[3.3.1]nonane, or monochloroborane, followed by thermal isomerization or reduction, respectively (69,70). The hydroboration of a simple hindered alkene, 2-methyl-2-butene, with borane–THF stops at the dialkylborane stage to give bis(3-methyl-2-butyl)borane [1069-54-1] (disiamylborane), $Sia_2BH$ (**14**) (71). The reagent is not stable over longer periods and it is recommended that it be used freshly prepared or stored at 0°C for only a few hours. It has high steric require-

ments, discriminates well between terminal and internal double bonds, and is often used in selective organic transformations (4,72).



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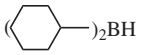
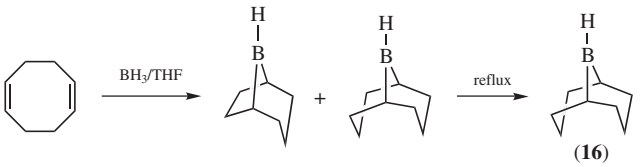


(**15**)

Dicyclohexylborane [1568-65-6], $Chx_2BH$ (**15**) is prepared in quantitative yield by the same method. It is a white solid, sparingly soluble in ether or THF. For most purposes, isolation is not necessary and it can be used as a slurry in these solvents. Its steric requirements are slightly lower as compared to $Sia_2BH$ (37,46,71–73). Much better thermal stability allows its use at higher temperatures.

9-Borabicyclo[3.3.1]nonane [280-64-8], 9-BBN (**16**) is the most versatile hydroborating agent among dialkylboranes. It is commercially available or can be conveniently prepared by the hydroboration of 1,5-cyclooctadiene with borane, followed by thermal isomerization of the mixture of isomeric bicyclic boranes initially formed (3,4,37,74).

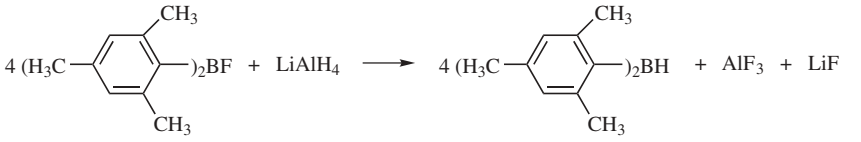


(**16**) (9)

Other procedures have also been reported (8,13,75). The properties and chemistry of 9-BBN have been reviewed (4,37,76). The reagent is a white crystalline solid, stable indefinitely at room temperature, soluble in hexane, carbon tetrachloride, benzene, THF, and diethyl ether. It exists as a dimer [21205-91-4] in the solid state and in non- or slightly complexing solvents, eg, hexane or diethyl ether. In THF and dimethyl sulfide the dimer partially dissociates to the solvent complexed monomer (31). The thermal stability of 9-BBN is remarkable. It distills at 195°C at 1.6 kPa (12 mm Hg) without dissociation to the monomer and can be heated for several hours to 200°C without loss of the hydride activity. The reactivity of 9-BBN toward alkenes of different structures varies over the range of $10^5$ and is somewhat lower compared to $Sia_2BH$ (77). The thermal stability of 9-BBN enables hydroborations at 60–80°C. At this temperature most alkenes react in 1 h. Even tetrasubstituted double bonds, which fail to react with $Sia_2BH$, are hydroborated with 9-BBN. It is less sterically demanding than $Sia_2BH$ and discriminates little between (*E*) and (*Z*) isomers (78). On the other hand, 9-BBN is quite sensitive to electronic factors. Thus, unique among dialkylboranes, it is more reactive toward alkenes than alkynes (79). The *B*-alkyl-9-BBN derivatives are exceptionally resistant to thermal isomerization. Consequently, isomerization sometimes encountered in the hydroboration of certain labile systems with borane can be circumvented by using 9-BBN (80). In many reactions of trialkylboranes, only one of the three groups is used. For

such reactions, eg, the Suzuki coupling (81), the use of *B*-R-9-BBN derivatives (R = alkyl, alkenyl, alkynyl, aryl) is advantageous, making possible full utilization of the R group.

The most hindered of all presently known hydroborating agents is possibly dimesitylborane, $Mes_2BH$, (**17**) an air-stable white solid, slightly soluble in THF, the best etheral solvent (37). It is commercially available or can be prepared according to the following reaction (82):



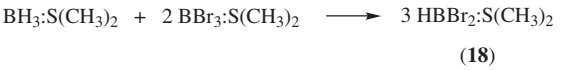

(10)

(**17**)

Its reactions with olefins, governed by steric rather than electronic factors, are very sluggish. Even simple 1-alkenes require 8 h at 25°C for complete reaction. In contrast, alkynes are hydroborated with great ease to alkenylboranes, high steric requirements of the reagent preventing dihydroboration (82).

Bis(pentafluorophenyl)borane provides acces to pentafluorophenyl organoboranes, cocatalysts for metallocene-based polymerization of olefins and for other synthetic applications (83,84). It is generated by the reduction of bis(pentafluorophenyl)chloroborane with dimethylchlorosilane (85). The reagent is a relatively strong Lewis acid and complexation with THF makes it unreactive for hydroboration. However, in a noncomplexing solvent, eg, benzene, it is highly reactive hydroborating simple alkenes and alkynes in minutes. 1-Alkynes react stepwise producing the corresponding (*E*)-aklenylboranes with 1 equiv of the reagent, and 1,1-diboryl derivatives with 2 equiv. The reaction with internal alkynes stops at the monohydroboration stage. Chemo- and regioselectivity of the reagent is comparable to 9-BBN (85).

Dihalogenoboranes are conveniently prepared by the redistribution of BDM with boron trihalide–dimethyl sulfide complexes (59,60), eg, for dibromoborane–dimethyl sulfide [55671-55-1] (**18**).




(11)

(**18**)

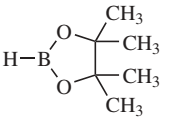
Dichloroborane complexes with diethyl ether and dimethyl sulfide are so strong that direct hydroboration does not proceed (86). The addition of a decomplexing agent, eg, boron trichloride, is necessary for hydroboration.

Dichloroborane-1,4-dioxane is readily prepared from dioxane–boron trichloride and sodium borohydride in the presence of catalytic amounts of tri- or tetraglyme. It is somewhat more reactive and shows remarkable selectivity toward two-substituted terminal olefins, such as 2-methyl-1-butene and β-pinene, when compared to simple terminal and hindered olefins (64). Alternatively, dichloroborane can be generated very conveniently by the reduction of boron trichloride with trimethyl- and triethylsilane or dimethylchlorosilane,

and used *in situ* in a noncomplexing solvent, eg, dichloromethane or without solvent, for the hydroboration of olefins and acetylenes (4,87).

Dibromoborane–dimethyl sulfide reacts directly with alkenes and alkynes to give the corresponding alkyl- and alkenyldibromoboranes (4,37,86,88). Dibromoborane differentiates between alkenes and alkynes hydroborating internal alkynes preferentially to terminal double and triple bonds (88). Unlike other substituted boranes it is more reactive toward 1,1-disubstituted than monosubstituted alkenes (89).

Simple dialkoxyboranes undergo readily disproportionation. However, certain 1,2-diols and phenols, such as pinacol (90), catechol (91) and 1,8-dihydroxynaphtalene (92), react with borane producing relatively stable 1,3,2-dioxaborolane and 1,3,2-dioxaborinane derivatives, 2,2,4,4-tetramethyl-1,3,2-dioxaborole (pinacolborane, PBH) (**19**), 1,3,2-benzodioxaborole (catecholborane, CBH) (**20**), and 1,3-dioxa-2-boraphenalene (**21**), respectively.



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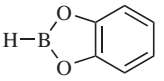

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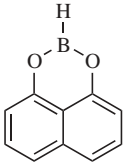


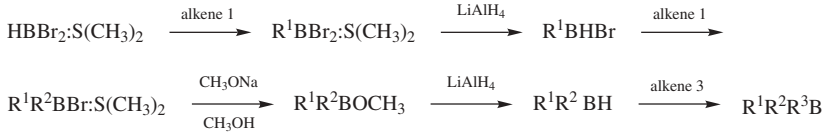
(**21**)

Pinacolborane and catecholborane are extensively used for catalytic hydroboration (see below). Catecholborane is a well-studied hydroborating and reducing agent (3,4,37). Both reagents are commercially available, and can be prepared by the reaction of pinacol and catechol with borane–THF or BMS. Compared with dialkylboranes their reactivity is decreased by the oxygen atoms. Consequently, hydroboration of alkenes and alkynes with catecholborane requires elevated temperatures, 100 and 70°C, respectively. Higher reactivity of alkynes allows selective hydroboration of triple bonds in the presence of double bonds (93). Catecholborane [274-07-7] and dialkoxyboranes hydroborate alkenes under mild conditions in the presence of lithium borohydride (94) and borane-*N,N*-diethylaniline adduct (95). Chiral 1,3,2-dioxaborole derivatives used for hydroboration of acetylenes, served as a chiral auxiliary in enantioselective cyclopropanation of the intermediate alkenylboronic ester (96).

Alkylchloro- and alkylbromoboranes are valuable reagents for the synthesis of di- and trialkylboranes having different alkyl groups. Thexylchloroborane (ThxBHCl) [75030-54-5] (**22**), is a very useful reagent.

It can be prepared by the reaction of monochloroborane with 2,3-dimethyl-2-butene (97), or from thexylborane and hydrogen chloride (98). It undergoes rapid redistribution in diethyl ether, but its complex with dimethyl sulfide is remarkably stable at room temperature. Thexylchloroborane reacts with unhindered alkenes, producing the corresponding alkylthexylboranes cleanly. With more hindered alkenes the reaction is slow and accompanied by redistribution, leading to side products (98). Thexylhaloboranes and thexylalkoxyboranes are the most selective hydroborating agents known (99, 100). Generally, the stepwise hydroboration of simple alkenes with monohaloboranes cannot be controlled

precisely, although in certain cases monoalkylchloroboranes can be obtained (63). The opposite approach, stepwise reduction, works better, providing access to di- and trialkylboranes with different alkyl groups (101).




(12)

Among chiral dialkylboranes, diisopinocampheylborane (**12**) is the most important and best-studied asymmetric hydroborating agent (4,102). It is obtained in both enantiomeric forms from naturally occurring α-pinene. Several procedures for its synthesis have been developed (103). The most convenient one, providing product of essentially 100% ee, involves the hydroboration of α-pinene with BMS in THF (104). Other chiral dialkylboranes derived from terpenes, eg, 2- and 3-carene (105), limonene (106), and longifolene (107), can also be prepared by controlled hydroboration. A more tedious approach to chiral dialkylboranes is based on the resolution of racemates. *trans*-2,5-Dimethylborolane, which shows excellent enantioselectivity in the hydroboration of all principal classes of prochiral alkenes except 1,1-disubstituted terminal double bonds, has been prepared by this method (108).

Hydroboration of alkenes and alkynes with certain higher boranes provides access to the corresponding alkyl and alkenyl derivatives. For example, olefin hydroboration with arachno-6,9-$S(CH_3)_2$-$B_{10}H_{12}$ produces *nido*-6-R-8-$S(CH_3)_2$-$B_{10}H_{11}$ which may be further transformed to *nido*-6-R-$B_{10}H_{13}$ (109). Aza-*nido*-dodecaboranes have also been used for the hydroboration of alkenes and alkynes (110). The addition proceeds via the 9-BH vertex.

**2.3. Solvents.** The hydroboration of olefins with diborane in the absence of solvent is sluggish requiring elevate temperatures and long reaction periods (14). In ethereal coordinating solvents, such as diethyl ether, THF, diglyme, the reaction is rapid and quantitative (1,3). Diborane dissolves also in chlorohydrocarbon solvents, such as dichloromethane, 1,2-dichloroethane, and 1,1,2,2-tetrchloroethane to form ∼0.5 *M* solutions in which it is in equilibrium with solvent–$BH_3$ adducts (8–15%). These solutions hydroborate olefins very rapidly even at −16°C (111). It is interesting to note that hydroboration with borane–amine complexes in dichloromethane is slowed down (46), presumably due to dipolar interreactions between the solvent and borane–amine adducts (111). Certain substituted borane derivatives may react without solvent, eg, dichloroborane with alkynes (4,87) or diethylborane with alkenes (112). Recently, the hydroboration of representative olefins under liquid–liquid phase-transfer catalysis conditions was shown to provide the corresponding alcohols in excellent yields (113).

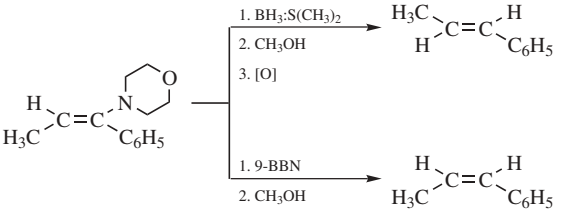
**2.4. Selectivity.** *Chemoselectivity.* Double and triple carbon–carbon bonds are more reactive toward borane and substituted boranes than most other functionalities. Consequently, many functional groups are tolerated in the hydroboration reaction (Table 1). Using a suitably chosen hydroborating agent, eg, dicyclohexylborane, even aldehydes and ketones may be unprotected

Table 1. **Reactivities of Representative Functional Groups Toward Selected Boranes**[a]

| Functional groups | $BH_3$/THF (**1**) | $ThxBH_2$ (**5**) | ThxBHCl (**22**) | $Sia_2BH$ (**14**) | 9-BBN (**16**) | CBH (**20**) |
|---|---|---|---|---|---|---|
| alkyne | f | f | f | f | f | m |
| alkene | f | f | f | f | f | s |
| aldehyde | f | f | f | f | f | f |
| ketone | f | f | f | f | f | f |
| carboxylic acid | f | vs | m[b] | n | vs | m |
| nitrile | f | vs | f | vs | vs | s |
| lactone | f | s | s | f | m | |
| carboxylic acid anhydride | f | f | f | vs | vs | m |
| epoxide | s | s | vs | s | vs | m |
| ester | s | vs | n | n | m | s |
| amide | s | s | vs | s | s | m |
| acid chloride | n | n | s | n | f | s |
| nitro | n | n | n | n | n | n |
| alkyl halide | n | n | | n | n | n |
| Reference | 114 | 115 | 116,117 | 118 | 119 | 120 |

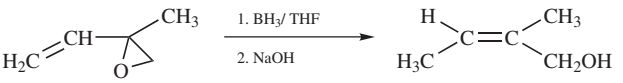
[a]f, fast; m, moderate; s, slow; vs, very slow; n, no reaction.
[b]Reduced to aldehyde.

