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Boron: boranes in organic synthesis. Annual Survey covering the year 1989 *

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Contents

1. Introduction

H.C. Brown and his coworkers first reported the hydroboration reaction in 1956 and provided a convenient route to a variety of organoboranes. Today, organoboranes and borohydrides are used in thousands of syntheses. Although Professor Brown remains a leader in the development of organoborane technology, new names continue to appear in the literature as the role of boron in organic synthesis continues to expand. This review focuses on reports concerning new methodology and/or reagents. The format for this year's review has not changed; though classifications are somewhat arbitrary, they are, presumably, logical.

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* No reprints available. For previous Annual Survey see *J. Organomet. Chem., 404* (1991) 1.

2. Borane reagents

2.1. Hydroborating agents

The hydroboration reaction has proven to be the most convenient route to synthetically important organoboranes. One of the most significant features of the hydroboration reaction is the fact that a large number of functional groups are tolerated by the various hydroborating reagents [1,2]. In this respect, organoboranes are rather unique synthetic intermediates in that functional groups can be introduced rather early in a multistep synthetic sequence.

2.1.1. BH_3

Kabalka and Bierer studied the protection of carboxylic acids during hydroboration reactions [3]. They report that the trimethylsilyl esters of carboxylic acids are inert to a variety of hydroborating agents and

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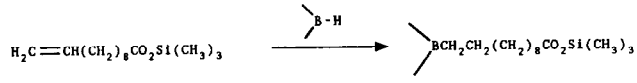
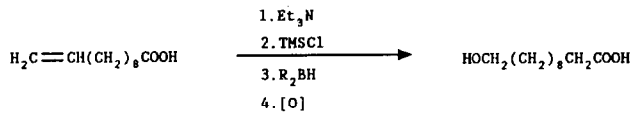
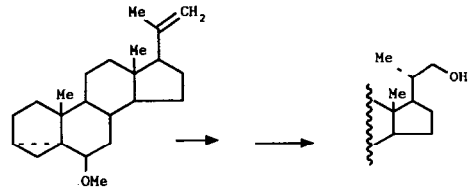
provide a convenient method for protecting the acid functionality during organoborane transformations. The authors also described a convenient, one-pot, proce-



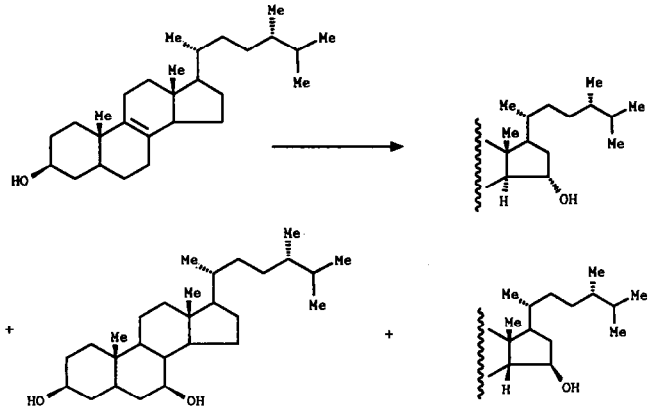
dure involving the protection of the carboxylic acid functionality without isolation of the TMS intermediate [4].



Ganem reviewed the catalytic asymmetric hydroboration of styrene [5]. Liu and Liang studied the stereoselective hydroboration/oxidation of 3,5-*cyclo*-6-methoxylpregn-20(22)-ene. They utilized $NaBH_4/BF_3 \cdot Et_2O$ in their study and the yields of the alcohol as well as three byproducts were found to be dependent on the molar ratios of $NaBH_4$ and $BF_3 \cdot Et_2O$ [6].

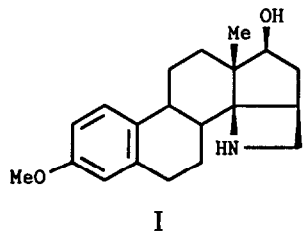


Allevi, Anastasia, Colombo and Fiecchi reported that hydroboration of 5α-ergost-8-en-3β-ol, followed by oxidation, gave three diols but that the previously reported 5α,9β-egostane-3β,7β-diol was not obtained [7].

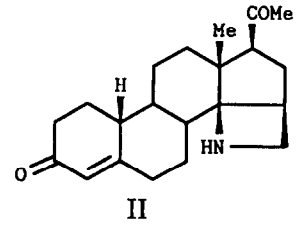


Ponsold, Prousa and Reck prepared 19-norpregnane derivatives with nitrogen-containing four-membered rings in the 14,15-position from estratrienol, **I**. Key steps involved the hydroboration of the 17-ethylidene derivative **III** to give a mixture of the 17α and 17β isomers of the pregnane derivative **IV** (R = $PhSO_2$).

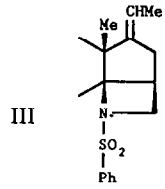
The crystal structure of 20-oxo derivative **VI** was also determined [8].



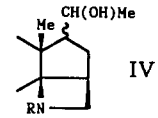
I



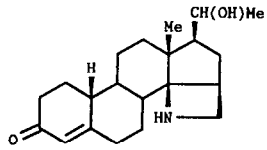
II



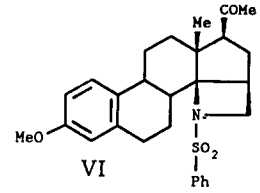
III



IV

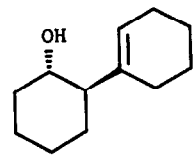


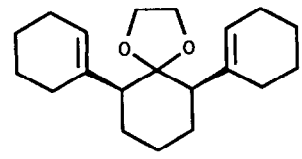
V



VI

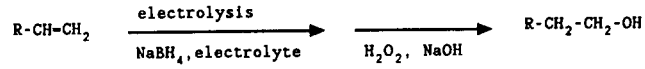
Bell and his coworkers studied the interannular diastereoselectivity in the hydroboration of functionalized 1-cyclohexylcyclohexenes. They report the reaction of t-hexylborane with 2-(1-cyclohexen-1-yl)cyclohexanone, *cis*-2,6-di(1-cyclohexen-1-yl)cyclohexanone and related alcohols and ketals. All reactions are selective for products with *erythro* linkages between cyclohexyl rings; diastereoselectivities ranged from 66 to 97%. Greatest *erythro* selectivities were observed for equatorial homoallylic alcohols and ethylene ketals. The configurations of all products were unambig-





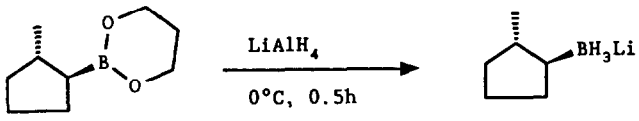
uously assigned by correlation with [1,1'-bicyclohexyl]-2,2'-diones and an *erythro*, *erythro* triketone [9].

Nishiguchi and his coworkers describe a novel method for hydroboration of olefins *via* electrolysis using a breaker-type undivided cell with a platinum foil as an anode and a stainless plate as a cathode [10].

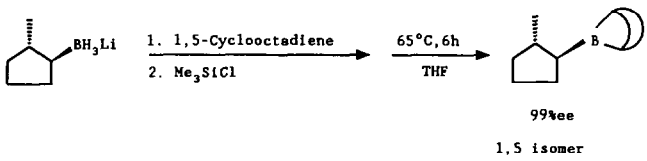


2.1.2. RBH_2

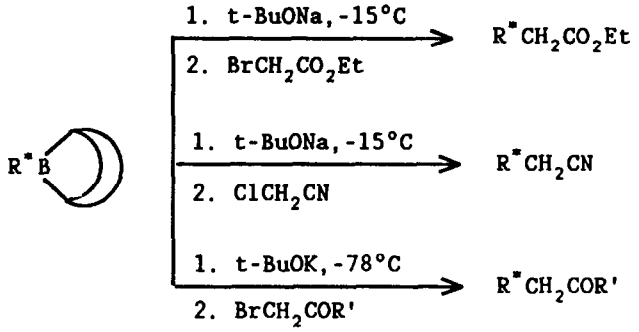
Brown and his group reported a convenient and simple procedure for the synthesis of various optically active B-alkyl-9-borabicyclononanes *via* chiral monoalkylboranes generated *in situ*. These are valuable reagents for chiral synthesis proceeding through boron intermediates. Since (+)- and (−)-α-pinene are readily available, both borane enantiomers can be prepared. Chiral alkylboronic esters and monoalkylboron hydrides are exceptionally promising intermediates for carbon–carbon bond-forming reactions. A major breakthrough involved the discovery that $LiAlH_4$ readily converts relatively inert chiral boronic esters



into reactive lithium monoalkylborohydrides which can then be utilized in hydroboration reactions with retention of chirality. These optically active B-alkyl-



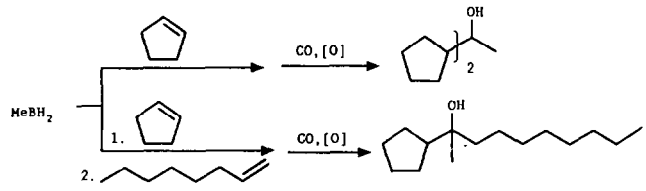
9-borabicyclononanes alkylate various α-halogenated derivatives stereospecifically in the presence of base. Consequently, it is now possible to synthesize a variety of optically active functional derivatives using asymmetric hydroboration coupled with a number of homologation reactions.



[where R* is chiral]

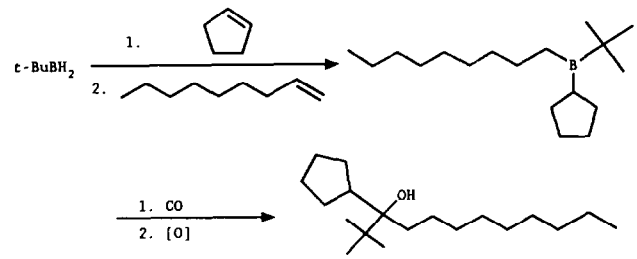
Attempts to use sterically hindered B-alkyl-9-borabicyclononanes such as B-(*trans*-2-methylcyclohexyl)-9-borabicyclononane gave poor results [11].

Srebnik, Cole, Ramachandran and Brown studied the controlled, sequential hydroboration of simple alkenes with monoalkylboranes and concluded that methylborane ($MeBH_2$), n-butylborane ($^nBuBH_2$), isopropylborane ($^iPrBH_2$), sec-butylborane ($^sBuBH_2$) and tert-butylborane ($^tBuBH_2$) all cleanly monohydroborate internal alkenes to yield mixed dialkylboranes, R^1R^2BH. $^tBuBH_2$ was found to be extraordinarily stable in THF at 0°C and room temperature. $MeBH_2$ is the only monoalkylborane that successfully hydroborates monosubstituted terminal alkenes such as

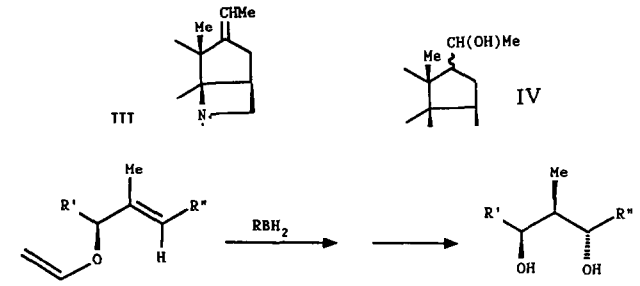


1-hexene. The readily available dialkylboranes R^1R^2BH can, in turn, be used as new hydroboration agents or transformed into borinic esters. Reaction

with different alkenes furnishes totally mixed trialkylboranes $R^1R^2R^3B$, which can then be converted into a number of difficult to obtain tertiary alcohols [12].