(121). Hydroboration of allylic and vinylic derivatives leads to α-, β-, or γ-substituted organoboranes prone to eliminations or rearrangements (see for example Ref. 122). In some cases, such transformations may be synthetically useful. For example, the hydroboration of enamines, leading to the corresponding amino alcohols (123), also enables a simple conversion of aldehydes and ketones into (*Z*)- or (*E*)-alkenes (124).



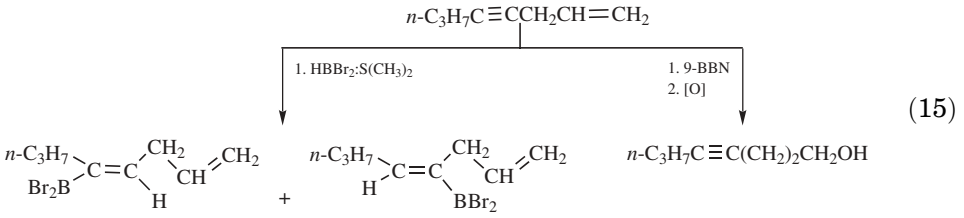

(13)

Conjugated ketones are either reduced to allylic alcohols (125) or undergo 1,4-addition to give enolboranes (126). Cisoid vinylic epoxides and aziridines give 1,4-addition products stereoselectively, probably via a six-membered transition state (127). However, sterically demanding hydroborating agents may react selectively with the double bond (128). The organoboranes initially formed from conjugated esters rearrange to the more stable borinates (129).



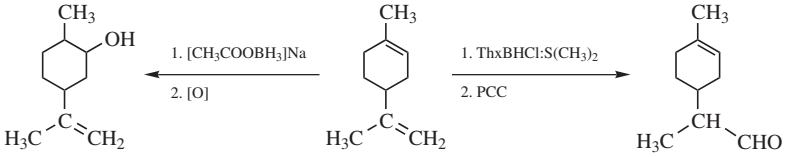

(14)

Many other examples illustrate the possibilities of chemoselective hydroborations (89,130,131). For example, selectivity between double and triple bonds has been shown (89).




(15)

Different reagents react with different bonds in the same molecule. Pyridinium chlorochromate is PCC.




(16)

*Regioselectivity.* Hydroboration of olefins and acetylenes involves predominant placement of the boron atom at the less hindered site of the multiple bond. The direction of addition is governed by polarization of the boron–hydrogen bond and by combination of steric and electronic effects of substituents at the multiple bond. Simple 1-alkenes react with borane to place 94% of the boron at the terminal position. For most purposes, this purity is sufficient. However, 6% of addition to the secondary position means that the organoborane may contain up to 18% of di-*n*-alkyl-*s*-alkylborane. This may complicate transformations involving selective migrations of alkyl groups. The selectivity of borane addition to disubstituted 1-alkenes and trisubstituted alkenes is higher, 98–99% of the boron going to the less substituted site. Internal disubstituted alkenes and alkynes are hydroborated with low selectivity even when the substituents differ in size, indicating low sensitivity of borane to steric effects. Most of these difficulties are circumvented by the application of substituted boranes showing high sensitivity to steric factors. Directive effects in the hydroboration of various alkenes and functional derivatives with representative hydroborating agents are shown in Figure 2. 9-Borabicyclo[3.3.1]nonane is probably the most often used substituted borane because of its excellent chemo- and regioselectivity and a broad range of reactivity toward structurally different olefins. Dibromoborane–dimethylsulfide and dimesitylborane show remarkable selectivity in the addition to internal alkynes (37,82,89).

Functional groups influence the regioselectivity of hydroboration by inductive, mesomeric, and steric effects, their magnitude depending on the proximity of the double bond and the functional group (122). An increased addition of boron to the secondary position (11–18%) is already observed for 3-butenyl derivatives (122). In allylic systems the electron-withdrawing substituents direct the boron atom to the β-position, the effect increasing with the increasing electronegativity

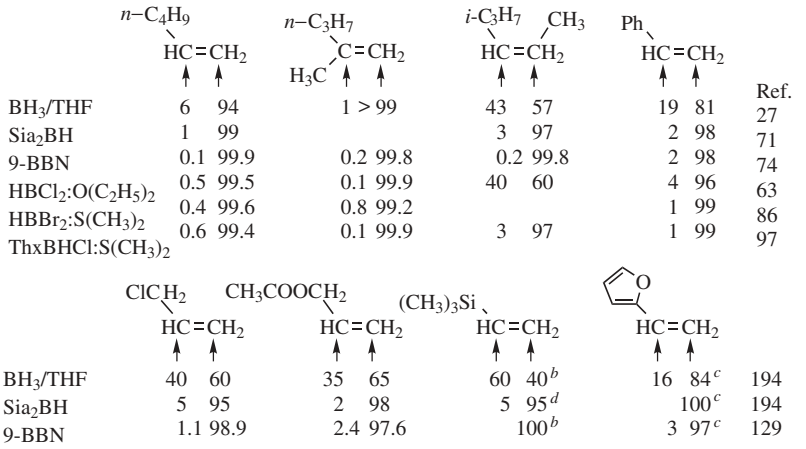



**Fig. 2.** Directive effects in the hydroboration of alkenes. [a]Numbers are percentages. [b]Ref. 27. [c]Ref. 130. [d]Ref. 131.

of the substituent. Vinylic substituents with a strong electron donating mesomeric effect, eg, OR and $NR_2$ direct boron to the β-position. The reverse is observed for electron accepting substituents such as silicon and boron. For example, *gem*-diboryl compounds are obtained by dihydroboration of terminal alkynes even with bulky dialkylboranes such as (**15**) (132). Directive effects in the hydroboration of functionalized alkynes are similar to the corresponding alkenes.

$$RC{\equiv}CH + 2\ Chx_2BH \longrightarrow RCH_2CH(BChx)_2 \quad (17)$$

(**15**)

$$R{-}C{\equiv}C{-}CH_2Cl \xrightarrow{Chx_2BH} \begin{matrix} R \\ H \end{matrix}\!\!>\!C{=}C\!<\!\begin{matrix} CH_2Cl \\ BChx_2 \end{matrix} \quad (18)$$

Generally, borane shows low regioselectivity in the addition to allylic and vinylic derivatives. Fortunately, sterically demanding substituted boranes can overcome the electronic effects of functional groups and react with high selectivity. The possibility of controlling the direction of addition is important for the preparation of isomerically pure substituted organoboranes (133) (Fig. 2).

Regioselectivity in the hydroboration of fluoroolefins depends on both electronic and steric interreactions with the reagent. Thus, tridecafluorooctene reacts with dicyclohexylborane to place the boron atom preferentially at the primary position, whereas the reaction with dichloroborane leads to the secondary product (134).

$$n\text{-}C_6F_{13}CH{=}CH_2 \xrightarrow[2.\ [O]]{1.\ HB<} n\text{-}C_6F_{13}CH_2CH_2OH + n\text{-}C_6F_{13}CHCHCH_3 \quad (19)$$

OH

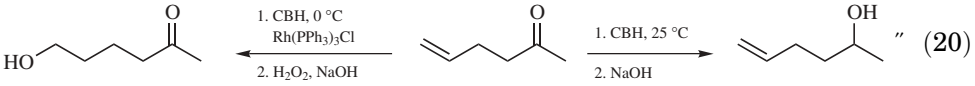
| | | |
|---|---|---|
| $Chx_2BH$ | 98 % | 2 % |
| $Cl_2BH$ | 5 % | 95 % |

When a methylene spacer is introduced between the perfluorohexyl group and the double bond a 1: 1 ratio of the alcohols is obtained from the hydroboration with dichloroborane. When two methylene spacers are introduced the ratio of the primary to secondary alcohol is 99: 1 for each of the reagents.

*Stereoselectivity.* The addition of a boron–hydrogen bond across the double bond proceeds cleanly in a cis fashion leading to simple diastereoselection for suitably substituted double bonds. Double bonds are approached by the hydroborating agent from the less sterically hindered face. The thermodynamically less stable addition products may result, as has been demonstrated for β-pinene (3) and camphene (135). Borane discriminates well between faces differing significantly in steric hindrance. When the difference is small, low selectivity results. Bulky, sterically demanding hydroborating agents, show higher stereoselectivity. Functional groups may influence the stereochemistry of addition. For example, unsaturated bicyclic amines by strong complexation of borane may have one face of the double bond more hindered, and the addition is directed to the opposite side. In contrast, weakly complexing groups like ethers may facilitate the addition from the same side.

Chemo-, regio-, and stereoselective hydroboration is extensively used in natural product synthesis. At present, it is often combined with metathesis as demonstrated in approaches to mono- and bifunctional dienes (136), cignatoxin (137), alkaloid (−)-swainsonine (138), isoquinoline derivatives (139), sporochnol (140), and polycyclic ethers corresponding to subunits of brevetoxins (141). Hydroboration and the Suzuki cross-coupling sequence is used in the approach to D-*erythro*- and L-*threo*-sphinganines (142), in a stereocontrolled total synthesis of (−)-ebelectone-A (143), and vinylphosphonates (144). Among other recent examples are syntheses of multifunctional indol alkaloids taxoids (147), prodrugs of betulenic acid derivatives (148), aspartyl protease inhibitors (149), derivatives of vitamin $D_3$ (150), and (*E*)-homoallylic alcohols from propargyl chloride and bromide (151,152). The synthesis of statine and norstatine involves the stereoselective reduction with borane catalyzed with oxazaborolidyne, followed by the transformation of a triple bond into a carboxylic group via hydroboration (153). Highly diastereoselective is the Markovnikov hydration of 3,4-dialkoxy-1-alkenes and 4,5-dialkoxy-2-alkenes (154). Many other examples are described in recent monographs and review articles (3,4,6,7,11,155).

**2.5. Catalytic Hydroboration.** Hydroboration of alkenes with relatively stable dialkoxyboranes, eg, catecholborane (CBH) at room temperature is sluggish. The reaction rate is dramatically increased in the presence of a catalytic amount Wilkinson's catalyst. Moreover, the catalyzed and uncatalyzed reactions of an unsaturated ketone show opposite chemoselectivities (156).



(20)

This result prompted intensive studies on the catalytic hydroboration of alkenes and alkynes that have been reviewed (157,158).

Catecholborane and pinacolborane are the reagents most often used. Other compounds, such as 1,3-dioxa-2-boraphenalene (92), 4,4,6-trimethyl-1,3,2-dioxa-

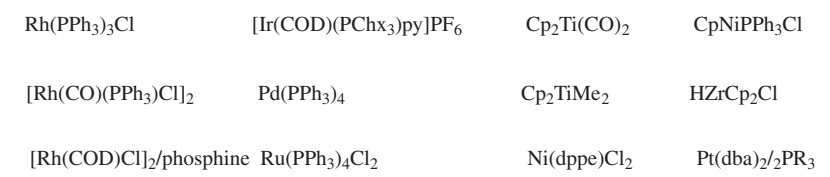



**Fig. 3.** Selected catalysts for catalytic hydroboration.

borane (156), 5-phenyl-3,4-dimethyl-1,3,2-oxazaborinane (159), and borazine (160), have also been tried. Titanium-catalyzed hydroboration of terminal olefins and unconjugated dienes with decaborane results in the exclusive, high-yield formation of monosubstituted alkyldecaborane derivatives 6-R-$B_{10}H_{13}$ and linked cage products, respectively, used as single-source precursors to boron carbide (161). The catalysts are complexes of rhodium, iridium, palladium, platinum, ruthenium, titanium, zirconium, and nickel (Fig. 3).

Recently, Rh(I) complexes with rigid phosphines (BABAR-phos) proved to be highly stable active catalyst precursors for hydroborations. The BABAR-phos compounds show very high thermal and chemical stability (162–164). The catalytic activity of simple metal salts, eg, $RhCl_3$, $SmI_3$, $Sm(Oi\text{-}C_3H_7)_3$ has also been observed (165). However, isomerization of organoborane products in the rhutenium catalyzed reaction may be a complicating factor.

The reaction mechanism of the catalyzed hydroboration depends on the catalyst and other factors, and is different from the uncatalyzed reaction (166,167). The proposed mechanism for the hydroboration of olefins with catecholborane in the presence of Wilkinson's catalyst involves an oxidative addition of the reagent to the metal center, followed by an olefin coordination and insertion to the metal–hydrogen bond, and the reductive elimination completes the process. Catalytic hydroborations are carried in common solvents ($Et_2O$, THF, $C_6H_6$, $CH_2Cl_2$, or better $ClCH_2CH_2Cl$). However, the carbon tetrachloride addition instead of catalytic hydroboration with pinacolborane was observed (168). Recently, ionic liquids (169), fluorinated solvents (170), and supercritical carbon dioxide (171,172) have also been used. Catalyst immobilization on a polymeric support makes possible the reaction in polar protic solvents (173).

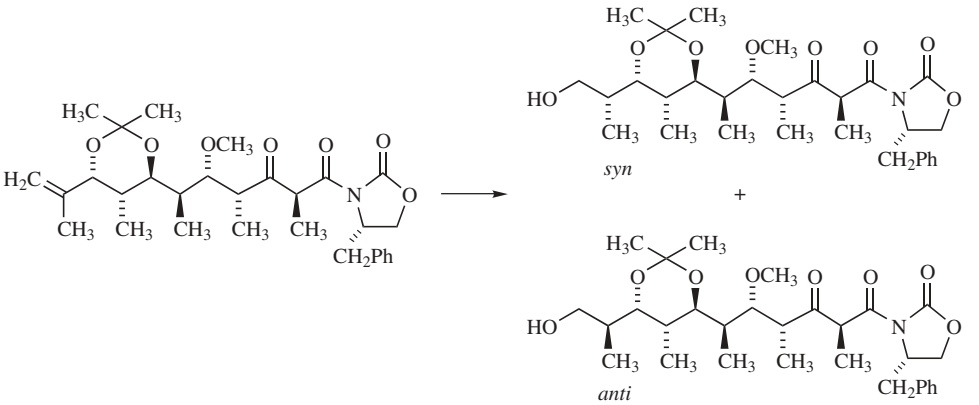
Catalytic hydroboration with catecholborane and pinacolborane provides a simple access to alkyl and alkenyl boronic acids, which are important reagents for the Suzuki cross-coupling reaction. The reaction depends significantly on the catalyst and even tetrasubstituted double bonds can be hydroborated in the presence of certain catalysts, eg, $[Rh(cod)(dppb)]BF_4$ (174). Generally, the catalyzed and uncatalyzed hydroboration of simple alkenes and alkynes involves the anti-Markovnikov cis addition (156,158,175). However, arylalkenes often react to give the Markovnikov product, and trans addition in the rhodium- and iridium-catalyzed hydroboration of 1-alkynes has been observed (176) (Fig. 4).

Regio- and stereoselectivities of the catalyzed and uncatalyzed hydroboration of functional derivatives of alkenes often differ for allylic and homoallylic

| | RCH=CH$_2$ | | PhCH=CH$_2$ | | RC≡CH | | PhCH≡CH | | |
|---|---|---|---|---|---|---|---|---|---|
| | R | | | | R | | | | Ref. |
| (**20**), uncatalyzed, THF | *n*-$C_8H_{17}$ | 2 98 | 8 | 92 | *n*-$C_4H_9$ | 6 94(*E*) | 9 | 91(*E*) | 37 |
| (**20**), $Rh(PPh_3)_3Cl$, THF | *n*-$C_4H_9$ | 1 99 | >99 | 1 | | | 41 | 59 | 167,179 |
| (**20**), $[Rh(COD)Cl]_2$, $4P(i\text{-}C_3H_7)_3$, $(C_2H_5)_3N$, cyclohexane | | | | | *n*-$C_8H_{17}$ | 99(*Z*) 1(*E*) | | 99(*Z*) 1(*E*) | 176 |
| (**19**), uncatalyzed, $CH_2Cl_2$ | | | | | *n*-$C_6H_{13}$ | 1 98(*E*) 1(*Z*) | | 96(*E*) 4(*Z*) | 177 |
| (**19**), $Rh(PPh_3)_3Cl$, $CH_2Cl_2$ | *n*-$C_6H_{13}$ | 99 | 35 | 65 | *n*-$C_6H_{13}$ | 29 71(*E*) | 52 | 48(*E*) | 175 |
| (**19**), $Rh(CO)(PPh_3)_2Cl$, $CH_2Cl_2$ | | | 1 | 99 | *n*-$C_6H_{13}$ | 1 99(*E*) | 2 | 98(*E*) | 175 |

**Fig. 4.** Directive effects in catalytic hydroboration of selected alkenes and alkynes.

derivatives, such as alcohols and amines (177,178), as illustrated in the synthesis of an antibiotic lonomycine A fragment (179).




(**20**), $Rh(PPh_3)_3Cl$ 2,3 *syn/anti* 94 : 6
9-BBN 2,3 *syn/anti* 8 : 92 (21)

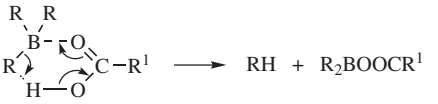
Many other examples are described in the reviews (eg, Ref. 158). Conjugated dienes and enynes react with catecholborane producing either 1,2- or 1,4-addition products, depending on the catalyst. In contrast to the uncatalyzed reaction isoprene shows higher reactivity than 1-decene in the competitive hydroboration with catecholborane catalyzed with $Ni(dppe)Cl_2$ (180). Vinylacetylene can be transformed into labile *B*-1,3-butadienylcatecholborane useful for the Diels-Alder reaction (181). Monohydroboration of terminal allenes with pinacolborane can be controlled by choosing an appropriate phosphine ligand in a $Pt(dba)_2/2PR_3$ catalyst (182). Clearly, the catalytic hydroboration is complementary to the uncatalyzed reaction, expanding the scope of the hydroboration reaction.

## 3. Reactions of Organoboranes

Organoboranes available by hydroboration and also by other methods are versatile synthetic intermediates. The organic groups attached to boron can be transferred, usually with high stereoselectivity, to hydrogen, oxygen, nitrogen, halogens, sulfur, selenium, metal atoms, and carbon. Consequently, carbon–heteroatom and carbon–carbon bonds can be constructed. The combination of hydroboration and functionalization corresponds overall to anti-Markovnikov addition of the elements of HX to a double bond.

$$RCH{=}CH_2 \xrightarrow{HB\diagup\diagdown} RCH_2CH_2B\diagup\diagdown \longrightarrow RCH_2CH_2X \qquad (22)$$

**3.1. Replacement of Boron by Hydrogen or a Heteroatom.** *Protonolysis.* Simple trialkylboranes are resistant to protonolysis by alcohols, water, aqueous bases, and mineral acids. In contrast, carboxylic acids react readily with trialkylboranes, removing the first alkyl group at room temperature and the third one at elevated temperatures. Acetic and propionic acids are most often used. The reaction proceeds with retention of configuration of the alkyl group via a cyclic, six-membered transition state (183).



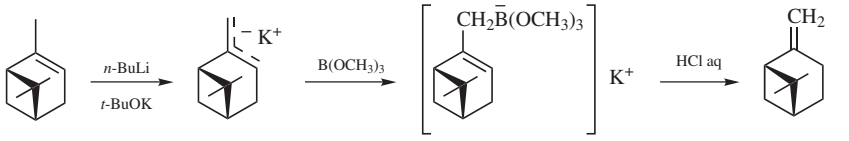
$$\longrightarrow RH + R_2BOOCR^1 \qquad (23)$$

Primary alkyl groups are more reactive than secondary and tertiary. Pivalic acid accelerates the rate of protonolysis of trialkylboranes with water and alcohols (184). The reaction can be controlled to give excellent yields of dialkylborinic acids and esters and has been applied for the protection of hydroxyl groups in sugars (185).

$$R_3B + HOR^1 \xrightarrow{(CH_3)_3CCOOH} R_2BOR^1 + RH \qquad (24)$$

Allylic, alkenyl, and alkynyl groups are more readily protonolyzed than alkyl groups. It is often sufficient to use water or methanol. For example, allylic organoboranes are hydrolyzed with water at room temperature, the reaction proceeding with the allylic rearrangement (186).

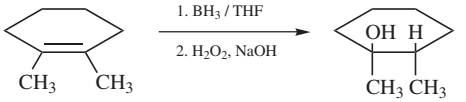
The reaction was used in the final step of a convenient contrathermodynamic isomerization of olefins by a metalation–transmetalation–hydrolysis sequence. (+)-α-Pinene, (+)-2-carene, and (−)-α-thujene, were transformed into optically pure (+)-β-pinene (187), (+)-3(10)-carene, and (+)-sabinene (188), respectively, and the sequence for the synthesis of (+)-β-pinene is shown below.




(25)

In general, hydroboration–protonolysis is a stereoselective noncatalytic method of cis-hydrogenation providing access to alkanes, alkenes, dienes, and enynes from olefinic and acetylenic precursors (189). Procedures for the protonolysis of alkenylboranes containing acid-sensitive functional groups under neutral or basic conditions have been developed (190).

*Oxidation.* The oxidation reactions of organoboranes have been reviewed (6,7,11). Hydroboration–oxidation is an anti-Markovnikov cis-hydration of carbon–carbon multiple bonds. The standard oxidation procedure employs 30% hydrogen peroxide and 3 *M* sodium hydroxide. The reaction proceeds with retention of configuration (191).




(26)

Sodium perborate can safely substitute for hydrogen peroxide (192). A variety of common organic functional groups, such as double or triple bonds, halogens, ethers, esters, ketones, nitriles, are unaffected under the reaction conditions. However, certain functionalized organoboranes and functional groups present in the target molecules, eg, vicinal halo- and alkoxyorganoboranes or aldehydes, are sensitive to the alkaline medium. In such cases, buffering (193), simultaneous addition of base and peroxide (194), or reagents other than hydrogen peroxide, eg, trimethylamine *N*-oxide (195–197) or peracids (198), are used. The reactivity order of alkyl- and alkenylboranes toward trimethylamine *N*-oxide decreases in the following order: tertiary > secondary > primary alkyl > alkenyl groups (195). Alkynyl groups are not oxidized by the reagent (199). Organoboranes containing different groups can be selectively oxidized (197).

Usually, organoboranes are sensitive to oxygen. Simple trialkylboranes are spontaneously flammable in contact with air. Nevertheless, under carefully controlled conditions the reaction of organoboranes with oxygen can be used for the preparation of alcohols or alkyl hydroperoxides (200). Free-radical oxidations of *B*-alkylcatecholboranes with 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) occur under mild conditions and do not require the use of base (201). Trialkylboranes are not oxidized under these conditions. Despite radical intermediates a fair level of stereoselectivity has been reached in the reported examples. Aldehydes are produced by oxidation of primary alkylboranes with pyridinium chlorochromate (202). Chromic acid at pH <3 transforms secondary alkyl and cycloalkylboranes into ketones; pyridinium chlorochromate can also be used (203). A convenient procedure for the direct conversion of terminal alkenes into carboxylic acids employs hydroboration with dibromoborane–dimethyl sulfide and oxidation of the intermediate alkyldibromoborane with chromium trioxide in 90% aqueous acetic acid (204).

*Halogenolysis.* Alkylboranes are readily converted into the corresponding alkyl chlorides by a free-radical reaction with nitrogen trichloride (205). The reactivity order of alkyl groups is tertiary > secondary > primary, reflecting

the stability of free radicals. The stereochemical integrity of alkyl groups is not retained, eg, tri(*exo*-2-norbornyl)borane gives 70% *exo*- and 30% *endo*-2-nobornyl chloride. Only two groups of the trialkylborane are readily accommodated in the reaction. Other reagents, such as copper(II) chloride, iron(III) chloride and dichloramine T can also be used (206). Although only one group is utilized by the latter reagent, its stereoselectivity is excellent.

The reactions of trialkylboranes with bromine and iodine are greatly accelerated by bases. The use of sodium methoxide in methanol gives good yields of the corresponding alkyl bromides or iodides. All three primary alkyl groups are utilized in the bromination reaction and only two in the iodination reaction. Secondary groups are less reactive and the yields are lower. Both Br and I reactions proceed with predominant inversion of configuration; thus, for example, tri(*exo*-2-norbornyl)borane yields >75% endo product (207). In contrast, the dark reaction of bromine with tri(*exo*-2-norbornyl)borane yields cleanly *exo*-2-norbornyl bromide (208). Consequently, the dark bromination complements the base-induced bromination.

The iodination reaction can also be conducted with iodine monochloride in the presence of sodium acetate (209) or iodine in the presence of water or methanolic sodium acetate (207,210). Under these mild conditions functionalized alkenes can be transformed into the corresponding iodides. Application of *B*-alkyl-9-BBN derivatives in the chlorination and dark bromination reactions allows better utilization of alkyl groups (211). An indirect stereoselective procedure for the conversion of alkynes into (*E*)-1-halo-1-alkenes is based on the mercuration reaction of boronic acids followed by *in situ* bromination or iodination of the intermediate mercuric salts (212). Both (*E*)- and (*Z*)-1-halo-1-alkenes can be prepared by hydroboration of 1-alkynes or 1-halo-1-alkynes followed by halogenation of the intermediate boronic esters (213). Differences in the addition–elimination mechanisms operating in these reactions lead to the opposite configurations of iodides as compared to bromides and chlorides. An alternative synthesis of (*Z*)-1-halo-1-alkenes involves hydroboration of 1-halo-1-alkynes, followed by protonolysis (214). Disubstituted (*E*)- and (*Z*)-alkenyl bromides can be prepared from (*E*)- and (*Z*)-alkenyl boronic esters, respectively, by treatment with bromine followed by base (215).

*Replacement of Boron by Nitrogen.* Organoboranes react with amino compounds containing good leaving groups, eg, chloramine, hydroxylamine-*O*-sulfonic acid, or mesitylsulfonylhydroxylamine to give primary amines (216). The replacement proceeds with retention of configuration (217). The yields are moderate because only one or two alkyl groups are utilized. However, this inconvenience can be circumvented by the use of alkyldimethylboranes (218).

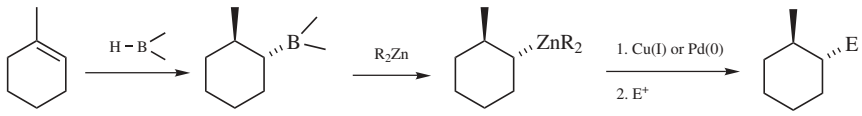
Secondary amines are obtained in excellent yields by the reaction of alkyldichloroboranes with alkyl-, cycloalkyl-, or aryl azides (216,219). Reagents containing two leaving groups on nitrogen, can also be used for the synthesis of secondary amines (220). Tertiary amines and other nitrogen compounds such as *N*-substituted aziridines (219), alkyldimethylamines (221), alkyl azides (222), and *N*-alkylsulfonylamides (223) can be prepared by the reaction of alkylboranes with β-iodoalkyl azides, *N*-chlorodimethylamine in the presence of galvinoxyl, sodium azide, and chloramine T, respectively.

*Replacement of Boron by Sulfur and Selenium.* Trialkylboranes are cleaved by dialkyl- and diaryldisulfides in an air-catalyzed radical reaction producing mixed thioethers (224).

(27)

Alkylthiocyanates and alkylselenocyanates are obtained by treatment of trialkylboranes with potassium thiocycanate (225) and sodium selenoisocyanate (226), in the presence of iron(III) compounds, respectively. Unsymmetrical trialkylboranes react preferentially at the more highly branched alkyl group. Alkenylphenyl selenides are obtained by the reaction of alkenylboronic acids with phenylselenyl bromide (227).