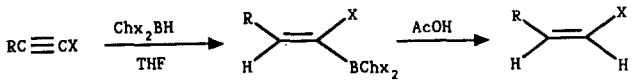
Harada, Matsuda, Uchimura and Oku described a highly stereoselective synthesis of 1,3-diols utilizing intramolecular hydroboration of allyl vinyl ethers using t-hexylborane [13].



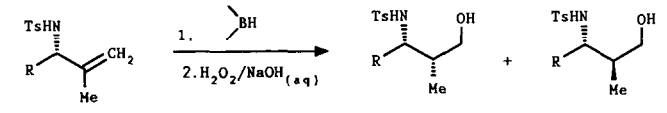
2.1.3. R_2BH

Brown and his coworkers report that the hydroboration of 1-halo-1-alkynes with dicyclohexylborane (Chx_2BH) yields C-1 monohydroboration products

which can be easily protonolyzed with acetic acid to give (*Z*)-1-halo-1-alkenes [14].

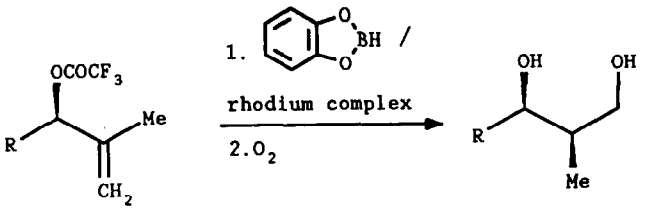


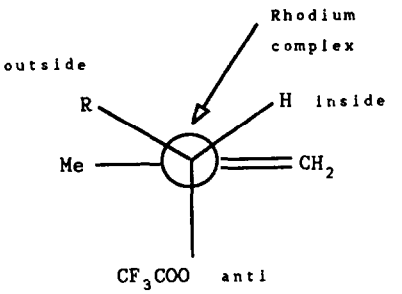
Burgess and Ohlmeyer describe substrate-controlled diastereoselectivity in catalyzed and uncatalyzed hydroborations of allylic amine derivatives. They conclude that rhodium catalyzed hydroborations tend to be *syn* selective and uncatalyzed hydroborations are *anti* selective [15].



	syn		*anti*
where R = $PhCH_2$ rhodium catalyzed	7.0	:	1.0
non catalyzed	1.0	:	1.0

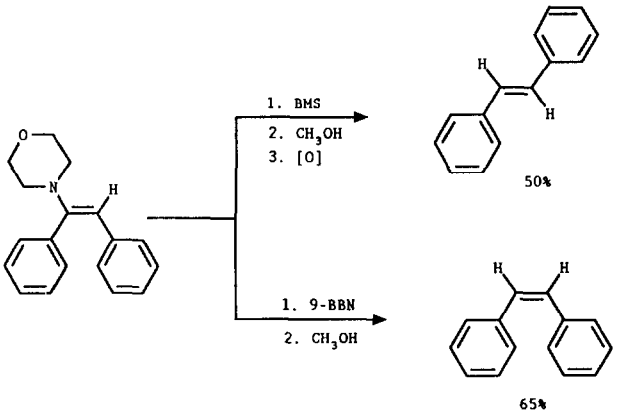
Burgess and Ohlmeyer developed a model for predicting the sense of diastereoselection in catalyzed hydroborations of allylic alcohols and amines derivatives. Electronic effects play an important role in reaction stereoselectivity. Trifluoroacetate (a good σ-acceptor) will orientate *anti* to the approaching



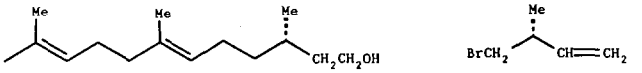


rhodium complex. In the non-catalyzed systems, the σ-donor occupies the conformational position *anti* to the approaching borane which follows Houk's [16] model for conventional hydroborations [17].

Brown and his coworkers developed a convenient conversion of aldehydes and ketones into the corresponding alkenes *via* hydroboration of their enamines. The appropriate selection of hydroboration procedures permits the conversion of a single acyclic ketone enamine into the corresponding (*Z*)- or (*E*)-alkene [18]. Hydroboration with BMS followed by methanolysis gives the corresponding dimethylboronate ester. The amino boronate ester on treatment with hydrogen peroxide affords the amine N-oxide which undergoes *cis* elimination. In contrast, hydroboration with 9-BBN affords the corresponding trialkylborane which on treatment with methanol undergoes a catalyzed *trans* elimination to produce the alkene.

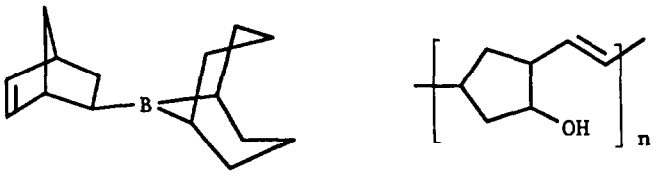


Moiseenkov, Koptenkova and Veselovskii developed a simple synthesis of (*S*)-(−)-terrestrol (**VIII**) in 65% yield *via* Grignard coupling of the chiral bromide (**VII**) with geranyl bromide followed by hydroboration with 9-BBN [19].



VIII VII

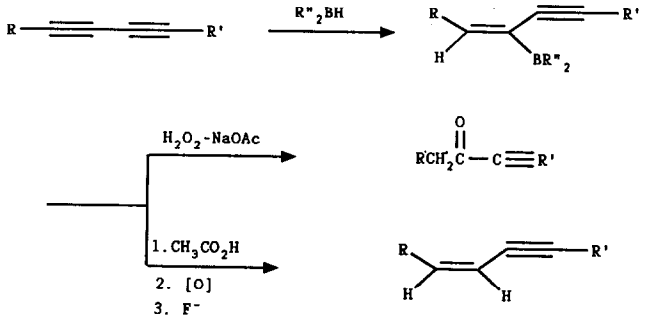
Chung and Ramakrishnan synthesized the hydroxyl group-containing polymer, poly(*exo*-5-hydroxynorbornene, **X**) by metathesis polymerization of **IX** (prepared by selective hydroboration of 2,5-norbornadiene with 9-borobicyclononane) at room temperature in the presence of WC_{16}–Me_4Sn catalysts and subsequent oxidation with alkaline H_2O_2 [20].



IX X

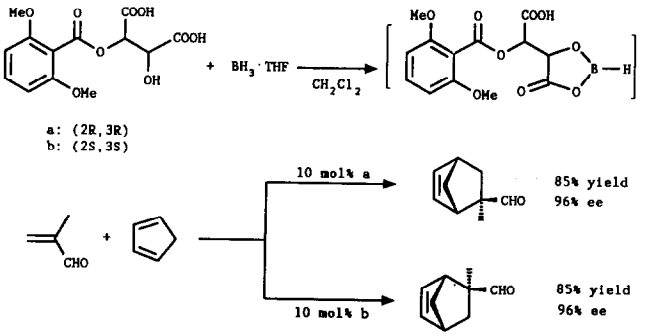
Zweifel and his group reported that chemo- and regioselective hydroboration of 1-(dimethyl-t-hexylsilyl)-1,3-diynes with dicyclohexylborane or with [bis(1,2-dimethylpropyl)borane] furnished organoboranes which

afforded, on protonation, (*Z*)-enynes and, on oxidation, alkynyl ketones [21].



R = n-C_6H_{13}, c-C_6H_{11}, Me_2thexylSi
R"= cyclohexyl (Cy), siamyl (Sia)
R'= Me_2thexylSi, (t-butyl)Me_2Si

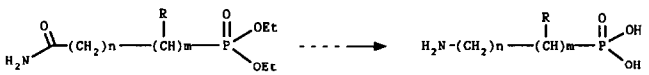
Furuta, Shimizu, Miwa and Yamamoto prepared chiral acyloxyborane (CAB) complexes as Lewis acid catalysts for the introduction of chirality. The practicality of this new method is one of its more attractive aspects; since chiral sources (tartaric acids) are easily obtainable in both enantiomeric forms, simple α,β-unsaturated aldehydes can be used without any derivatization, making further transformation of the adduct straightforward; only a catalytic quantity is needed [22].



2.2. Reducing agents

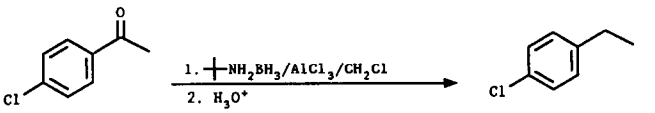
2.2.1. BH_3

Wasielewski, Dembkowski and Topolski used borane-dimethyl sulfide for the reduction of dialkoxyphosphorylcarboxamides as a new route to aminoalkylphosphonic acids [23].

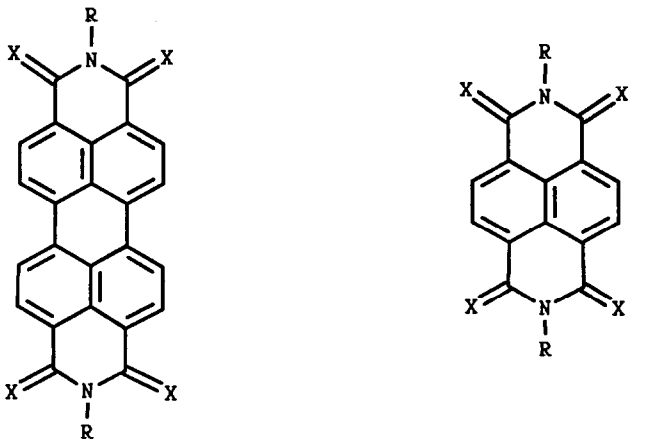


n = 1, 2, 3 m = 0, 1 R = H, CH_2, C_6H_5

Lau and his coworkers reported the reductive deoxygenation of aryl aldehydes and ketones by tert-butylamine-borane and aluminum chloride in chloromethane. The optimum ratio of reagents was found to be 1:3:6 for substrate (ketone or aldehyde) to aluminum chloride to tert-butylamine-borane substituent [24].

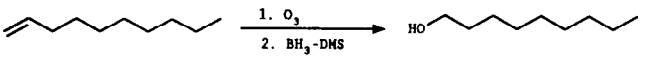


Hsu and Chiang used BH_3·THF in an efficient reduction of aromatic bis-imides to their amine derivatives in over 85% yield [25].