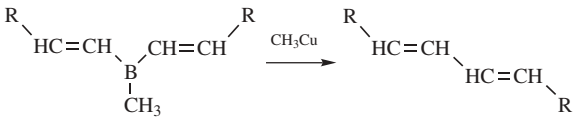
*Replacement of Boron by Metal.* The scope of organoboranes has been considerably enhanced by a boron–zinc exchange reaction providing organozincs that react with a broad range of electrophiles. Generally, the overall transformations proceed with retention of configuration leading to derivatives of tin, sulfur, bromine, phosphoranes, and to carbon–carbon bond formation (228–231).



(28)

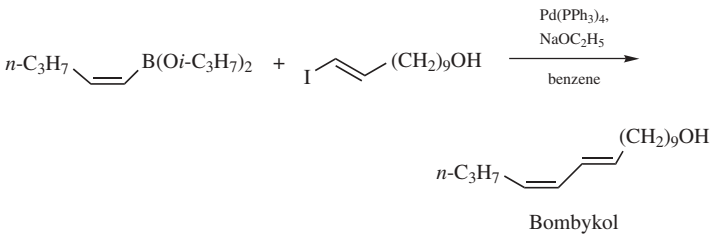
Mercury(II) salts react with alkyl-, alkenyl-, and arylboranes to yield organomercurials, which are useful synthetic intermediates (232). For example, dialkylmercury and alkylmercury acetates can be prepared from primary trialkylboranes by treatment with mercury(II) chloride in the presence of sodium hydroxide or with mercury(II) acetate in tetrahydrofuran (3). Mercuration of *s*-alkylboranes is sluggish and requires prolonged heating. Alkenyl groups are transferred from boron to mercury with retention of configuration (212).

**3.2. Carbon–Carbon Bond Formation.** *Coupling of Organic Groups Attached to Boron.* Treatment of alkylboranes with alkaline silver nitrate solution results in coupling of the alkyl groups. Yields obtained for primary and secondary groups are in the range of 60–80% and 35–50%, respectively. Unsymmetrical products can be obtained by the use of an excess of one substrate. The reaction probably proceeds through the formation of unstable silver alkyl intermediates breaking down into silver and free radicals undergoing dimerization (3). Methylcopper couples dialkenylalkylboranes (233). Alkenyldialkylboranes are also coupled with complete retention of configuration by copper(I) compounds (234).



(29)

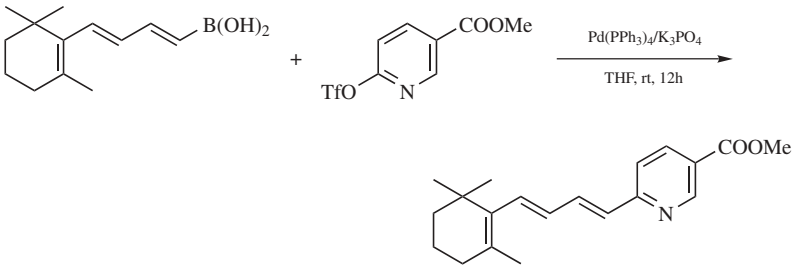
*Cross-Coupling of Organoboranes with Organic Halides and Triflates.* In the last two decades the palladium catalyzed cross-coupling of the variety of aryl-, alkenyl-, alkyl-, and alkynylboranes with organic halides and triflates has emerged as one of the widely used methodology for the carbon–carbon bond formation (5,235,236). The crucial role of bases in the reaction has been demonstrated by Suzuki, Miyaura, and co-workers, and the reaction is often referred to as the 'the Suzuki coupling'. It offers several advantages: mild reaction conditions, many functional groups are tolerated, nontoxic reagents, very small amounts of catalyst, both aqueous and heterogeneous reaction media, good regio- and stereoselectivity. An example of the synthesis of a highly functionalized compound is the cross-coupling betwen (*E*)-1-alkenylboronic acid and (*Z*)-iodoalkene used for the formation of C-75–C-76 bond of palyotoxin (237). A highly stereoselective synthesis of a pheromone bombykol has been achieved in the same way (238).




Bombykol

(30)

Very mild reaction conditions make possible the synthesis of thermally unstable compounds, eg, common retinoids (239).




(31)

Many other examples are described in monographs and reviews (5,81,235,236). At present, alkyl–alkyl coupling is least advanced, although the reaction proceeds with *B*-alkyl-9-BBN derivatives and alkyl iodides (240).

Coupling of alkylboranes, *B*-alkenyl-9-BBN derivatives and lithium trialkylmethylborates with organic halides is also catalyzed by copper(I) compounds (241). In general, palladium- and copper-catalyzed cross-couplings proceed with retention of configuration of the organic groups.

*Organoborate Rearrangements.* A variety of carbon–carbon bond forming reactions involving alkyl-, alkenyl-, and alkynylborates are anionotropic

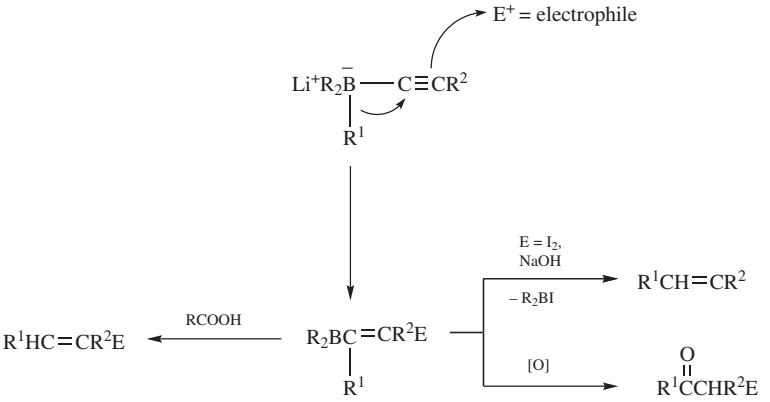



**Fig. 5.** Migration of an alkyl group from boron to carbon.

rearrangements in which an organic moiety migrates from electron-rich boron to electron-deficient carbon. The electron deficiency can be created either by a polar bond, eg, to halogen, or by the action of electrophiles on unsaturated borates. If the electrophile is iodine, the intermediate iodoorganoborane obtained from alkenyl- or alkynylborates breaks down to give an alkene or alkyne, respectively. For most other electrophiles the intermediate is stable and can be oxidized, hydrolyzed, or used for other transformations (Fig. 5). Retention of configuration of the migrating group is usual for this type of mechanism. Tertiary alkyl and methyl groups show low migratory aptitude. The general Zweifel alkene synthesis starts (Fig. 6) with the hydroboration of 1-alkynes or 1-haloalkynes with dialkylboranes (242). Treatment of the intermediate 1-alkenyldialkylborane with iodine and base yields (*Z*)-alkene. Base is sufficient to induce the rearrangement to (*E*)-alkenes since the electron-deficient center is already present in the haloalkenyl group. The scope of the original approach, limited by the availability of dialkylboranes, is considerably extended by the application of dialkylhalo- and alkyldibromoboranes as the precursors, and by the use of thexylborane derivatives (242–244).

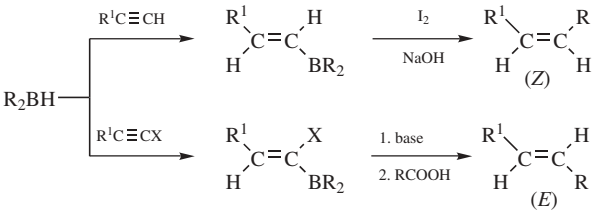
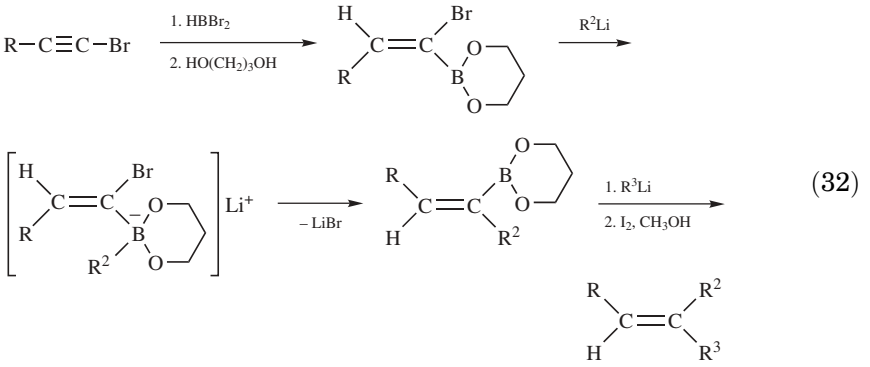



**Fig. 6.** The Zweifel alkene synthesis.

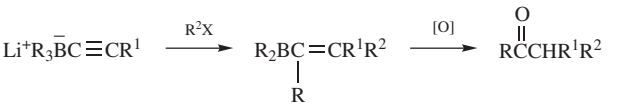
A general synthesis of trisubstituted alkenes containing three different alkyl substituents is achieved by the following methodology (245).




(32)

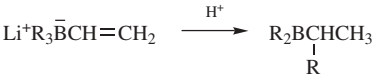
The organoborate intermediates can also be generated from alkenylboronic esters and alkyllithium or Grignard reagents, or from trialkylboranes and alkenyllithium compounds. Conjugated symmetrical and unsymmetrical diynes (246), stereochemically pure 1,3-dienes (247), and 1,3-enynes (248) including functionalized systems can be prepared (249).

Various electrophiles other than iodine have been used to induce alkenyl coupling. Alkyl halides and protic acids react with alkynylborates to yield mixtures of stereoisomeric alkenylboranes. Nevertheless, oxidation of these products is synthetically useful, providing single ketones (250,251). Alcohols are obtained from the corresponding alkenylborates.



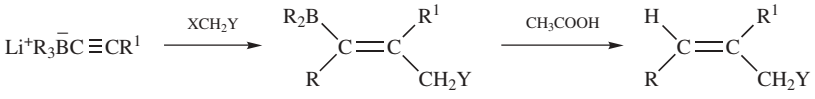

(33)

Markovnikov boranes not available by direct hydroboration can be prepared by protonolysis of alkylethenyl- and alkylalkynylborates (251).




(34)

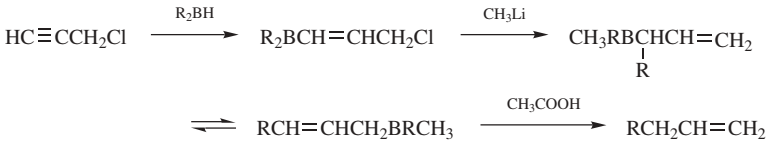
Aldehydes react with alkenylborates to give 1,3-diols upon oxidation of the intermediate (252). Alkynylborates are transformed by epoxides into homoallylic alcohols, and alkenylborates into 1,4-diols (252,253). Carbon dioxide reacts with alkenylborates to yield carboxylic acids (254). The scope of these transformations is further extended by the use of functionalized electrophiles and borates, often reacting with high stereoselectivity. For example, in the reactions of alkynylborates with α-bromocarbonyl compounds and related derivatives or trimethylsilyl chloride (255), the incoming group is placed cis to the migrating one (250).



(35)

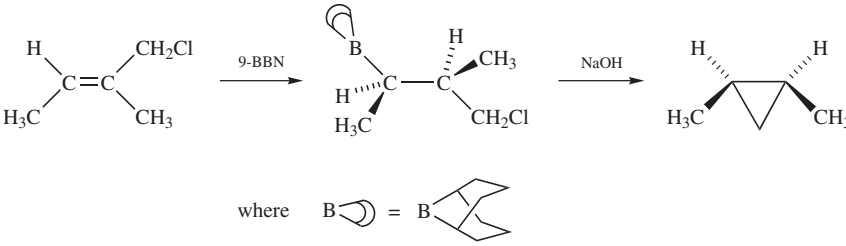
where X = Br; Y = $COR^2$, $COOR^2$, and C≡CH

Similar selectivity is observed in the synthesis of allylsilanes where $X = CF_3SO_3^-$ and $Y = Si(CH_3)_3$ (256). Alkenyl- and alkynylborates containing a leaving group in the γ-position rearrange to allylic and allenic boranes, respectively (257).



(36)

Properly substituted organoborates can undergo elimination with ring formation. Thus, cyclopropanes or cyclobutanes are formed when the organoboranes prepared by the hydroboration of allylic, propargylic, or homopropargylic chlorides and tosylates with 9-BBN are treated with base (258). The cyclopropane ring closure is stereospecific involving antiparallel alignment of the boron atom and the leaving group (259).

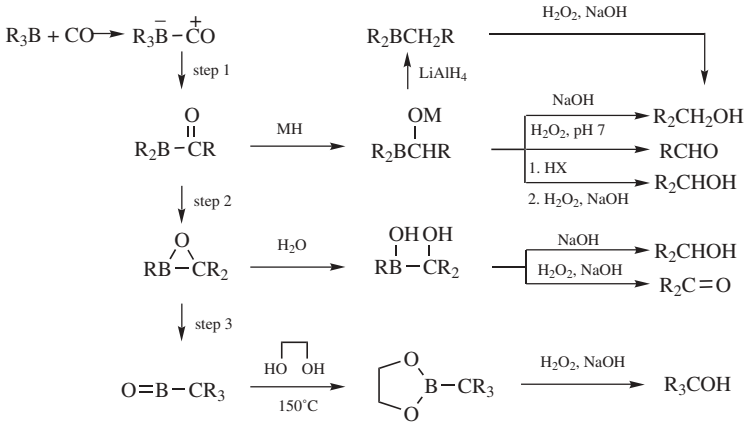


(37)

Cyclopropanes can also be obtained by the reaction of vinyltrialkylborates with aldehydes followed by treatment with phosphorus pentachloride and base (252), and by the rearrangement of δ-substituted alkynyltrialkylborates (260). It is also possible to utilize this approach for the synthesis of five- and six-membered rings. Trans-1,4-elimination in cyclic systems leads to the formation of stereodefined acyclic 1,5-dienes or medium-ring dienes, depending on the starting compound (261).

*Single–Carbon Insertion Reactions.* Carbonylation, cyanidation, and related reactions are convenient general processes developed to bring about the transfer of organic groups from boron to a single-carbon atom.

*Carbonylation.* Trialkylboranes react with carbon monoxide at elevated temperatures and pressures (262), or more conveniently at 100–125°C in diglyme solution (263) (Fig. 7). Oxidation of the organoborane product yields a tertiary alcohol. The reaction proceeds stepwise and the migration of alkyl




MH = $Li[Al(OMe_3)_3H]$; $K[B(Oi\text{-}C_3H_7)_3H]$; $LiBR_3H$; HX = HCl, $CH_3COOH$

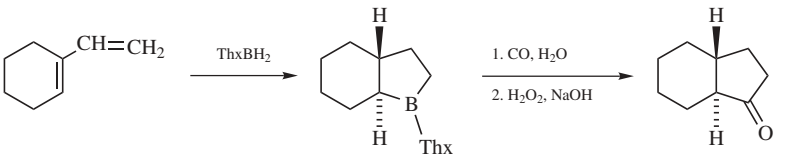
**Fig. 7.** Carbonylation of trialkylboranes.

groups can be controlled to give the products of one, two, or three groups transfer. Primary, secondary, and tertiary alcohols, aldehydes, and ketones can be obtained, depending on the reaction conditions. Configuration of the migrating group is retained. Many functional groups, eg, ethers, esters, nitriles, and chloro are tolerated.

The rate of carbon monoxide absorption is greatly increased in the presence of hydrides and the reaction proceeds at much lower temperatures (264). The intermediate formed after the first group migration (step 1) is reduced by the hydride (MH is potassium triisopropoxyborohydride or lithium trialkoxyaluminum hydride). Hydrolysis of the reduction product yields the methylol derivative $RCH_2OH$ (264), oxidation yields the aldehyde RCHO (265), treatment with acid, inducing migration of the second alkyl group, followed by oxidation provides the secondary alcohol, $R_2CHOH$ (266). For better utilization of alkyl groups it is advantageous to use the *B*-alkyl-9-BBN derivatives in these reactions (267).

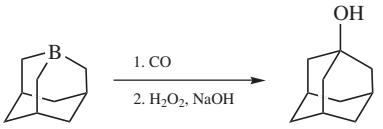
The presence of water in the carbonylation mixture makes it possible to halt the reaction after the second group migration (step 2). Oxidation of the intermediate boraglycol yields the corresponding ketone, $R_2CO$, and alkaline hydrolysis affords the secondary alcohol, $R_2CHOH$. A blocking group of low migratory aptitude, eg, thexyl, allows complete utilization of alkyl groups (268).

A convenient annulation procedure based on cyclic hydroboration–carbonylation of 1-vinyl- and 1-allylcycloalkenes with thexylborane provides trans-fused bicyclic ketones (269).



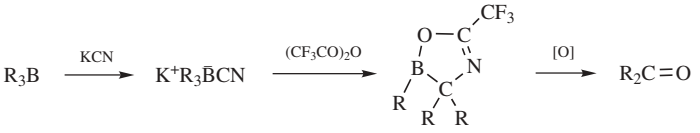

(38)

Moderate yields of acids and ketones can be obtained by palladium-catalyzed carbonylation of boronic acids and by carbonylation cross-coupling reactions (270). In an alternative procedure for the carbonylation reaction, potassium trialkylborohydride in the presence of a catalytic amount of the free borane is utilized (271). Finally, various tertiary alcohols including hindered and polycyclic structures become readily available by oxidation of the organoborane intermediate produced after migration of three alkyl groups (263,269).




(39)

*Cyanidation.* The cyanide ion is isoelectronic with carbon monoxide. It coordinates with trialkylboranes, giving stable cyanoborate salts that must be treated with a suitable electrophile, eg, trifluoroacetic anhydride, to bring about the migration of groups from boron to carbon (272). Two groups migrate readily at room temperature to give a cyclic intermediate which can be oxidized with hydrogen peroxide to the ketone $R_2CO$. The third group migrates upon warming the intermediate with an excess of trifluoroacetic anhydride to give $R_3COH$ (6, 272). Conjugated ketones are obtained from alkenylboranes (273).




(40)

The cyanidation reaction proceeds under mild conditions and no special equipment is required. Stereochemistry of the product usually is the same as in the carbonylation reaction. However, in hindered systems stereoisomeric products may be formed (44). Annulation by hydroboration–cyanidation finds application in the synthesis of natural products (274).

*Carbanion Coordination.* The coordination of alkylboranes with carbanions generated from various halogeno- and thiomethane compounds, eg, chloroform, chlorodifluoromethane, dichloromethane, trimethylsilylchloromethane, tris(phenylthio)methane, 1,1-dichloromethyl methyl ether [4885-02-3] (DCME), and others, results in the migration of alkyl groups from boron to carbon (275). Generally, these reactions proceed under mild conditions, often at low temperatures. Very hindered trialkylboranes undergo transformation into the corresponding tertiary alcohols by the DCME reaction even the thexyl group migrates under mild conditions (276). The reaction is also useful in the synthesis of ketones (277).


(41)

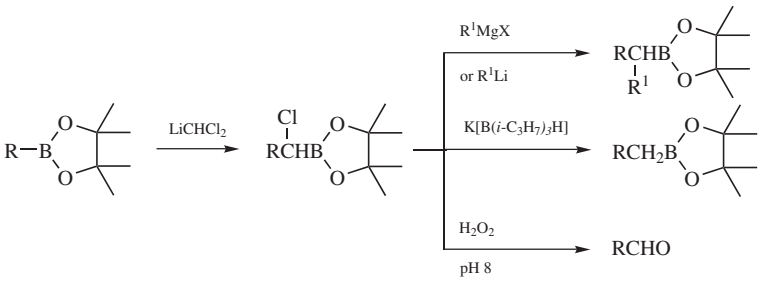
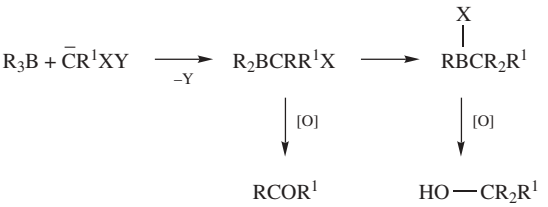



**Fig. 8.** Homologation of boronic esters.

Dichloromethyllithium generated at −100°C reacts with boronic esters to give dichloromethylborates, rearranging upon warming to the homologated α-chloroboronic esters. Displacement of the chlorine atom with an alkyl group yields the homologated boronic ester and the sequence can be repeated (278). Primary, secondary, and tertiary alkyl, alkenyl, and aryl groups undergo migration. Functionalities, eg, benzyloxy, remote ketal, and ether groups are tolerated. The process has been developed into a useful methodology for the synthesis of optically active boronic acids and carbon compounds (9) (Fig. 8).

Similarly, various boronic acid esters have been homologated with $LiCH_2X$. The reactivity is in the order $X = I > Br > Cl$. The reagents $LiCH_2X$ and $LiCHCl_2$ generated by *in situ* procedures are useful for the synthesis of boronic acids not available via hydroboration (279).

*Reactions with Acyl Carbanion Equivalents.* Alkyl substituted carbanions with potential leaving groups X, Y, and acyl carbanion equivalents react with alkylboranes, providing products with mixed alkyl groups derived from both reagents.

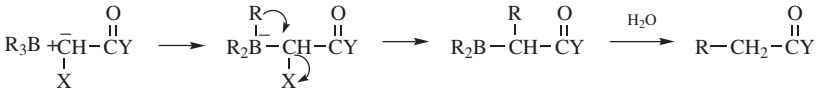



(42)

Lithiated thioacetals and sulfur ylides are convenient reagents for these transformations. Thus, the anions derived from 2-substituted 1,3-benzodithioles are less sterically demanding than 1-lithio-1,1-bis(phenylthio)alkanes developed earlier and are advantageous for the synthesis of hindered ketones and tertiary alcohols (280). The first migration is spontaneous, the second requires the addition of an electrophile ($HgCl_2$ or hazardously toxic $FSO_2CH_3$). The preferential migration of primary to tertiary and 9-BBN groups has been observed (280). Sulfur ylides react with alkyl- and alkenylboranes to give the homologated organoboranes (281,282). The leaving ability of the thioalkoxy group is increased by the addition of an electrophile, eg, methyl iodide (281), or mercury(II) halides (281,283). Organoboranes react also with α-heterosubstituted carbanions

containing a heteroatom-leaving group other than halogen or sulfur. Examples include lithiated enol ethers (283) and aldimines (284), nitrogen and phosphorus ylides (285), and ortho-lithiated furans and pyridines (286).

*α-Alkylation of Carbonyl Compounds and Derivatives.* The organoborate intermediates generated by the reaction of alkylboranes with carbanions derived from α-halocarbonyl compounds and α-halonitriles rearrange to give α-alkylated products.

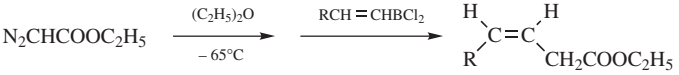


(43)

where X = halogen; Y = H, R, OR

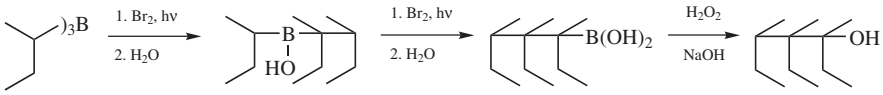
Two different groups can be introduced consecutively starting with α,α-dihalonitriles. The anions are generated by sterically hindered bases, eg, *tert*-butoxide, or better, 2,6-di-*tert*-butylphenoxide for sensitive compounds. Groups unreactive in $S_N2$ displacements such as alkenyl, aryl, or norbornyl can be introduced. Double alkylation with two secondary alkyl groups is possible. The use of *B*-alkyl-9-BBN derivatives instead of trialkylboranes allows better utilization of alkyl groups in the synthesis of ketones (287), esters (287), and nitriles (287). Malononitrile and 4-bromocrotonic acid can also be used (288).

α-Diazocarbonyl compounds react with trialkylboranes directly, in the absence of bases at 0–25°C (289). Mild conditions are advantageous when functionalities labile to bases are present (290). Di- and monoalkylchloroboranes are used for better utilization of alkyl groups (291). β,γ-Unsaturated carboxylic esters can be prepared in excellent isomeric purity by the reaction of 1-alkenyldichloroboranes with ethyl diazoacetate (292).



(44)

*α-Bromination Transfer.* The photochemical α-bromination of organoboranes with bromine proceeds readily. Weak bases such as water or THF are sufficient to induce the migration of alkyl groups from boron to the α-brominated carbon. Consequently, bromination of an organoborane in the presence of water results in a facile carbon–carbon bond formation. All three alkyl groups are utilized (293). It is also possible to halt the reaction after the first group migration.



(45)

Selective bromination at the more substituted position makes possible connection of two different alkyl groups. The use of dialkylthexylboranes and dialkylhaloboranes allows full utilization of alkyl groups (294). Bicyclic and more complex

boracycles can be transformed into carbon structures not readily available by other methods (295).

*Addition to Carbonyl Compounds.* Unlike Grignard and alkyllithium compounds, trialkylboranes are inert to carbonyl compounds. The air-catalyzed addition to formaldehyde is exceptional (296). Tetraorganoborate anions are more reactive and can transfer alkyl groups to acyl halides. The reaction provides a convenient method for the synthesis of ketones (297).

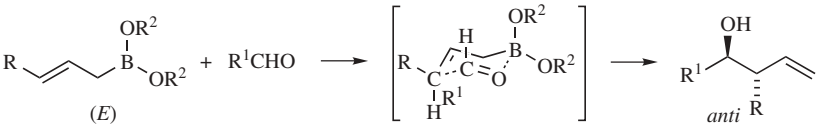
$$R_3B + R^1Li \longrightarrow LiR_3BR^1 \xrightarrow{R^2COX} R^1COR^2 + R_3B + LiX \qquad (46)$$

R = *n*-Bu, *c*-$C_5H_9$; $R^1$ = *n*-Bu, $PhCH_2$; X = Cl, Br

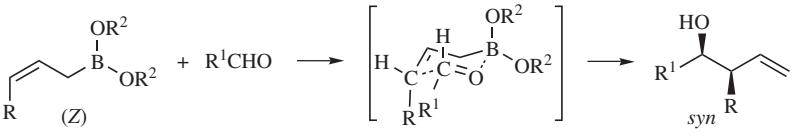
$R^2$ = *n*-Bu, $CH{=}CH(CH_2)_8$, $MeOOC(CH_2)_2$, Ph, 4-$IC_6H_4$, 4-$NO_2C_6H_4$

The migration aptitude increases in the following order: secondary alkyl < prim-primary alkyl < allyl, benzyl.

*Allylboration, Allenylboration, and Propargylboration.* In contrast to alkylboranes, allylic organoboranes add readily to carbonyl compounds (4,298–300). Acid chlorides, esters, and amides undergo double addition (300). The reaction with aldehydes and ketones proceeds via a cyclic transition state with complete allylic rearrangement to give the homoallylic alcohols. Allylic organoboranes are prone to the allylic rearrangement leading to the loss of stereochemical integrity of the allylic group. In an equilibrium, the boron atom favors the least substituted position (186). The sensitivity to this process depends on the substituents at the boron atom. Oxygen and nitrogen atoms attached to boron prevent the rearrangement at ambient temperatures but the reactivity of allylic boronic esters is lower compared to allylic dialkylboranes (301). The latter compounds must be used at low temperatures to avoid the rearrangement (302). The addition of stereodefined allylic organoboranes to aldehydes and ketones is highly stereospecific, leading from (*E*)-allylic boranes predominately to anti-products and from (*Z*)-isomers to syn products. The stereochemical course of the addition can be interpreted assuming a chair-like transmission state (4,7).




(47)




(48)

Typical diastereoselectivities are in the range of 80–95%. These additions are of importance finding application in the synthesis of natural products. A number of other synthetically useful additions of allylic organoboranes to carbonyl and other compounds, has been described (4,299,303).