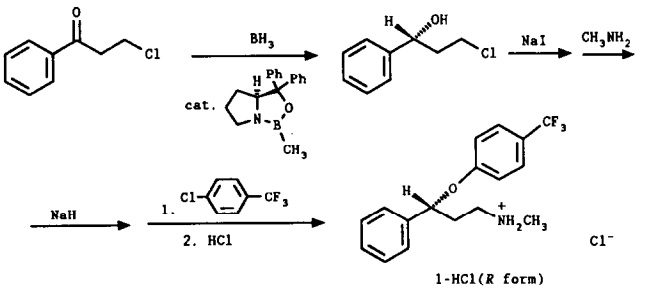


R = $C_{10}H_{21}$ X = O [before reduction]
X = H_2[after reduction]

Flippin and his coworkers developed a convenient method for the reduction of ozonides to alcohols with borane-dimethyl sulfide in methylene chloride solution. Employed at room temperature, the reagent is tolerant of the carboxylic ester functionality; in addition, the hydrolytic workup allows the application of this method to the preparation of water soluble alcohols [26].

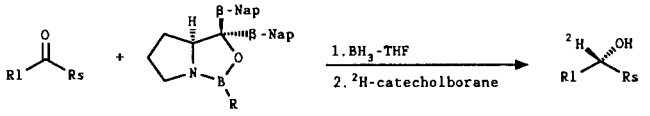


Corey and Reichard reported an efficient synthetic route to either (*R*)- or (*S*)-fluoxetine using a chiral, enzyme-like catalyst (chemzyme) to create the stereocenter of these enantiomerically pure therapeutic agents [27].

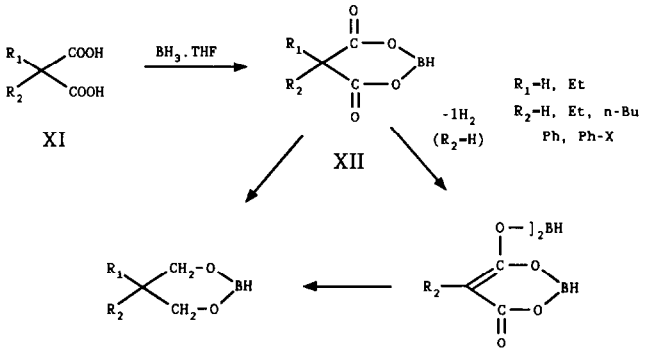


1-HCl(*R* form)

Corey and Link also prepared a new chiral catalyst for the enantioselective synthesis of secondary alcohols and deuterated primary alcohols by carbonyl reduction [28].

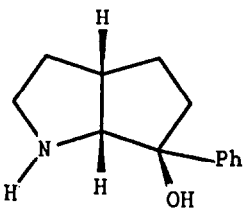


Choi and his coworkers monitored the effect of temperature on borane reduction of representative malonic acids, **XI**. The relatively stable cyclic intermediate **XII** has been synthesized and characterized. The exceptionally slow reduction seen in some cases is due to the intermediate formation of **XIII**. The data indicate that the use of low temperatures (−20°C) prevents formation of **XIII** (except for phenylmalonic acid, **XI**, R = Ph, which requires −30°C) [29]. At −20°C, most malonic acids are completely reduced in

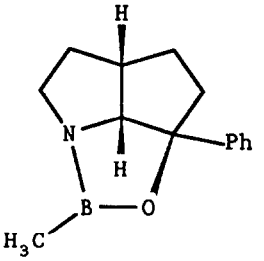


times ranging from 24 hours for aliphatic to 3 days for aromatic compounds.

Corey and Reichard described an efficient synthesis of (+)-1(*S*),5(*R*),8(*S*)-8-phenyl-2-azabicyclo[3.3.0]octan-8-ol, **XIV**, and its enantiomer. The B-methyloxazaborolidine derivatives, **XV**, are excellent catalysts for the enantioselective reduction of a variety of achiral ketones to chiral secondary alcohols, *e.g.* acetophenone, 98% ee; pinacolone, 98% ee; α-tetralone, 97% ee; and 2-bromo-2-cyclohexen-1-one, 98% ee [30].

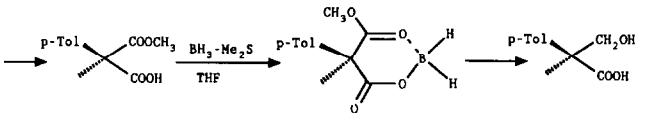


XIV

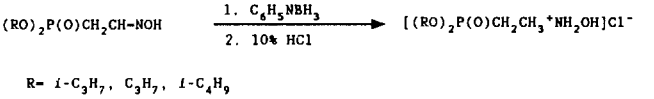


XV

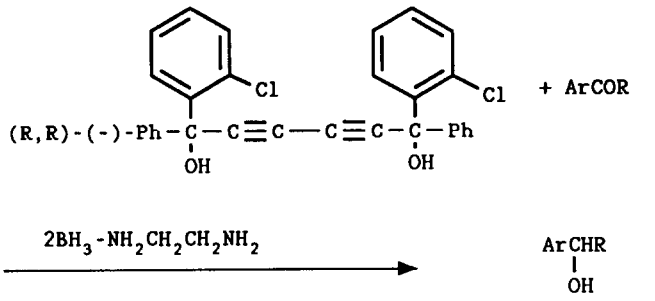
Fadel, Canet and Salaun report the reverse chemoselective borane reduction of an optically active malonic acid ester, with a likely formation of the six-membered ring monoacyloxyborane intermediate followed by an intramolecular hydride transfer [31].



Liorber, Pavlov and Khamatova, in studying organophosphorus compounds containing hydroxylamine groups, found pyridine-borane (in the presence) of HCl to be an effective reducing system for phosphorylacetaldehyde oximes. The corresponding hydroxylamines are separated as hydrochlorides [32].

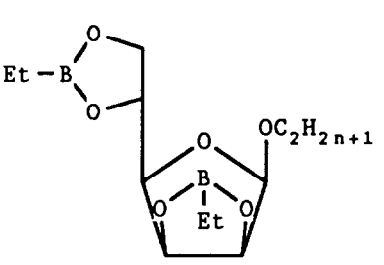


Toda and Mori found that host–guest inclusion compounds, formed from ketones and (*R*,*R*)-(−)-1,6-di(*o*-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol, were enantioselectively reduced with BH_3-ethylenediamine complex to the (*R*)-alcohols [33].

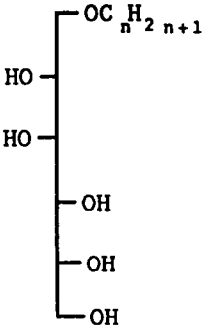


2.2.2. RBH_2

Dahlhoff used 9-methanesulfonyloxy-9-borabicyclo [3.3.1]nonane and ethyldiborane in the regioselective reduction of a homologous series of mannofuranosides, **XVI**. After deboronation, the mesogenic mannitols, **XVII**, are obtained [34].



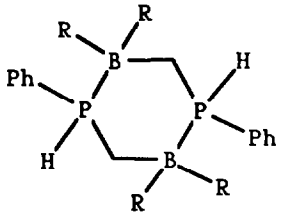
XVI



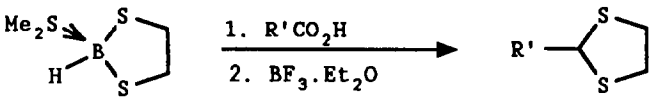
XVII

2.2.3. R_2BH

Efremov and Nekhoroshkov studied the interaction of dicyclohexylborane with [(dimethylamino)methylene]phenylphosphine. Reaction of 2 equivalents of R_2BH (R = cyclohexyl) with $PhP{=}CHNMe_2$ in $THF \cdot Et_2O$ gave 66% of the dimer [35].



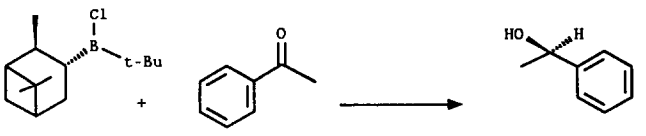
Kim, Lin and Kim prepared a dithiaborolane complex from 1,2-ethanedithiol and $Me_2S \cdot BH_3$ and treated it with $R'CO_2H$ (R' = alkyl, alkenyl, cyclohexyl, adamantyl, Ph, BrC_6H_4, tolyl, anisyl, substituted alkyl, PhCH=CH) and $BF_3 \cdot Et_2O$ to give dithiolanes [36].



2.2.4. R_3B

Yamamoto, Maruoka, Furuta and Naruse reviewed new approaches for natural product syntheses using main group organometallic reagents; organoboron-mediated asymmetric reactions play an important role [37]. Midland reviewed asymmetric reductions with organoborane reagents in which the active hydride is derived from the alkyl group of the organoborane [38]. Woodling described the development and mechanism of asymmetric reducing and hydroborating reagents [39].

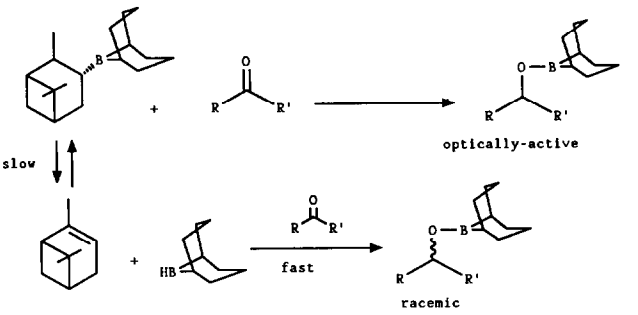
Brown and his group studied the effect of the steric requirements of the alkyl substituent in isopinocampheylalkylchloroboranes for the asymmetric reduction of representative ketones. They prepared IpcBRCl where R = Me, Et, ^{i}Pr, Cyp, ^{t}Bu, and Thx. ^{d}IpcB^{t}BuCl holds promise as a complementary reagent to ^{d}Ipc$_2$BCl; the chiral auxiliary α-pinene is available in both enantiomeric forms and it can be recovered completely. The reagent is superior to ^{d}Ipc$_2$BCl both for enone reductions and for the reduction of α-keto esters [40]. The study demonstrates the importance of the R group,



R, 90% ee

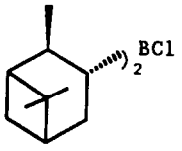
importance of the R group, both on the effectiveness of the chiral reduction and on the absolute configuration of the product.

Midland and his coworkers reported the asymmetric reductions of prochiral ketones with B-3-pinanyl-9-borabicyclo[3.3.1]nonane (alpine-borane) at elevated pressures. The reduction of unhindered ketones provides a simple means of forming chiral, nonracemic alcohols of known absolute configuration in high enantiomeric purity. A dehydroboration–reduction mechanism leading to the racemic alcohol is believed to be responsible for erosion of the enantiomeric efficiency with more hindered ketones. The use of elevated pressures (2000–6000 atm) accelerates the asymmetric reduction mode while suppressing the undesired dehydroboration mode. In studying the reduction of ketones containing chiral centers, the absolute configur-

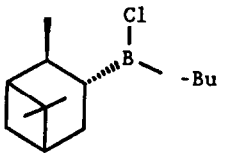


ation of the product can be predicted based on a simple model. The relative steric requirements of groups on the ketone may be categorized as very small (C≡CH, C≡N, H, D); small (CH_3, CO_2CH_3); medium (n-alkyl, *trans*-RHC=CH); medium large (CF_3, ^{i}Pr); large (Ar); and too large (tert-butyl). Effective asymmetric reductions are achieved when groups from non-adjacent catagories are attached to the carbonyl [41].