*B*-Alkenyl-9-BBN derivatives transfer the alkenyl group to aldehydes providing (*E*)- or (*Z*)-allylic alcohols. Methyl vinyl ketone gives the 1,4-addition product (304). *B*-Alkynyl-9-BBN compounds are very mild, nonbasic reagents, showing no reactivity toward various functional groups, eg, acid chlorides, anhydrides, esters, amides, nitriles, sulfoxides, and diethyl malonate. They can differentiate the sterically less hindered among aldehydes and ketones, eg, addition of *B*-alkynyl-9-BBN to a mixture of cyclopentanone and cyclohexanone results in a 71% yield of 1-alkynylcyclohexanol and <1% of 1-alkynylcyclopentanol (305). The simplest representative, *B*-ethynyl-9-BBN, decomposes above −78°C but *B*-2-trimethylsilyl(ethynyl)-9-BBN is a stable reagent (306).

Allylborating reagents bearing functional groups in the allyl moiety expand the scope of allylboration making possible the synthesis of functionalized products (307–309). Allenyl and propargylic organoboranes react with aldehydes to give homopropargylic and homoallenyl alcohols, respectively (310). It is possible to prepare highly unsaturated enynols and trienols (310). The availability of higher crotyl and propargylboronates offers advantages over other corresponding main groups organometallic reagents that lack the isomeric integrity. Several applications of these compounds to the synthesis of dienyl and propargylic alcohols have been reported (7,311,312).

*Boron-Stabilized Carbanions.* Carbanions α to boron are stabilized by the mesomeric effect. The difficulty in deprotonation of alkylboranes lies in a strong tendency of bases to coordinate with boron rather than abstract a proton. Consequently, either very hindered bases or hindered groups attached to boron must be employed to suppress the rate of complex formation and enhance deprotonation. A highly hindered base, lithium 2,2,6,6-tetramethylpiperidide, deprotonates *B*-methyl-9-BBN, but it fails to generate carbanions from *B*-alkyl-9-BBN derivatives (313). Primary alkyldimesitylboranes and allyldimesitylborane are deprotonated by moderately hindered bases such as lithium dicyclohexylamide or mesityllithium (314). *gem*-Diboronic esters and more conveniently heterosubstituted boronic esters, eg, phenylthio- or trimethylsilylmethylboronates can also be deprotonated (315). Alternatively, boron-stabilized carbanions are generated by nucleophilic addition to hindered vinylic boranes (316) and by deboronation of *gem*-trialkylboranes (317) or methanetetraboronic esters. The anions add readily to aldehydes and ketones to give olefins, the so-called boron Wittig reaction (7,318) (Fig. 9). Stereoselective addition can be achieved. The reaction is sensi-

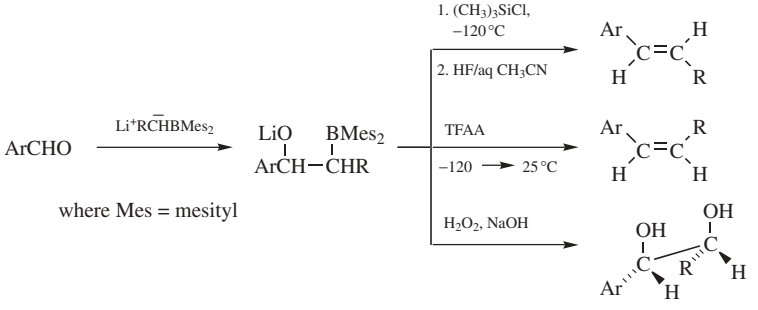


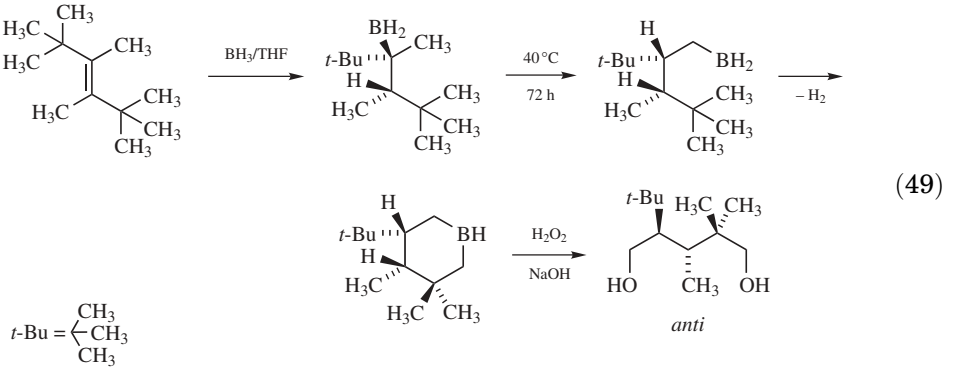

**Fig. 9.** The boron Wittig reaction.

tive to temperature and the amount of trifluoroacetic anhydride (TFAA) must be carefully controlled.

Other reactions of boron-stabilized carbanions involve alkylation by primary alkyl halides (319), addition to esters (320), and transformation into silyl-, tin-, and sulfur-substituted products and *gem*-dibora derivatives (321).

**3.3. Thermal Isomerization of Organoboranes.** Trialkylboranes undergo isomerization under the action of heat, generally at temperatures >100°C, the boron atom moving to the least hindered site of the alkyl group (322). It migrates past a tertiary, but not a quaternary center. The rate of isomerization depends on the organoborane structure. Thus, the relatively unhindered dichloroboryl, dibromoboryl, and 9-BBN groups migrate very slowly, whereas bulky hindered groups such as bis(2,5-dimethylcyclohexyl) boryl migrate readily (323). The isomerization appears to involve a dehydroboration–hydroboration mechanism. The addition of an excess of another olefin of equal or greater reactivity results in the displacement of the olefin from the organoborane (324). Consequently, the combination of hydroboration, isomerization, and displacement makes possible contrathermodynamic isomerization of olefins (325). In certain cases, the displacement with an aldehyde is more convenient (104).

Certain organoboranes are thermally labile, eg, di-4-isocaranylborane undergoes isomerization in refluxing THF (326). Similarly, *cis*-myrtanylborane obtained by hydroboration of β-pinene is readily transformed into the trans isomer upon heating (327). Tertiary organoboranes undergo thermal isomerization at temperatures much <100°C, and migration of boron to the adjacent position is often stereoselective. The diastereoselective synthesis of various acylic and cyclic compounds with stereocontrol of up to three adjacent carbon centers has been achieved (328). A remote stereoselective C–H activation has also been observed (329).

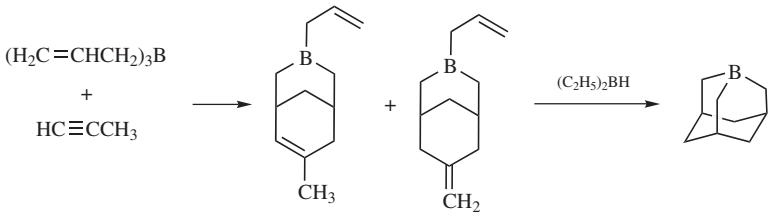



(49)

Long-chain primary alcohols, eg, triacontanol, can be prepared by the hydroboration–isomerization–oxidation of the corresponding internal alkenes (330). Alternatively, triacontanol can be prepared by cometathesis of cycloolefins with 1-alkenes followed by hydroboration–oxidation–hydrogenation (331).

**3.4. Concerted Reactions of Organoboranes.** Allylic organoboranes react via cyclic transition states not only with aldehydes and ketones, but also

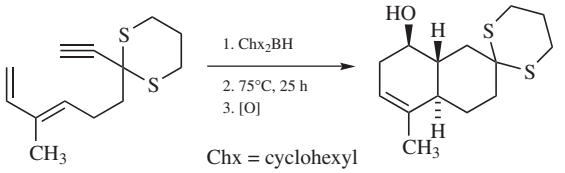
with alkynes, allenes, and electron-rich or strained alkenes. Bicyclic structures, which can be further transformed into boraadamantanes, are obtained from triallyl- or tricrotylborane and alkynes (332).




(50)

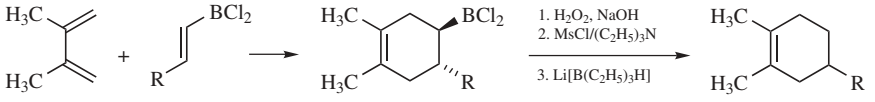
The addition proceeds in three discrete steps and the intermediates can be isolated. Simple alkenes are less reactive than alkynes and do not undergo the addition to allylic boranes, but electron-rich alkyl vinyl ethers react at moderate temperatures to give 1,4-dienes or dienyl alcohols (333).

*The Diels-Alder Reaction.* Vinylic organoboranes are useful dienophiles and dienes for the Diels-Alder reaction (4,334). Chiral organoboranes serve as highly effective catalysts for the asymmetric Diels-Alder additions (335). The reactivity of organoborane dienophiles depends on the boryl group, and increases in the order $B(OR)_2 < BR_2 < BCl_2 < BBr_2$. The activating effect of the dihaloboryl group is remarkable, eg, dichloro- and dibromovinylborane react with 2,3-dimethyl-1,3-butadiene below 0°C (336). Regioselectivity and stereochemistry of the addition is influenced both by the structure of the alkenyl group and the substituents on boron, eg, the endo-boryl group is favored for the adducts of 1,3-cyclopentadiene with dichlorovinylborane and *B*-vinyl-9-BBN, whereas the exo-boryl group is favored in the reaction with *B*-2-propenyl-9-BBN (336). The use of organoborane dienophiles provides a convenient stereoselective access to cyclohexanols and bicyclic alcohols (337).




(51)

Ethenyl- and 1-alkenyldichloroborane are synthetic equivalents of sluggishly reacting ethylene and 1- alkenes. The organoborane adducts are transformed into the corresponding olefins by the oxidation-mesylation–reduction sequence (336).

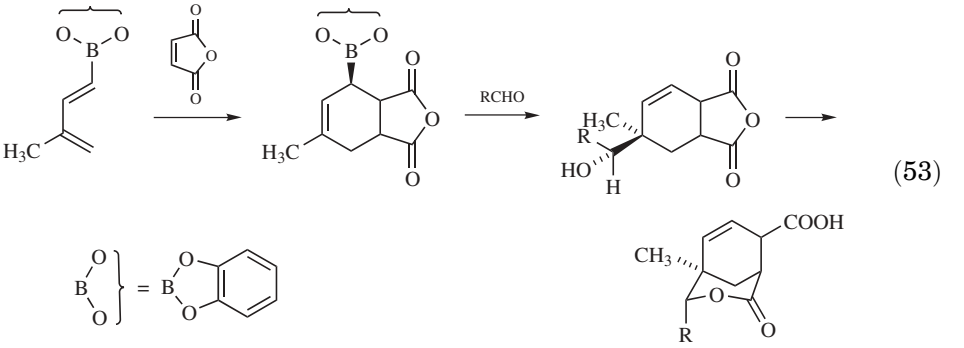



(52)

Ms = $CH_3SO_2$

3-Borylacrolein is an example of a functionalized dienophile. The electron-withdrawing carbonyl group enhances the reactivity, and the adducts can be transformed into β-functionalized aldehydes (338). Other electron-withdrawing groups can also be introduced in the β-position (339).

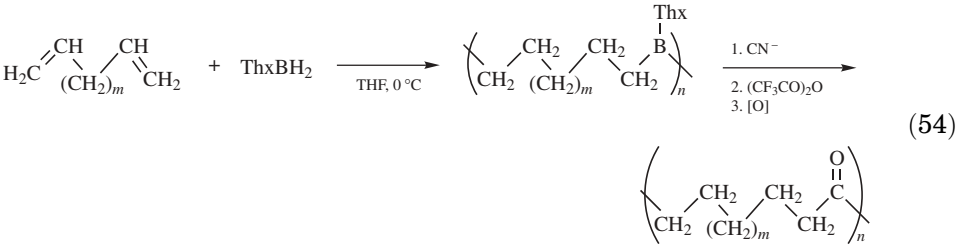
Dienylboranes are available by the monohydroboration of 1,3-enynes (181, 340), via the coupling of 2-bromovinylboronic esters with alkenyl zinc halides (341), and by other methods (342). The adducts of dienylboranes are allylic boranes, which can be further transformed, eg, by allylboration of aldehydes (340).




(53)

This tandem sequence has been applied to the synthesis of clerodin (343). Recently, chiral 1,3-dienylboranes have been described (344).

**3.5. Polymerization.** Hydroboration of α,ω-dienes with monoalkylboranes gives reactive organoboron polymers that can be transformed into polymeric alcohols or polyketones by carbonylation, cyanidation, or the DCME reaction followed by oxidation (345).




(54)

Air-stable boron-containing polymers can be prepared by the reaction of dicyano compounds with the *tert*-butylborane–trimethylamine complex (346). New II-conjugated organoboron polymers have been prepared by hydroboration–polymeryzation of aromatic diynes with mesitylborane, and other reagents (347,348). Hydroxylation of polystyrene-block-polyisoprene by hydroboration oxidation was used in studies of nanostructured polymers (349,350). Dendric carbosilanes containing double bonds were hydroxylated by hydroboration with 9-BBN and oxidation. Modification of polymers by hydroxylation via hydroboration was also used to obtain crystal growth modifiers of calcium carbonate (351),

improved stretchable fabrics (352), and olefin block copolymers with low homopolymer content (353), and in other applications (354,355).

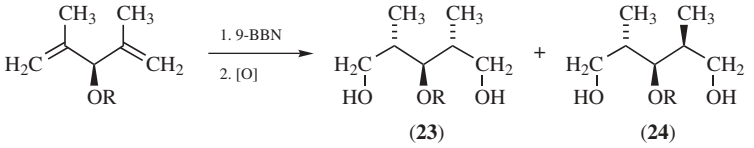
**3.6. Synthesis of Isotopically Labeled Compounds.** Organoborane reactions have been applied for the synthesis of isotopically labeled compounds important in chemical and biological research and in modern medical imaging techniques, such as positron emission tomography (pet) and magnetic resonance imaging (mri). Organoboranes tolerate a wide range of physiologically active functionalities, and hence are well-suited intermediates in radiopharmaceutical pathways. Such use has been reviewed (356). Various isotopes both stable and short lived can be incorporated into organic compounds via organoboranes. In $RCH_2CH_2B \rightarrow RCH_2CH_2X$, R can contain $NO_2$, CN, COOR, halogen, OR, aryl, metal, etc, and X = D, T, $^{11}C$, $^{13}C$, $^{15}O$, $^{13}N$, $^{15}N$, $^{123}I$, $^{82}Br$, etc. The stereoselective deuteration by deuterioboration or hydroboration–deuteriolysis is straightforward (184, 357). Olefins monodeuterated in the allylic position are readily prepared by deuteriolysis of allylic organoboranes (358).

Special methodologies are often required for the incorporation of short-lived isotopes or due to the most convenient source of the isotope. For example, molecular oxygen is readily available labeled with essentially all known oxygen isotopes. Consequently, oxidation of organoboranes with molecular oxygen is preferred for the synthesis of alcohols (359). Bromination and iodination are carried out using halides instead of the free halogens due to the dangers and cost associated with radiohalogens. *In situ* generation of chloramine from ammonia has been developed for the amination reaction of organoboranes (360). Carbonylation and cyanidation with isotopically labeled carbon monoxide or cyanide ion, respectively, is used for the incorporation of carbon isotopes (361). Isotopically labeled steroids, carbohydrates, amino acids, and other compounds have been prepared by these methods (356).

## 4. Asymmetric Synthesis Via Chiral Organoboranes

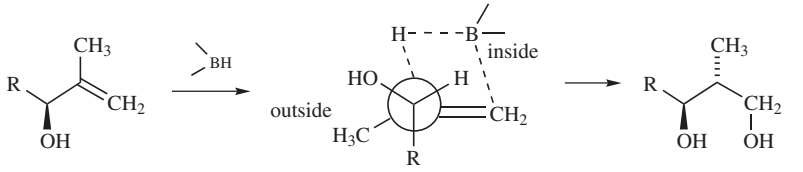
Asymmetric synthesis via chiral organoboranes has been reviewed (4,102,335,362–367). Asymmetric induction in the hydroboration reaction may result from the chirality present in the olefin (asymmetric substrate), the reagent (asymmetric hydroboration), or the catalyst (catalytic asymmetric hydroboration).

**4.1. Origins of Asymmetry.** *Asymmetric Substrate.* Excellent stereoselectivity is achieved in borane addition to rigid cyclic systems having one face of the double bond significantly more hindered than the other, eg, α-pinene (327). Less rigid monocyclic systems usually give mixtures of isomeric products (368). Electronegative substituents in allylic cycloalkenyl derivatives direct the boron atom to the trans-2-position (369). However, addition in the cis-2-position may be preferred for substituents complexing the hydroborating agent, eg, phosphinites (370). Acyclic diastereoselection is controlled by allylic, homoallylic, and more remote chiral centers (371–375) as in the following (375), in which $R = Si(CH_3)_2C(CH_3)_3$ and the product ratio of (**23**)/(**24**) 13:1. See also equation (21).




(55)

The stereochemical outcome of these reactions can be explained by considering the transition-state geometry. For example, applying the Houk model (376) to allylic alcohols and their derivatives, the smallest substituent at the preexisting chiral center is oriented "inside" over the face of the transition-state ring and the oxygen atom "outside" (372).




(56)

High levels of asymmetric induction have been achieved in the hydroboration of substituted 1,3-, 1,4-, and 1,5-dienes with thexylborane (371–374). The first chiral center is formed by an intermolecular reaction. In the second step, the organoborane intermediate undergoes an intramolecular hydroboration, creating the second chiral center with high diastereoselectivity.

*Asymmetric Hydroboration.* Hydroboration–oxidation of (*Z*)-2-butene with diisopinocampheylborane producing (*R*)-(−)-2-butanol in 87% ee was the first highly enantioselective asymmetric synthesis (375). Since then, several asymmetric hydroborating agents have been developed (376). Enantioselectivity in the hydroboration of significant classes of prochiral alkenes with representative asymmetric hydroborating agents is shown in Table 2.

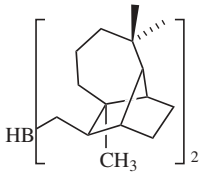
Table 2. **Enantioselectivity in the Hydroboration of Prochiral Alkenes with Various Hydroborating Agents**[a]

| Class Alkene | $Ipc_2BH$ (**12**) | 2-$Icr_2BH$ (**25**) | $Lgf_2BH$ (**26**) | TDMB[b] (**28**) | $IpcBH_2$ (**10**) | $EapBH_2$[c] (**27**) |
|---|---|---|---|---|---|---|
| placeholder for callout chemical structures 5 | 21 | 15 | 1 | 1 | 1.5 | 2 |
| placeholder for callout chemical structures 6 | 98.1 | 93 | 78 | 95.2 | 24 | 30 |
| placeholder for callout chemical structures 7 | | 30 | 25 | 97 | 73 | 76 |
| placeholder for callout chemical structures 8 | 13 | 37 | 70 | 94.2 | 53 | 68 |
| Reference | 103 | 105 | 107 | 108 | 377 | 378 |

[a] Numbers are % ee of the product alcohol.
[b] *trans*-2,5-Dimethylborolane = TDMB.
[c] Mono(2-ethylapoisopinocampheyl)borane = $EapBH_2$.

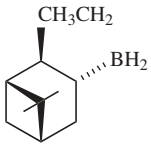
2-$Icr_2BH$ is bis(2-isocaranyl)borane [114533-27-6] (**25**), and $Lgf_2BH$ is dilongifolylborane (**26**).


(**25**)

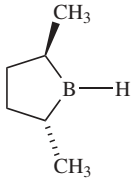



(**26**)

Simple terminal prochiral alkenes are hydroborated with low selectivity by all asymmetric hydroborating agents known. The chiral centers of the reagent are probably too far from the incipient chiral center to exert good asymmetric induction. However, such alkenes may react with higher selectivity in catalytic asymmetric hydroboration. Chiral terminal alkenes may also react with high selectivity (379). Disubstituted (*Z*)-alkenes react readily with all asymmetric dialkylboranes. Diisopinocampheylborane (**12**) is the reagent of choice for this class, producing alcohols of very high optical purity with the same absolute configuration for similar structures. Functionalized disubstituted alkenes and cycloalkenes are also hydroborated with high enantioselectivity (380). The relatively more hindered (*E*)-isomers and trisubstituted alkenes react sluggishly with diisopinocampheylborane. The reaction proceeds with the displacement of α-pinene and the organoborane product shows low optical purity. Less sterically demanding monoisopinocampheylborane (**10**) reacts readily with all classes of alkenes. Enantioselectivity of the addition to disubstituted (*Z*)-alkenes is low. In contrast, the (*E*) isomers and trisubstituted alkenes are hydroborated with much higher selectivity. Mono- and diisopinocampheylboranes are complementary hydroborating agents to each other. Mono(2-ethylapoisopinocampheyl)borane, $EapBH_2$ (**27**), shows slightly higher selectivity than monoisopinocampheylborane. However, its precursor, 2-ethylapopinene, is not commercially available. Similarly, TDMB (**28**), hydroborating three primary classes of alkenes with excellent selectivity, is not readily available. Sterically varied bis(terpenyl)haloboranes are petentially important, readily accessible, new asymmetric hydrobotrating reagents (381). New chiral monoalkylboranes bearing a nonstereogenic, chirooptic center lead to enantioselectivites of up to 64% ee from cyclic olefins, and 38% ee from 1-phenylcyclopentene (382). Models predicting the product configuration in the hydroboration of alkenes with mono- and diisopinocampheylboranes, based on the minimum energy calculations of the transition states, have been proposed (376).




(**27**)




(**28**)

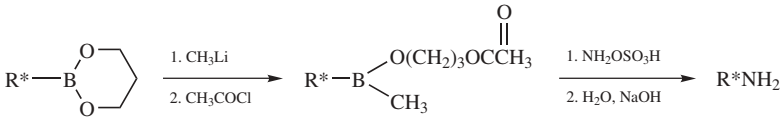
As follows from the data presented in Table 2, the range of organoboranes produced in high optical purity directly by hydroboration is rather limited. Fortunately, the following features of the organoboranes obtained by hydroboration with mono- and diisopinocampheylborane considerably increase their potential as intermediates in asymmetric synthesis. First, the optical purity of IpcR*BH and $Ipc_2R^*B$, where R* is a chiral group, can often be upgraded to essentially 100% ee by crystallization. Second, the chiral auxiliary isopinocampheyl group is readily removed from the organoborane by treatment with an aldehyde. Controlled treatment of $Ipc_2R^*B$ with aldehydes produces chiral boronates with higher enantiomeric purity than the substrate (383). Third, the boronates can be reduced by lithium aluminum hydride or lithium monoethoxyaluminum hydride to the corresponding mono- and dialkylborohydrides, which are stable over long periods (384). Mono- and dialkylboranes can be conveniently generated from the borohydrides by treatment with hydrogen chloride, methyl iodide, or chlorotrimethylsilane (56). In this way, optically pure mono- and dialkylboranes become available for further transformations into enantiomerically pure carbon compounds.

Finally, kinetic resolution of racemic olefins and allenes can be achieved by hydroboration. The reaction of an olefin or allene racemate with a deficient amount of an asymmetric hydroborating agent results in the preferential conversion of the more reactive enantiomer into the organoborane. The remaining unreacted substrate is enriched in the less reactive enantiomer. Optical purities in the range of 1–65% have been reported (376).

*Catalytic Asymmetric Hydroboration.* This reaction has been reviewed (4,335,362–364). The hydroboration of olefins with catecholborane (an achiral hydroborating agent) is catalyzed by cationic rhodium complexes with a variety of chiral bidentate P/P (385), P/N (386), P/S and P/Se (386) ligands, eg, $[Rh(cod)_2]BF_4$BINAP, and BINAP is 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl. The enantioselectivities are moderate; only vinylarenes give secondary product alcohols >90% ee. Noteworthy is higher enantioselectivity (69% ee) of the catalyzed hydroboration of 2,3,3-trimethyl-1-butene a terminal alkene, as compared to that achieved by the best asymmetric hydroborating agents (387). Efficient kinetic resolution in the hydroboration of 1,2-dihydronaphthalenes with catecholborane catalyzed with rhodium–QUINAP complex, has been achieved (388). Highly enatioselective syntheses of primary α-arylalkylamines in up to 97% enantiomeric excess via catalytic hydroboration of vinylarenes has been developed (389). Rhodium-catalyzed hydroboration of styrene followed by one carbon homologation with $LiCHCl_2$ was employed to the highly enantioselective synthesis of 2-phenylpropionic acid (390). Advantages of the use of achiral hydroborating agents and only small amounts of chiral ligands make catalytic asymmetric hydroboration very attractive (391). Recyclable catalyst systems are under development (392).

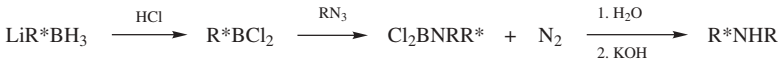
**4.2. Synthesis of Chiral Molecules.** *Synthesis of Chiral Alcohols, Ketones, Halides, Deuterated Hydrocarbons, and Amines.* The chiral organoboranes produced by asymmetric hydroboration can be transformed into the heterosubstituted chiral products applying methodologies developed for achiral organoboron compounds. Thus, in most cases described above, the organoboranes obtained from alkenes are oxidized to the corresponding chiral alcohols (Table 2). Among other examples are the alcohols derived from heterocyclic olefins (393),

dienes (302), functionalized olefins (379,380), and deuterium- or tritium-labeled chiral alcohols (394). Chiral ketones, eg, norcamphor, can be obtained by oxidation of chiral secondary alkylboranes with chromic acid (395). The hydroboration of (*Z*)-2-butene with diisopinocampheylborane followed by iodination with iodine in the presence of base or with iodine monochloride in the presence of sodium acetate affords 2-iodobutane of 87% optical purity (207,209). Chiral deuterated alkanes can be prepared either by asymmetric hydroboration–deuteriolysis or by asymmetric deuterioboration–protonolysis (394). Optically pure boronic esters available either by asymmetric hydroboration or homologation are particularly important intermediates, leading to optically pure products. Thus primary amines of high enantiomeric purity are produced through the intermediate formation of alkylmethylborinic esters (396).



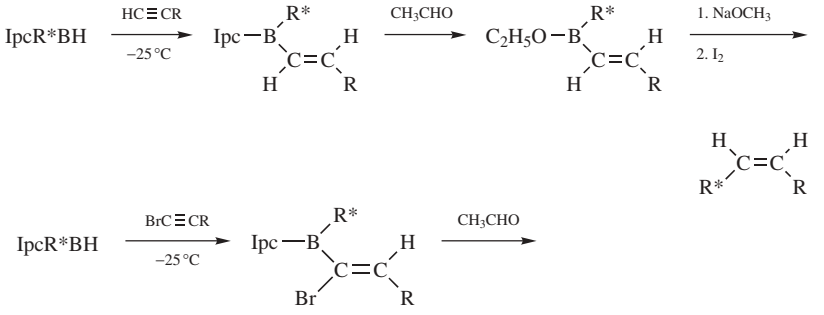

(57)

Secondary amines having one or two chiral groups attached to the nitrogen atom are prepared from boronic esters by their conversion into alkyldichloroboranes, followed by treatment with organic azides (397). The second chiral group can be derived from an optically active azide.

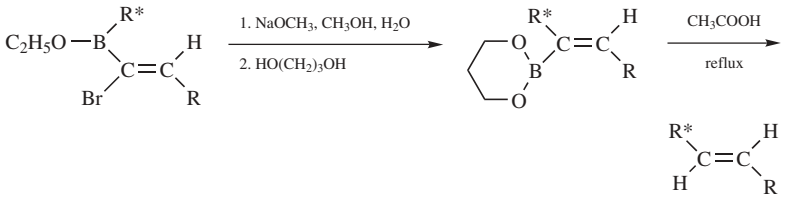



(58)

*Synthesis of Chiral Alkanes, Alkenes, and Alkynes.* An efficient general synthesis of α-chiral (*Z*)- and (*E*)-alkenes in high enantiomeric purity is based on the hydroboration of alkynes and 1-bromoalkynes, respectively, with enantiomerically pure IpcR*BH readily available by the hydroboration of prochiral alkenes with monoisopinocampheylborane, followed by crystallization (398).