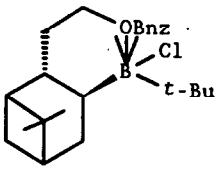
Brown and Ramachandran studied the asymmetric reduction of prochiral ketones by iso-2-methyl-, iso-2-ethyl-, and [iso-2-[2-(benzyloxy)ethyl]apopinocampheyl]-tert-butylchloroboranes. The data support the hypothesis that the steric requirements of the substituent at the 2-position of apopinene is a major factor in achieving successful asymmetric induction. The authors synthesized two new reagents, [iso-2-[2-(benzyloxy)ethyl]apopinocampheyl]-tert-butylchloroborane, **XX**, and (iso-2-ethylapopinocampheyl)-tert-butylchloroborane, **XXI**, and compared them with diisopinocampheylchloroborane, **XVIII** and isopinocamphyl-tert-butylchloroborane, **XIX**, for the chiral reduction of aliphatic ketones. **XX** and **XXI** were very effective in transferring chirality to the reduction products, although the rates of reduction were slow [42].



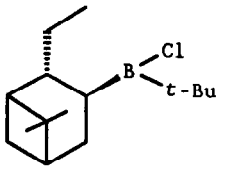
XVIII



XIX



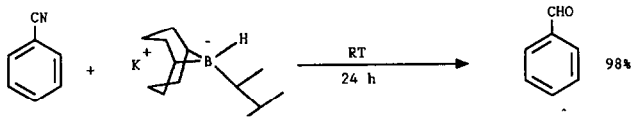
XX



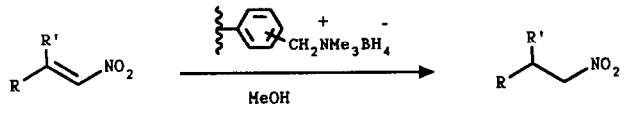
XXI

2.2.5. R_4B^-

Cha and Yoon prepared potassium 9-sec-amyl-9-boratabicyclo[3.3.1]nonane and used it in a selective reduction of aromatic nitriles to aldehydes in 60–98% yields; aliphatic nitriles were unaffected [43].



Kabalka and his group reported the use of borohydride supported on an ion exchange resin in the reduction of α,β-unsaturated nitroalkenes to nitroalkanes in high yields. The isolation of the pure products by simple filtration is the key feature of this method [44].



Yoon, Yang and Hwang describe $KBHEt_3$ as a selective reagent for the reduction of esters. Ethyl esters are selectively reduced in the presence of tert-butyl esters [45].

Wrackmeyer and Horchler prepared trimethyllead-lithium, $[Me_3Pb]Li$ in THF and used it in a stoichiometric 1 : 1 reaction with $BH_3 \cdot THF$ leading to a lithium trimethylplumbyltrihydridoborate, $[Me_3PB \cdot BH_3]Li$, an unstable borate that decomposes above $-30°C$ [46].

Hubbard described a convenient general method for the preparation of sodium trialkylhydroborates. Trialkylboranes in THF, even those with large steric requirements, react readily with toluene solutions of sodium diethyldihydroaluminate in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) [47].

$$NaEt_2AlH_2 + R_3B \longrightarrow NaR_3BH + Et_2AlH$$

Herdewijn studied the reaction of lithium triethylborohydride with the 2',3'-di-*o*-*p*-tolylsulfonyl derivatives of 9-β-D-ribofuranosyladenine, 9-β-D-arabinofuranosyladenine, 9-β-D-xylofuranosyladenine and 9-β-D-lyxofuranosyladenine [48].

2.3. Mechanism and theory

2.3.1. Theory

Ruscic, Schwarz and Berkowitz, studied the molecular structure and thermal stability of diborane(4) and tetrahydrodiboron(1 +) (B_2H_4 and $B_2H_4^+$) species. The adiabatic ionization potential of B_2H_4 (9.70 ± 0.02 eV) and the vertical value (≃ 10.4 eV) are obtained from the photoion yield curve. The values, and the shape of this curve, are consistent with a doubly bridged, C_{2v} structure for both the neutral and ionic species. The fragment ion $B_2H_2^+$ is observed with an appearance potential of 11.535 ± 0.03 eV. This value, combined with previous results, yields $DO(B_2H_4\text{–}H) =$ 40.1 kcal mol^{-1}, whereas $DO(B_2H_5\text{–}H) \leqslant 102.7$ kcal mol^{-1}. The $B_2H_2^+$ fragment may have as its neutral precursor an isomeric B_2H_4 (D_{2d}), with approximately the same stability as the C_{2v} species [49].

The same authors generated the B_2H_5 radical by the reaction of F + B_2H_6 and studied the photoionization mass spectrometry of the radical. The photoion yield curve for $B_2H_5^+$ (B_2H_5) is extremely weak at the adiabatic threshold (≃ 6.945 eV), at least three orders of magnitude weaker than at its maximum (≃ 9.67 eV). This observation provides support for recent *ab initio* calculations, which predict a singley bridged B_2H_5 and a triply bridged $B_2H_5^+$ as ground states. Coexistence of a doubly bridged B_2H_5 isomer, ≃ 0.3 kcal mol^{-1} higher in energy was also observed. From the appearance potential of $B_2H_3^+$ (B_2H_5), a B_2H_5–H bond energy of 102.7 kcal mol^{-1} is obtained. From the photoion yield curve of $B_2H_3^+$ (B_2H_5), at least one, and perhaps two, excited states of B_2H_5 can be inferred. The lower one also branches into parent B_2H_5 which is an apparent violation of QET [50].

Barone and Minichino performed an *ab initio* MO calculation on the binary association complexes of B_2H_6 and aluminum boron hydride ($AlBH_6$). The greater stability towards neutral dissociation of $AlBH_6$ with respect to B_2H_6 obtained at the Hartree–Fock level employing the 6-21G* basis set (≃ 10 kcal mol^{-1}) is reduced to only 2 kcal mol^{-1} when the basis set is sufficiently saturated and correlation energy properly included. The value of the activation energy for the

hydrogen scrambling in $AlBH_6$ is much less sensitive to the method used, although correlation still plays a significant role reducing the potential energy barrier from 11.4 to 7.7 kcal mol^{-1} [51].

Curtiss and Pople carried out theoretical studies on diborane(4) and tetrahydrodiboron(1 +) (B_2H_4 and $B_2H_4^+$). They refined the energies to the G1 level. The theoretical work is consistent with a bridged structure for B_2H_4. Theory also predicts an unbridged neutral isomer of comparable energy [52].

The same authors also presented an *ab initio* MO study of trihydrodiboron(1 +), diborane(2) radical ion(1 +), and diborane(2)ylium ($B_2H_3^+$, $B_2H_2^+$, and B_2H^+) at the G1 level of theory, including correlation energy beyond fourth-order perturbation theory and large basis sets. The structures of these ions are found to contain no hydrogen bridges in contrast to the to the $B_2H_6^+$, $B_2H_5^+$, and $B_2H_4^+$. Good agreement is found with a recent photoioization measurement of the appearance potentials of the $B_2H_3^+$ and $B_2H_2^+$ ions from B_2H_6 [53].

Cooper, Wright, Gerratt, and Hyams studied the comparative electronic structure of benzene, borazine and boroxine. They applied the spin-coupled theory to the π electrons, and they found marked differences between the spin-coupled descriptions of organic benzenoid systems and of the inorganic rings. Whereas the benzenoid aromatic molecules are stabilized by coupling the spins of the π electrons, this is not an important effect in borazine and boroxine. The spin-coupled π orbitals for the boron heterocycles take the form of two distorted 2p orbitals on each N or O atom. One orbital is very localized while the other shows very significant delocalization onto neighboring B centers. Any special stabilization of these two molecules must arise almost entirely from distortion effects in the orbitals. However, borazine and boroxine are very similar and it is suggested that neither molecule has significant aromatic character [54].

Li and Kendall carried out an *ab initio* investigation focused on the chair and twist-boat transition structures for the reaction of HCHO with allylborane and allylboronic acid. The twist-boat transition structure is predicted to be 8 kcal mol^{-1} less stable than the chair.

Schulman and Disch studied the aspects of the thermochemistry of borabenzene and borepin by homodesmic reactions and *ab initio* 6-31G* SCF energies. The model compounds they used for these analyses include divinylborane, 3-boraheptatriene, and the pentadienyl and heptatrienyl cations [56].

Bock, Cederbaum, VonNiessen, Paetlu, Rosmus and Solouki identified the organo(oxo)borane, MeB≡O, spectroscopically through pyrolysis of 2-methyl-1,3,2-dioxaborolane-4,5-dione. The He(I)-photoelectron spectrum, MNDO MO calculations, and thermodynamic stability of MeB≡O were discussed [57].

Wickham-Jones, Moran and Ellison studied the photoelectron spectra of BH_3^- and BD_3^- and the electron affinities of borane were measured, $E_A(BH_3) = 0.038 \pm 0.015$ eV and $E_A(BD_3) = 0.027 \pm 0.014$ eV. The peak splittings and intensities demonstrate that the BH_3^- ion and neutral BH_3 have very similar geometries; the spectra are consistent with a planar structure for both species. An *ab initio* model verifies equivalent, planar geometries for both BH_3 and BH_3^-, with $re(BH_3^-) = 1.207$ Å and $re(BH_3) = 1.188$ Å [58].

Vormann and Dreizler investigated and interpreted the ^{11}B-quadrupole hyperfine structure in the rotational spectrum of phenyldifluoroborane in the torsional ground state of the BF_2 group. The measurements were made with a microwave Fourier transform spectrometer in the fre qu ency range between 5 and 8 GHz [59].

2.3.2. Kinetics

Nelson and her coworkers found good to excellent correlations of ionization potentials *vs.* relative reactivities of a variety of alkenes toward bromination, oxymercuration and hydroboration. The use of alkenes having a broad range of steric requirements and electronic effects reveals that bromination is independent of steric effects, while oxymercuration and hydroboration each exhibit a natural separation into sterically similar groups within which alkene IP's correlate with relative reactivities. The data indicate that the transition states of the rate-determinating steps of oxymercuration and hydroboration are similar but both are different from that of bromination [60].

Meads, Marsden, Harrison and Phillips used NMR spectroscopy to study the reaction between BX_3 (X = F or Br) and $TiCl_4$ with $R_1CH{=}CHCH_2SnR_3$ (R = Me, Bu or cyclohexyl; R_1 = H or Me). They report allyl group–bromine exchange occurs at −60°C. At higher temperatures (25°C), the allyltin reagent reacts readily with $BF_3 \cdot Et_2O$; the predominant solution tin product being Me_2Sn. $TiCl_4$ rapidly produces R_3SnCl and $[RCH{=}CHCH_2]TiCl_3$ at 30°C [61].

2.3.3. NMR / IR

Kirwan and Roberts studied the electron spin resonance of radicals derived from primary amine-boranes. Photochemical generated tert-butoxy radicals react with the primary amine-boranes ($RNH_2 \rightarrow BH_3$) to form the nucleophilic amine-boryl radical, ($RNH_2 \rightarrow B \cdot H_2$) which subsequently abstracts hydrogen from the parent amine-borane to give the more stable isomeric aminylborane radical ($RN \cdot H \rightarrow BH_3$). The amine-boryl radicals can be intercepted by alkyl bromides or chlorides

or by nitriles, with which they react by halogen-atom abstraction or by addition to the CN group to give iminyl radicals, respectively. The ESR spectra of the aminyl-borane radicals show the presence of extensive hyperconjugative delocalization of the unpaired electron onto the BH_3 group. Monoalkylaminyl-borane radicals react readily with alkenes, with arenes, and with conjugated or cumulated dienes to transfer a β-hydrogen atom from boron to give alkyl, cyclohexadienyl, or allyl radicals, respectively [62].

Van Haveren, Peters, Batelaan and Kieboom, used ^{11}B and ^{1}H NMR spectroscopy, to determine that the apparent association constants for borate esters of 2-amino-1,3-diols are pH dependent. The studies also showed that boric acid ester formation can be detected using ^{11}B NMR [63].

Chapelle and Verchere used ^{11}B and ^{13}C NMR spectroscopy to study the structures of borate complexes of D-allose, D-talose, and D-psicose. They report that two 1: 2 complexes can be formed, depending on whether the sugar is α or β. The main species involved *cis*-HO-1,2. D-Psicose formed a single complex at HO-2,3. A second species was formed by D-talose (10%), D-ribose (30%), and D-allose (30%), which involved *cis*-HO-2,3 with *trans*-HO-1,2. They show the order of stabilities of the complexes was D-psicose > D-ribose > D-talose > D-allose. They also discussed the high affinity of ribo sugars towards borate. They found there was no correlation between the stability constants and the relative proportions of 1:2 complexes [64].

Currie, Bowie, Downard and Sheldon discussed the possibility of the formation of tetrahedral intermediates upon addition of nucleophiles to organoboranes in the gas phase. Nucleophilic addition of CD_3O^- to Me_2BOMe gives the same addition product as the corresponding reaction between Me_2BOCD_3 and MeO^- as evidenced by the identical collisional activation mass spectra of the products. This is interpreted in terms of exclusive formation of a boron product ion of tetrahedral geometry [65].

Kabalka and his group developed whole-body magnetic resonance imaging and spectroscopy protocols as tools for investigating pharmacokinetics for boron neutron capture therapy. ^{11}B MRI images hold promise for quantification of BNCT agents in organs such as liver and brain [66].

2.3.4. Structure

Matteson and his group prepared [(1*R*)-1-acetamido-3(methylthio)propyl]boronic acid and studied the X-ray structure of its ethylene glycol ester. They found that the oxygen atom of the acetamido group is coordinated to the weakly acidic boron atom. The five-membered 1,3,2-dioxaborolane ring is nonplanar, in accord with the chiral induction properties of 4,5-disubstituted 2-alkyl-1,3,2-dioxaborolanes in their reactions with (dihalomethyl)lithiums [67].

Imamoto and Oshiki synthesized organic-phosporus compounds containing a linear P–B bond chain. They note that some charge alternations may exist in these molecules, since phosphorus and boron atoms possess +1 and −1 formal charges, respectively. These characteristic bond sequences might be responsible for peculiar properties of the compounds [68].

Schmidbaur, Wimmer, Grohmann, Steigelmann and Mueller prepared 1 : 2 addition compounds, *e.g.* $H_2BrBPMe_2PMe_2BBrH_2$, from Me_2PPMe_2 with BH_3, BH_2Br, $BHBr_2$, BBr_3, and BH_3. Open chain and cyclic phosphineborane cations were obtained. Compounds in the molar ratio 2:1 or 1:1 were obtained from Me_2PPMe_2 and $H_2BrB \cdot SMe_2$, respectivly [69].

Brooks, Cole and Robins report that cyclic boronate derivatives of some alkaloid and terpenoid diols are suitable derivatives for gas chromatography-mass spectrometry. Cyclic ferroceneboronates of the alkaloidal diols retronecine, platynecine, rosmarinecine and swainsonine, and the bis-methaneboronate of aphidicolin were presented as examples [70].

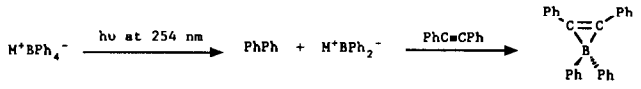
Karsch, Hanika, Huber, Meindl, Koenig and Krueger used X-ray crystallography to determine the influence of the boron substituents on the structures of monomeric diphosphinoboranes. They show that the phosphorus–boron (P–B) multiple bonding may be inferred from the molecular structure [71].

Fehlhammer, Hoffmeister and Boyadjiev reported the X-ray structure analysis of (*trans*-4,5-dimethyloxazolidin-2-ylidene)triphenylboron. (Oxalato)(2,4-hexanedionato)boron was synthesized by the reaction of boric acid with 2,4-hexanedione and oxalic acid, the structure consists of discrete molecules containing tetrahedrally coordinated B atoms with an average B–O distance of 1.461(6) Å. The acetylacetonato moiety is consistent with the fully delocalized and symmetrical description [72].

Economou, Papageorgiou and Kopf prepared and studied the structure of (oxalato)(2,4-hexanedionato) boron. The structure consists of discrete molecules containing tetrahedrally coordinated B atoms with average B–O distance of 1.461(6) Å [73].

2.4. Synthesis

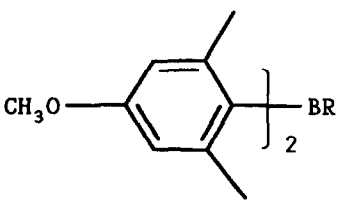
Eisch and his coworkers studied the photochemical generation of the diphenylborate anion from metal tetraphenylborates in aprotic media, they repudiated a contravening claim [74].



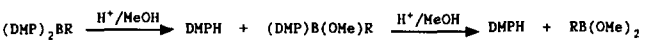
Brown prepared optically pure borinic esters $RR'BOR^2$ (R = chiral organyl moiety; R' = achiral aliphatic, alicyclic, aromatic, heterocyclic or alkynyl moiety; R^2 = cyclic organyl compounds < 10 C atoms) by treating $RB(OR^2)_2$ with R'Li and then with ethereal HCl, AcCl or Me_3SiCl at −78°C [75].

Gol'dberg, Abele, Liepins and Shimanskaya prepared sodium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate from the Grignard reagent and NaBF4 [76].

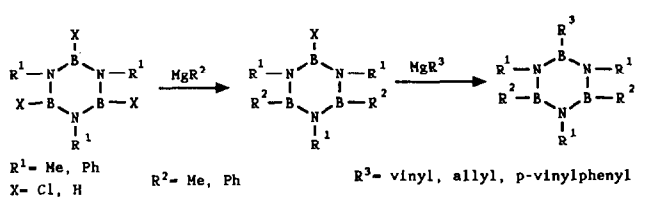
Pelter, Drake and Stewart developed bis[2,6-dimethyl-4-methoxyphenyl]boron, $[(DMP)_2B]$, as a new, readily solvolyzed carbanion stabilizing group. $(DMP)_2$ BR compounds are readily prepared *via* hydroboration



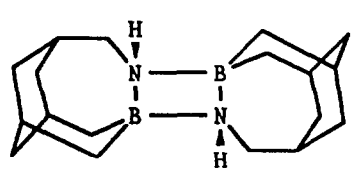
or metal exchanges. These agents undergo proton abstraction to yield boron stabilized carbanions. Interestingly, mineral acid solvolysis removes the DMP groups while leaving alkyl and alkenyl groups bonded to boron which provides an alternate route to a variety of boronic acids [77].



Jackson and Christopher prepared a series of unsymmetrically B-substituted, N–Me and N–Ph borazines by the substitution reaction of $Cl_3BN_3Me_3$ and $H_3B_3N_3Ph_3$ with a Grignard reagent [78].



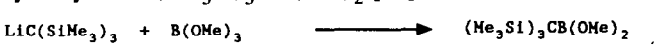
The molecular structure and synthesis of the 4-aza-3-borahomoadamantane dimer was described. An isomeric mixture of the title dimer was prepared by adding NaOCl to 1-boraadamantane ammoniate followed by heating to 180°C. The following dimer was identified [79].



Wang described the synthesis of potassium tetra(*m*-chlorophenyl)borate [80]. Haubold and his coworkers found that the pyrolysis of alkyldichloroboranes such as CH_3BCl_2, $Cl_2BCH{=}CHBCl_2$, $Cl_2BCH_2BCl_2$ or $(Cl_2B)_3CH$ at 450°C forms hexachlorohexaboradamantane as detected by X-ray diffraction and spectroscopic data [81].

Preparation of trityl tetraphenylborate from trityl triflate and $NaBPh_4$ was reported. The reagent is a useful hydride and methyl anion abstractor. It reacts with $(\eta^5\text{-}C_5Me_5)(PMe_3)_2RuMe$ to give the fulvene complex $[(\eta^4\text{-}C_5Me_4CH_2)(PMe_3)_2RuMe]BPh_4$, and with $(\eta^5\text{-}C_5H_5)_2ZrMe_2$ in acetonitrile-d_3 to afford the cationic methyl derivative $[(\eta^5\text{-}C_5H_5)_2ZrMe(NCCD_3)]BPh_4$ [82].

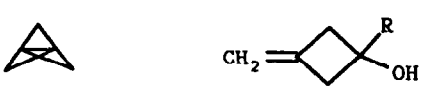
Eaborn, Smith and their coworkers described the preparation of tris(trimethylsilyl)methyl derivatives of boron, $(Me_3Si)_3CB(OMe)_2$. The latter converted by hydrolysis to $(Me_3Si)_3CB(OH)_2$ [83].



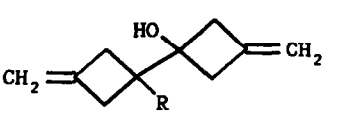
Koester, Schuessler and Yalpani studied the reduction of polycyclic arenes with boranes where naphthalene, anthracene or phenanthrene reacted with tetraalkyldiboranes at ⩾ 130°C to form borylated hydroarenes [84].

Yalpani, Lunow and Koester reported that tetrapropyldiborane and triethylborane catalyze the regioselective, partial hydrogenation of naphthalene and a number of substituted naphthalenes at 170–200°C. Naphthalene derivatives are mainly hydrogenated in the least substituted ring. In the case of alkyl substituents, Lewis acid catalyzed migration and, to a lesser extent, C–C bond rupture lower the yield of the main tetralin derivative. Chlorinated naphthalenes and O-derivatized naphthols also undergo partial loss of oxygen or chloro functional groups [85].

Bubnov, Lavriovich, Ignatenko, Sadovaya, Surmina, Koz'min and Zefirov demonstrated the electrophilic cleavage of propellane **XXII**, with R_3B (R = Pr, allyl) borane intermediates which were oxidized to give cyclobutanols **XXIII** and dicyclobutanols **XXIV** [86].

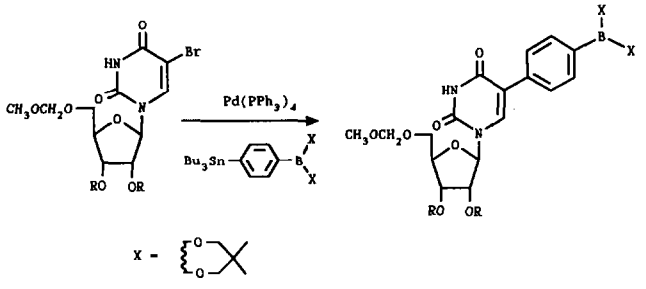


XXII XXIII



XXIV

Yamamoto and his coworkers described a new method for the synthesis of boron-10 containing nucleosides for potential use in neutron-capture therapy. The reaction proceeds chemoselectively at the C–Sn bond rather than the C–B bond to give the desired product [87].