(59)

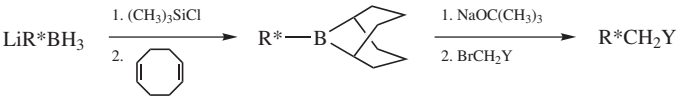



(60)

In the earlier, longer approach to (*Z*)-and (*E*)-alkenes, ThxR*BH was used instead of IpcR*BH. It is also possible to prepare α-chiral acetylenes and alkanes by this method (56). In a shorter synthesis of α-chiral alkynes, a prochiral disubstituted (*Z*)-alkene is hydroborated with diisopinocampheylborane and the trialkylborane produced is treated with alkynyllithium followed by iodine (399). Optical purity of the product is the same as the intermediate trialkylborane. The scope of this method is limited to alkenes handled by diisopinocampheylborane.

*Synthesis of α-Chiral and Homologated Aldehydes, Acids, and β-Chiral Alcohols.* A general approach to these compounds is based on the reaction of dichloromethyllithium with boronic esters. Rearrangement of the complex followed by reduction with potassium triisopropoxyborohydride provides the homologated boronic ester, which can be oxidized to the corresponding alcohol or transformed into the homologated aldehyde by reaction with methoxy-(phenylthio) methyllithium (400). β-Chiral alcohols not available in high optical purity by asymmetric hydroboration of terminal alkenes are readily prepared by this method.

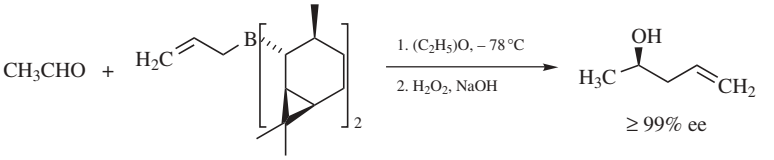
*Synthesis of α- and β-Chiral Ketones, Esters, and Nitriles.* Chiral boronic esters are convenient precursors of α-chiral ketones (R*COR′), which can be prepared via the dialkylborinic ester or dialkylthexyl route (401). The conversion of chiral boronic esters into optically pure *B*-alkyl-9-BBN derivatives followed by reaction with α-bromoketones, α-bromoesters, or α-bromonitriles leads to the homologated β-chiral ketones, esters, and nitriles, respectively (402).




(61)

where Y = COR, COOR, CN

*Asymmetric Allylboration.* Optically active allylic boronates and allylic dialkylboranes transfer the allylic group to aldehydes enantioselectively. For example, acetaldehyde reacts with allyldi(2-isocaranyl)borane to give optically pure pent-4-en-2-ol (403).




(62)

The asymmetric allyl- and crotylboration of aldehydes has emerged as an effective alternative to the aldol methodology in reactions involving acyclic stereoselection. Several reagents have been developed (Fig. 10), and their selectivity has been compared (4,403). The methodology has been applied to the synthesis of 2-deoxyhexoses (404); the AB disaccharide unit of olivomycin A (405); the C-17–C-27 segment of rifamycin S (406); benzoyl-pedamide, the

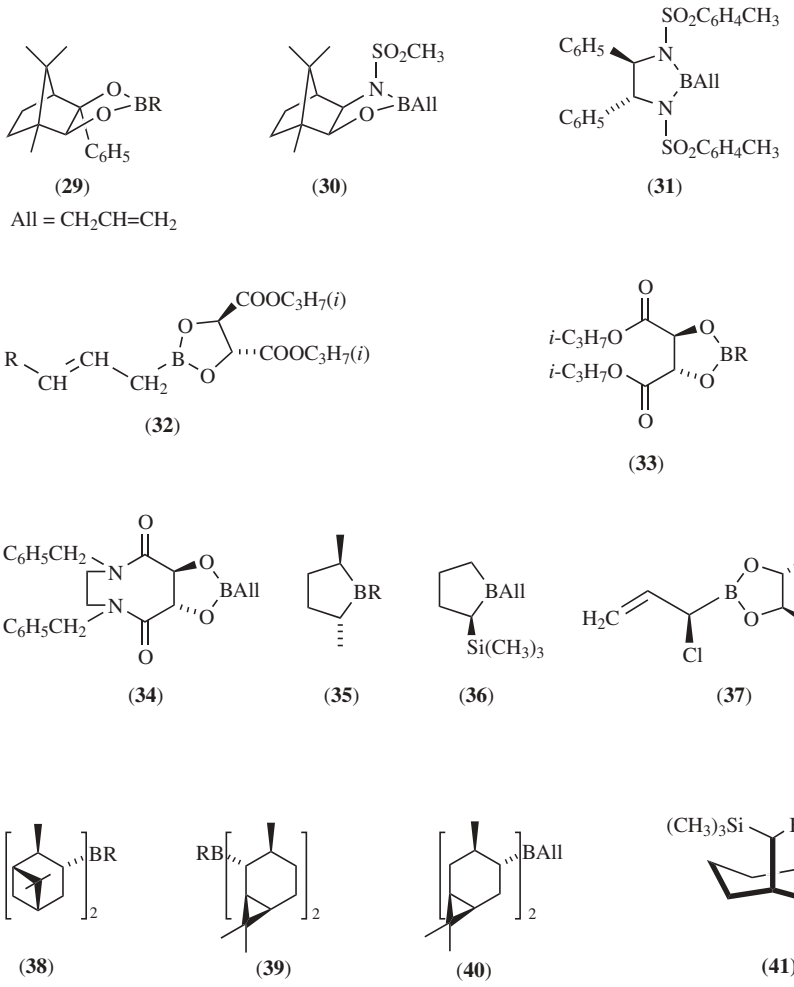
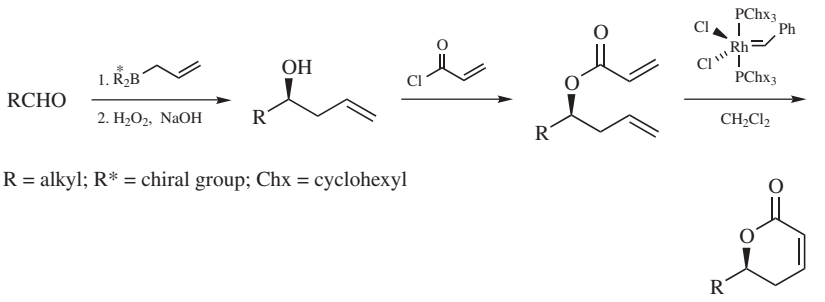



**Fig. 10.** Representative allylboration reagents. (**29**), R = allyl or crotyl ; (**30**); (**31**); (**32**) (R = H) is 2-(2-propenyl)-1,3,2-dioxaborolane-4,5-dicarboxylic acid diisopropyl ester [99417-55-7]; (**32**), R = $(C_6H_{11}O)(CH_3)_2Si$- and (**32**), R = $C_6H_5(CH_3)_2Si$- (**33**), R = allyl or crotyl; (**34**); (**35**), R = allyl or crotyl; (**36**); (**37**); (**38**) (R = allyl) is *B*-allyldiisopinocampheylborane [85116-38-7], or R may be crotyl; (**39**) (R = allyl) is *B*-allylbis(2-isocaranyl)borane [124821-92-7], or R may be crotyl; (**40**) is *B*- allylbis(4-isocaranyl)borane [125762-12-1]; (**41**) is *B*-allyl-10-trimethylsilyl-9-borabicyclo[3.3.2]decane.

key building block of pederin (407); ipsdienol (408); lactones, ω-allyl and ω-propyllactones (409); β-hydroxy-δ-lactone unit of statin drug analogues (410), several heterocyclic compounds (411); and to the α- and γ-hydroxyallylation and γ-chloroallylation of aldehydes (407).

A combination of allylboration and metathesis expands the synthetic potential of both reactions, and is a general route to lactons, as exemplified by the syntheses of (+)-goniodiol (412), goniothalamin, hexadecanolide, massoia

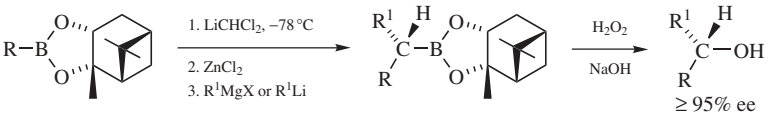
lactone, parasorbic acid (413), argentilactone (414), tarhonanthuslactone (415), and umuravumbolide (416).




(63)

A further extention is the possibility of allenyl- and homoallenylboration of aldehydes.

*Homologation of Boronic Esters.* A convenient general method of enantioselective carbon–carbon bond formation, not involving hydroboration, is based on the homologation reaction of boronic esters derived from optically active 1,2-diols, eg, 2,3-pinanediol (4,9). The -ate complex formed by treating the boronate with dichloromethyllithium undergoes 1,2-migration of the alkyl group. The second alkyl group is introduced using an alkyllithium or Grignard reagent (qv). Oxidation provides a chiral alcohol of high optical purity.




(64)

Consecutive chiral centers can be introduced by repeating the homologation sequence. Ultrahigh diastereomeric ratios (1000:1) for each new chiral center introduced have been achieved using boronic esters derived from 1,2-diols with C2 symmetry (417). This chemistry has been applied to the synthesis of labile molecules, eg, (2*S*,3*S*)-2-methyl-3-benzyloxypentanal, the drugstore beetle *Stegobium paniceum* (Anobiidae), beetle pheromones stegobiol, and stegobione, and carbohydrates (418).

## 5. Enolboration

The aldol reaction is one of the most powerful methodologies for the formation of carbon–carbon bonds in a stereodefined manner. Boron enolates are important intermediates for this transformation, since transition states of boron-mediated aldol reactions appear tightly organized, transmitting well the spatial arrangement to the aldol product (419). The stereochemical outcome of the addition to aldehydes depends on the configuration of the enolate, eg, (*Z*)-isomers of enol borinates produce the syn aldols, and (*E*)-isomers produce the anti-aldols (4) (Fig. 11).

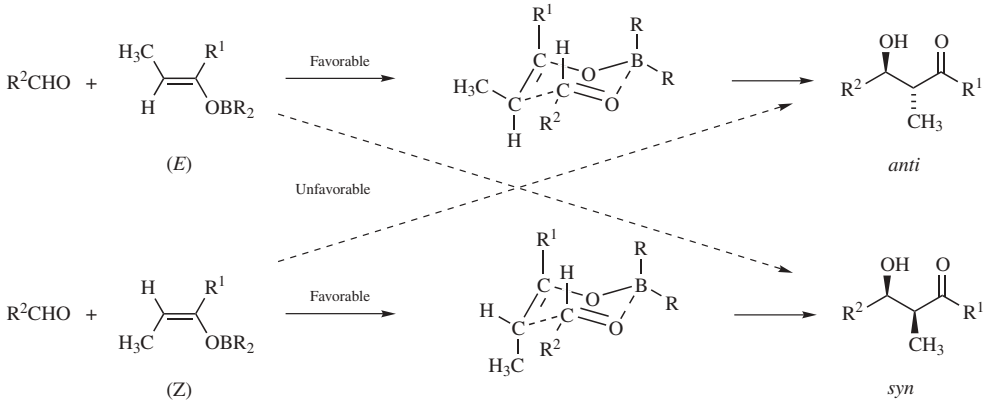



**Fig. 11.** Aldolization of (*E*) and (*Z*) enolborinates.

Enolboration of aldehydes and ketones is best achieved with dialkylborane derivatives $R_2BX$ in the presence of amines, where X is a good leaving group, eg, triflate or halogen (420). Representative chiral boron reagents for enolboration are shown in Figure 12.

The stereoselective formation of (*E*)- or (*Z*)-enolates is influenced by substitutents on boron and the ketone, and also by the amine (420). Molecular modeling has been applied to design optimal chiral groups on boron for the anti-aldol products. *B*,*B*-Dihaloterpenylboranes are convenient reagents for the synthesis of (*Z*)-enoloborinanes leading to syn-aldols (421).

Enolborinates can also be prepared by the addition of boranes to conjugated ketones (126). Boron enolates have been extensively applied to the synthesis of macrolides, ionophore antibiotics, and other compounds (422).

Enolboration of conjugated cyclohexenones with chlorodicyclohexyl borane produces the corresponding dienolborinates. The reaction with aldehydes leads to aldolization in the six-position and to the Morita-Baylis-Hillman-type products, depending on substituents of the cyclohexenone (423).

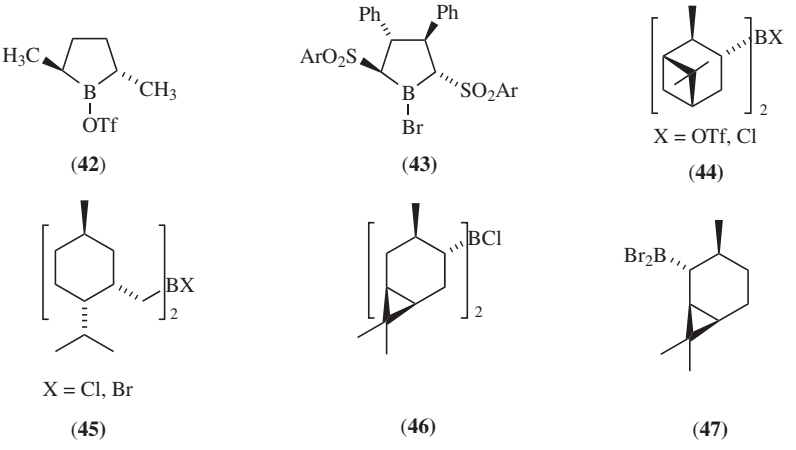



**Fig. 12.** Representative chiral boron reagents for enolboration.

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MAREK ZAIDLEWICZ
Nicolaus Copernicus University