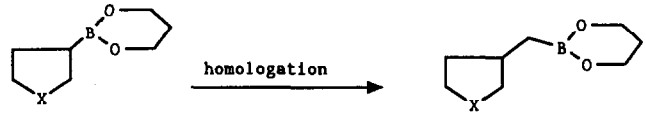


3. C–C bond formation

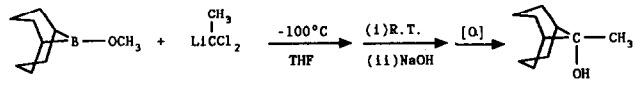
3.1. Homologation

Many synthetic methods involving carbon–carbon bond formation are now based on organoborane chemistry [88]. In the last decade new reactions and reagents have emerged for the conversion of organoboranes into complex organic molecules under very mild conditions [89]. Carbanionic reagents bearing a potential leaving group at the α-position can be utilized in borane homologation reactions; the reactions proceed through the formation of a borate complex followed by a 1,2-migration of the organic group from boron to the adjacent center with concomitant displacement of the leaving group. This offers a convenient and practical way to achieve C–C bond formation *via* organoboranes.

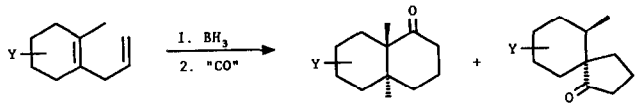
Brown and his group expanded the one-carbon homologation to reactions with heterocyclic boronic esters. The procedure involves the use of $LiCH_2Cl$, generated *in situ* by the reaction of $BrCH_2Cl$ and BuLi in THF at $-78°C$ in the presence of an enantiomerically pure heterocyclic boronic ester. The heterocyclic boronic esters were prepared *via* asymmetric hydroboration of representative heterocyclic olefins bearing either an endo-cyclic or exo-cyclic double bond using either Ipc_2BH or $IpcBH_2$ [90].



Hongxun and his coworkers reported that the reaction of various borinic esters with (1,1-dichloroalkyl) lithium, followed by treatment with base and hydrogen peroxide, provides a facile route to tertiary carbinols [91].

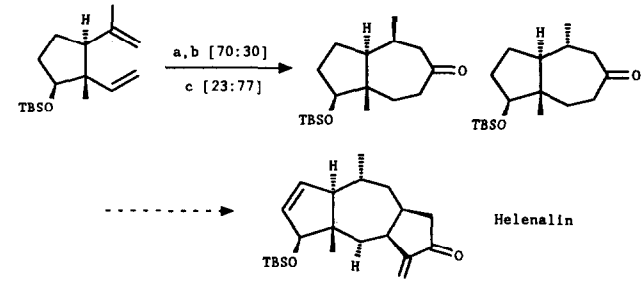


Akers and Bryson studied boron decalone annulations employing tetrasubstituted olefins. They report that the electronic β-effect of allylic silicon strongly influences the hydroboration selectivity [92]. The *trans*-decalin system was formed exclusively with the



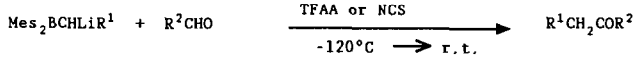
β-$Si(CH_3)_2Ph$ derivative. The reaction also proved to be selective for *trans*-decalin formation *vs.* spiroannulation with $Y = (OCH_2)_2$.

Welch and Bryson also studied the stereochemical aspects of boron cycloheptanone annulation; they synthesized (±)-helenalin [93].



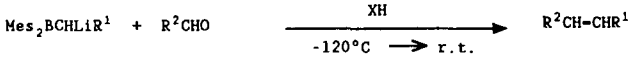
a $ThxBH_2$; NaCN; $(CF_3CO)_2O$; NaOH, H_2O_2
b ThxBrBH, KIPBH; NaCN; $(CF_3CO)_2O$; NaOH, H_2O_2
c H_2BBr-DMS, C_5H_{12}; CH_3ONa, CH_3OH; Et_3COLi, CH_3OCHCl_2, THF; NaOH, H_2O_2

Pelter, Smith and coworkers investigated Boron–Wittig reactions. A unique [94] variant of the Boron–Wittig provided ketones from aliphatic aldehydes in the presence of trifluoroacetic anhydride (TFAA) or N-chlorosuccinimide (NCS).



R^1= alkyl; ≠ H
R^2= alkyl

A stereoselective synthesis of alkenes using aliphatic aldehydes was [95] described.

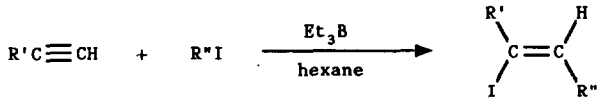


R^1= H, alkyl
R^2= alkyl
XH= CH_3CO_2H, CF_3CO_2H, CF_3SO_3H, HCl

Matteson reviewed α-halo boronic ester intermediates [96] in syntheses and also the use of boronic esters [97] in stereodirected synthesis.

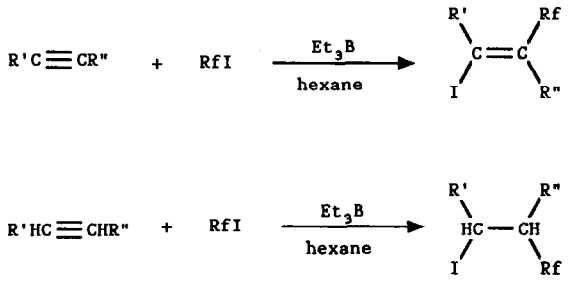
Oshima, Utimoto and coworkers treated terminal acetylenes with secondary or tertiary alkyl iodides in

the presence of triethylborane to yield the corresponding alkenyl iodides [98].



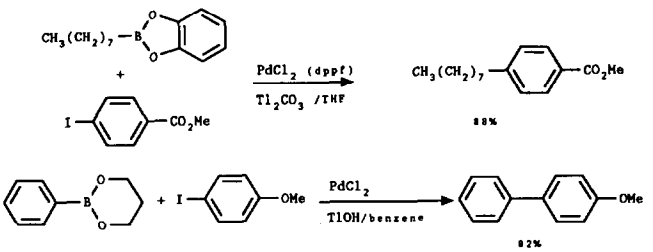
R'= Me_3Si R"= Et, n-C_6H_{13}, cyclohexyl, Me_3SiCH_2

Oshima and Utimoto also treated terminal or internal acetylenes bearing a variety of substituents with perfluoroalkyl iodides in the presence of a catalytic amount of triethylborane to provide the corresponding perfluoroalkenes. They described the addition of perfluoroalkyl iodides to olefins [99].

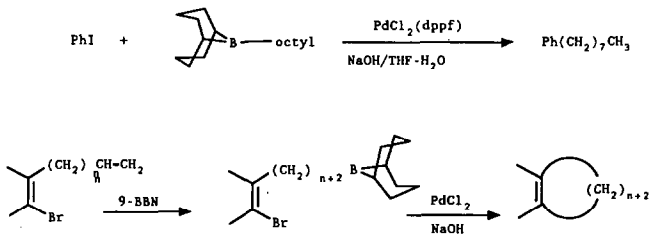


R'= n-$C_{10}H_{21}$, $HOCH_2CH_2CH_2$, $EtOOC(CH_2)_8$, Ph
R"= H, n-C_5H_{11}
Rf= C_6F_{13}, $(CF_3)_2CF$, CF_3

Suzuki and his group reported that the cross-coupling reaction of alkylboronic acid esters with 1-alkenyl or aryl halides is successfully catalyzed by $PdCl_2$ or $Pd(PPh_3)_4$ in the presence of thallium(I) to give the corresponding alkenes or arenes in good yields [100].

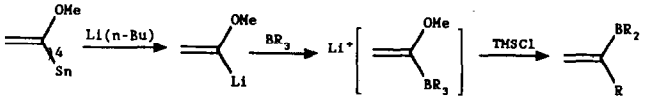


Suzuki also carried out an extensive study on palladium-catalyzed inter- and intramolecular cross-coupling reaction of B-alkyl-9-borabicyclo[3.3.1]nonane derivatives with 1-halo-1-alkenes or haloarenes. They studied the syntheses of functionalized alkenes, arenes and cycloalkenes *via* a hydroboration-coupling sequence [101].



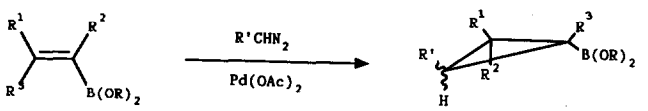
3.2. *Alkenylborate and arylborate*

Soderquist and Rivera prepared pure α-methoxyvinyllithium using a Sn/Li exchange reaction and found that the reagent reacts with trialkylboranes to form the corresponding "ate" complexes. These complexes rearrange in the presence of chlorotrimethylsilane to provide an efficient route to Markovnikov vinylboranes [102].



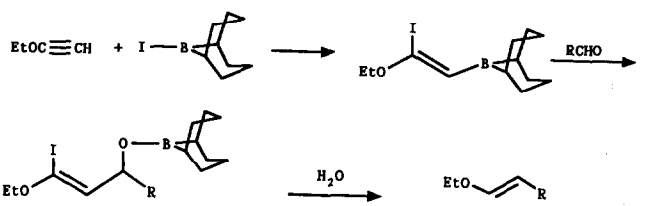
R_3= $(n\text{-}Pr)_3$, $(\text{-}Bu)_3$, $(CH_2TMS)_3$, Me-9-BBN, (n-Bu)-9-BBN

Carboni and his coworkers described a convenient, highly stereoselective synthesis of cyclopropylboronates. The carbenes, generated from diazo compounds in the presence of palladium acetate, add to vinylboronates thus achieving highly functionalized cyclopropylboronates [103].



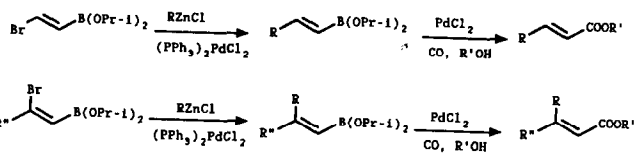
R^1= H, n-C_4H_9, Cl-$(CH_2)_3$, $(CH_3)_3Si$, CH_3OCO, $PhSCH_2$, CH_3, PhS
R^2= H, n-C_4H_9, CH_3
R^3= H, CH_3
R'= H
$B(OR)_2$= 

Suzuki and his coworkers described a haloboration adduct, formed by the reaetion of B-iodo-9-borabicyclo[3.3.1]nonane with ethoxyethyne, which in turn reacts with aldehydes chemoselectively under very mild conditions. The subsequent hydrolytic work-up affords *trans*-α,β-unsaturated esters in good yields [104,105].

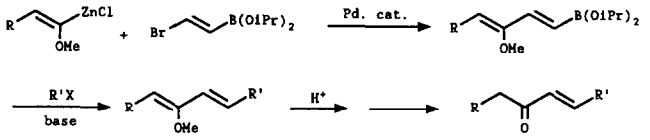


The thermal instability of the haloboration adduct prevented its full characterization.

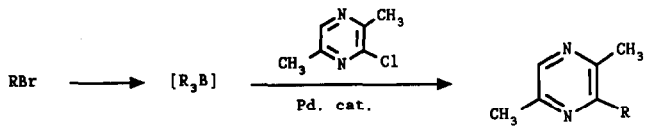
Suzuki and his coworkers reported the preparation of β-mono and β,β-disubstituted esters stereoselectively and in good yields by the stepwise alkylation and alkoxycarbonylation of 2-bromo-1-alkenylboronates [106]. The Suzuki group also reported the stereoselec-



tive synthesis of α,β-unsaturated ketones by the stepwise cross-coupling reaction of (*E*)-(2-bromoethenyl)diisopropoxyborane using a palladium catalyst [107].

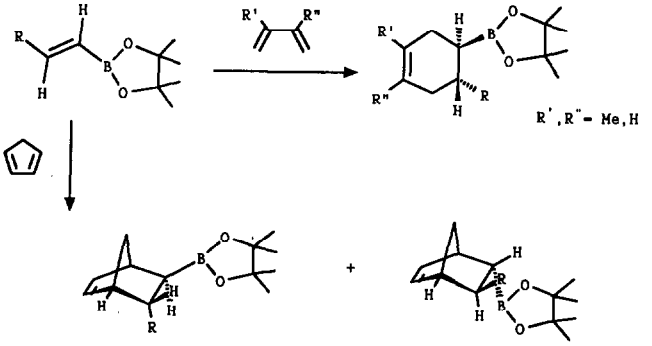


Ohta and his group described the palladium-catalyzed cross-coupling reaction of chloropyrazines with organoboron compounds prepared from Grignard reagents [108].



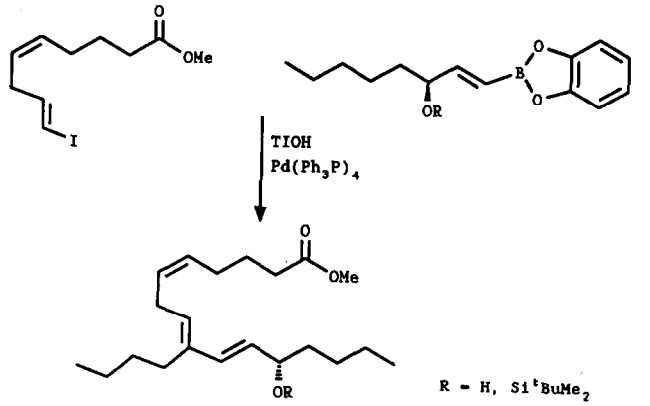
R = $CH_2CH_2CH(CH_3)_2$, $CH(CH_3)CH_2CH(CH_3)_2$

Vaultier and Fresneda describe the synthesis of *E*-vinylboronates β-substituted by an electron withdrawing group. They show that this new type of electron-deficient olefin undergoes a clean Diels–Alder cycloaddition to typical 1,3-dienes [109].



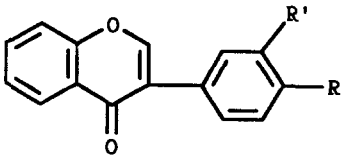
R= CO_2Me, PhSO, $PhSO_2$

Nicolaou and his coworkers prepared the methyl ester of the major metabolite of arachidonic acid, 12(*s*)-hydroxy-5*Z*,8*E*,10*E*-heptadecatrienoate based on a Pd^0-TlOH catalysed coupling reaction of the vinyl iodide and the vinylborane [110].



R = H, Si^tBuMe_2

Yokoe, Sugita and Shirataki prepared isoflavones by the cross-coupling reaction of 3-iodochromone with 4, 3-RR'$C_6H_3B(OH)_2$ catalyzed by $Pd(PPh_3)_4$ [111].

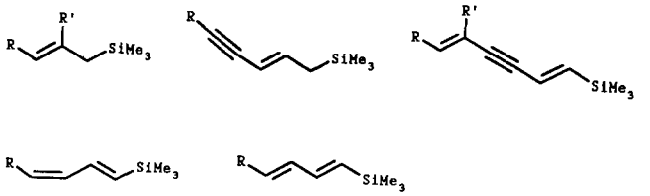


R = H, Me, OMe, R' = H; R = R' = OMe; RR' = OCH_2O

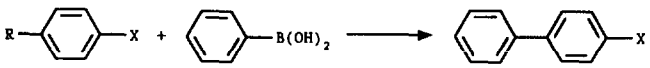
Soderquist and Colberg converted (*Z*)-2-(9-borabicyclo[3.3.1]non-9-yl)-1-propenyl(triisopropyl)silane to the corresponding (*E*)-2-substituted 1-triisopropylsilylpropenes in 80–90% yield and isomeric (> 99% *E*) purity [112].

Bumagin, Bykov and Beletskaya reported that the cross-coupling of aryl iodides with $PhB(OH)_2$ in H_2O containing Na_2CO_3 was catalyzed by $Pd(OAc)_2$ [113].

Andreini, Carpita, Roosi and Scamuzzi reported the palladium-catalyzed diastereoselective syntheses of (*E*)-1trimethylsilyl-2-alkenes, (*E*)-1-trimethylsilyl-1-alken-3-ynes, (1*E*,5*E*)-1-trimethylsilyl-1,5-alkadien-3-ynes, (1*E*,3*Z*)- and (1*E*,3*E*)-1-trimethylsilyl-1,3-alkadienes [114].

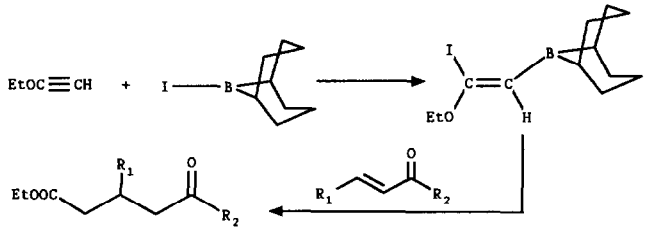


Huth, Beetz and Schumann describe the reaction of aromatic triflates of phenols with boronic acids as a valuable supplement to known arylation techniques. This method allows the replacement of an aromatic hydroxy group by an aromatic ring, avoiding the problem of working with tin or zinc compounds [115].



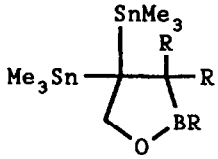
R = OSO_2CF_3
X = OCH_3, NO_2

Suzuki's group also reacted α,β-unsaturated ketones with B-iodo-9-borabicyclo[3.3.1]nonane/ethoxyethyne adduct *via* a Michael-type addition to give δ-keto esters in excellent yields [116].

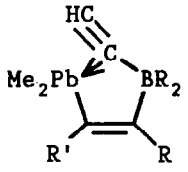


3.3. Alkynylborate

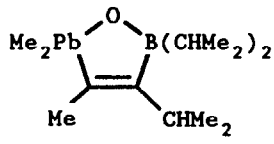
Wrackmeyer and his group studied the reactions of 3-(trimethylstannyl)-2-propynyl-1-ethers with trialkylboranes, they report that the product distributions are dependent on the substituents on boron, and on the presence of a Me_3SnO-group as well as on the substituents at the C-1 carbon atom. $Me_3SnC{\equiv}CR$ (R = CH_2OSnMe_3), when reacted with Me_3B, gave the new heterocycles, 2,3,3-trialkyl-4,4-bis(trimethylstannyl)-1,2-oxaborolanes in quantitative yields [117].



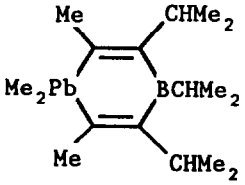
Wrackmeyer and his group also prepared alkynylborate-stabilized triorganolead cations **XXV** from $Me_2Pb(C{\equiv}CR')_2$ and R_3B. **XXVI** decomposed by intramolecular rearrangement to give **XXVI** and in the presence of MeOH to give **XXVII** [118].



XXV

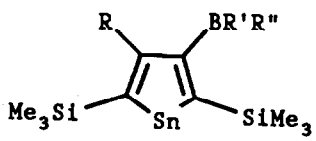


XXVI

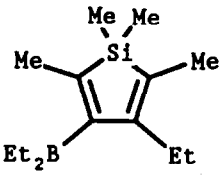


XXVII

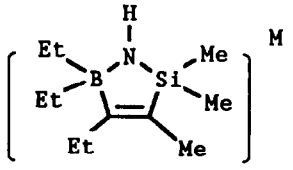
Wrackmeyer also studied the organoboration of bis(trimethylsilylethynyl)dimethylstannane by various noncyclic trialkylboranes and B-alkyl-9-borabicyclo [3.3.1]nonanes. In all cases stannacyclopentadienes were formed as the final products with Me_3Si groups in the 2,5-position and the boryl group in 3-position [119].



Wrackmeyer and his group prepared a substituted silol by the reaction of $Me_2Si(C{\equiv}CMe)_2$ with BEt_3. Reactions of MNH_2



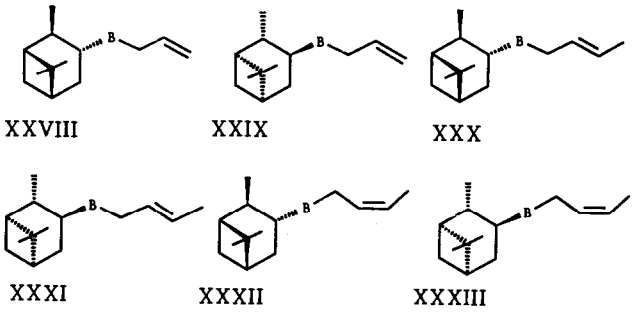
(M = Na, K) and (*E*)-[M]CMe=CMeBEt$_2$ ([M] = $SiMe_3$) below 0°C gave $MNH_2BEt_2CMe{=}CMe[M]$ which on warming eliminated alkane to give the azasilaborole [120].



Deng and Zhang reported *E*-addition reactions of lithium trialkylalkynyl borates with allyl acetate in the presence of $Pd(PPh_3)_4$ gave *E*-allylated alkenes as the major products in 70–83% yields [121].

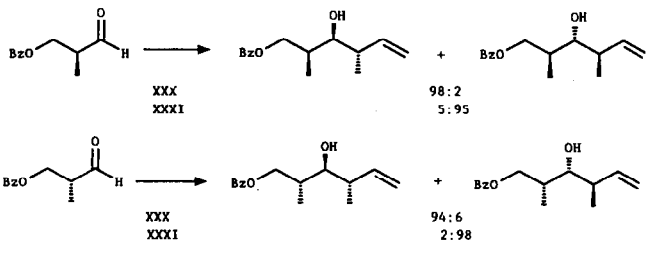
3.4. Propargyl and allylboranes

Brown and his coworkers prepared the B-allyldiisopinocampheylboranes (**XXVIII, XXIX**), (*E*)-crotyldiisopinocampheylboranes (**XXX, XXXI**) and (*Z*)-crotyldiisopinocampheylboranes (**XXXII, XXXIII**) for generating diasteriofacial selectivity in their reactions with α-substituted chiral aldehydes [122]. The crotylboranes, **XXX–XXXIII**, are highly diasterioselective reagents and the corresponding (3,4 and 4,5)-*anti,syn*, -*anti,anti*, and -*syn,anti* products have been obtained with very high selectivities.

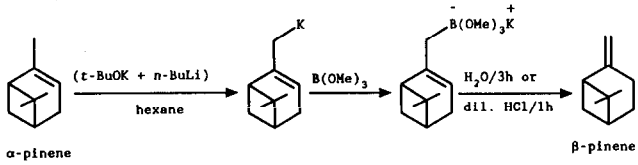


XXVIII XXIX XXX

XXXI XXXII XXXIII

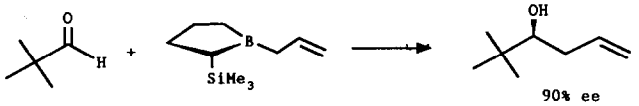


Brown and his group also improved the Schlosser allylic metalation of α-pinene. The (+)-α-pinene was added to the Schlosser reagent (1 : 1.5 molar ratio) and the organopotassium intermediate (without isolation) was treated with trimethoxy borate providing the "ate" complex which was hydrolyzed at room temperature to obtain the β-pinene in 80% yield ($\geq$ 99% isomeric purity) [123].

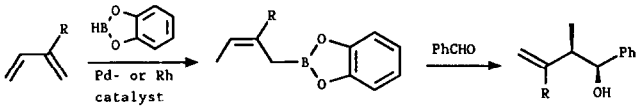


Short and Masamune used B-allyl-2-(trimethylsilyl) borolane reagents in asymmetric allylboration with a large number of aldehydes [124]. These reagents were more effective in asymmetric allylboration reactions

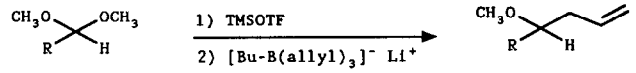
than the earlier reported *trans*-2,5-dimethylborolanes.



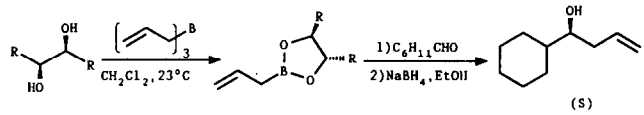
Suzuki and his group described a new convenient approach to the preparation of (*Z*)-allylic boronates *via* catalytic 1,4-hydroboration of 1,3-dienes with catecholborane [125].



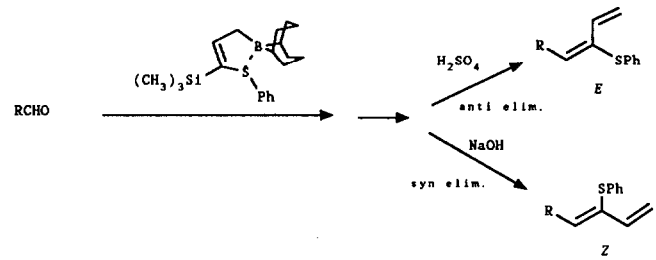
Hunter and Tomlinson reported a novel allylation procedure involving lithium n-butyltriallylborate acetals activated by trimethylsilyl trifluoromethanesulphonate (TMSOTF). They discussed the importance of compatibility of the Lewis acids and organometallic compounds [126].



Roush and his coworkers studied the rate and enantioselectivity of the asymmetric allylboration reaction and their dependence on the diol auxiliary. They concluded that the rates of these reactions are influenced by the structure of the diol. Steric effects decrease the reactivity (ethanediol ester > butanediol ester); inductive effects which increases the Lewis acidity of the boron atom increase the reactivity (tartrate esters are more effective than oxazoline derivatives R=CON-(Bzl)$_2$) [127].

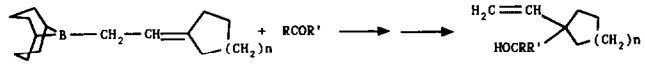


In an effort to apply their recent intramolecular cyclization methodology of azides with 2-(phenylthio)-1,3-butadienes [128] to alkaloid synthesis, Pearson and his coworkers developed an efficient method to prepare these dienes in a stereoselective fashion from aldehydes [129]. The allylborane was prepared from an

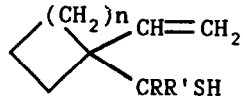


allene (available from 1-(phenylthio)-1-propyne by deprotonation) and 9-BBN.

Bubnov, Zheludeva and Ignatenko describe the addition reaction of allylic boranes containing exocyclic double bonds with RCOR' which proceed with complete allylic rearrangement; deboronation of the intermediate esters gives cycloalkylcarbinols. The boranes similarly react with EtOC≡CH to give divinylcycloalkanes [130].

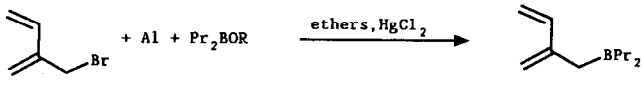


Bubnov, Zheludeva and Ignatenko described a new method of synthesising homoallyl mercaptans *via* reaction of thioketones with the appropriate allyl derivative of 9-BBN and subsequent treatment with $HOCH_2CH_2NH_2$ [131].

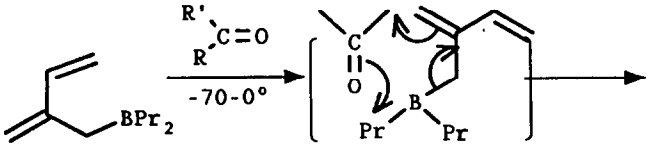


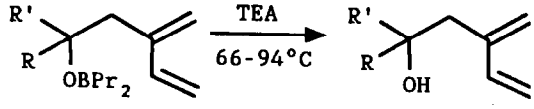
Sugano and Naruto reported that the aldol condensation of $PhCH_2OCH_2CO_2R'$ with RCHO and $CF_3SO_3BR_2$ gave mixtures of *syn*- and *anti*-compounds [132].

Bubnov, Etinger and Ignatenko prepared 2-dipropylborylmethyl-1,3-butadiene, from the reaction of 2-bromomethyl-1,3-butadiene, aluminum and alkoxy(dipropyl)borane.



The authors also developed a convenient method for obtaining dienyl and polyenyl alcohols, ketone, and vinyl esters. The method is based on the isoprenylation of carbonyl compounds, esters, and ethoxyacetylene by means of 2-dipropylborylmethyl-1,3-butadiene [133].

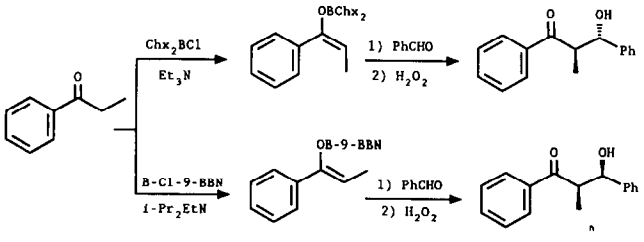




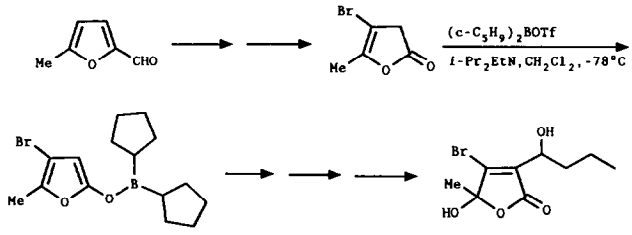
Bubnov, Gursky and Geiderikh reported a novel allylboration for the synthesis of diboryl derivatives of olefins and dienes. Treating Me_2C=CHMe, *Z*-MeCH=CHMe, or 1,5-hexadiene with BuLi · Me_3CO and then with two equivalents of R_2BCl gave $(Et_2BCH_2)_2C$=CHMe, *E*- and *Z*-Pr_2BCH_2CH=$CHCH_2BPr_2$, and Et_2BCH_2CH=CHCH=CHCH$_2BEt_2$ (mixtures of *cis* and *trans* isomers), respectively [134].

3.5. Enol borinates

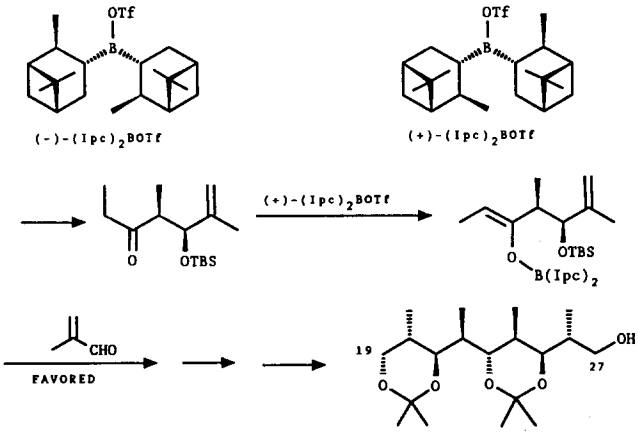
Brown and his group studied the major effect of the leaving group in controlling the stereospecific conversion of ketones into either (*E*)- or (*Z*)-enol borinates. They concluded that the stereochemical outcome of the reaction varies not only with steric requirements of R_2B and the amine but also with the nature of the leaving group [135].



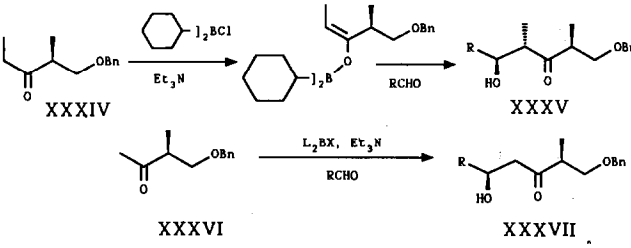
Jefford and his coworkers synthesized (±)-bromobeckerelide, a secondary metabolite of the red marine algae *Becherella subcostatum*, from 5-methylfurfural by exploiting the regiospecific aldolization of a dialkylboro-2-furanolate [136].



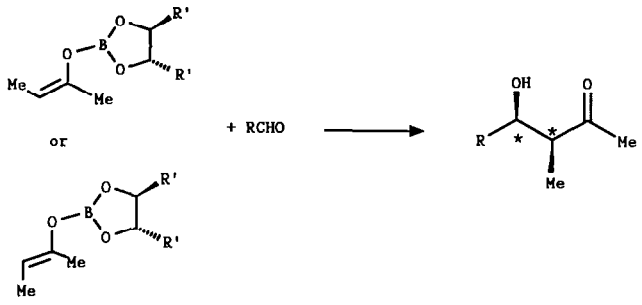
Paterson and his group describe a short asymmetric synthesis of a C_{19}–C_{27} segment of the antibiotic *rifamycin s* by the kinetic resolution in the Aldol reaction of ethylketones usinq chiral boron reagents [137].



Paterson and his group used (c-C_6H_{11})$_2$BCl in the *anti*-selective aldol reaction of the α-chiral ethylketone, **XXXIV**, which leads to high stereoselectivity (> 94%) for the 1,2-*anti*-2,4-*anti* isomer **XXXV**. The related α-chiral methylketone aldol reaction, **XXXVI** to **XXXVII**, proceeds with 84–93% diastereoselectivity for a range of boron reagents [138].

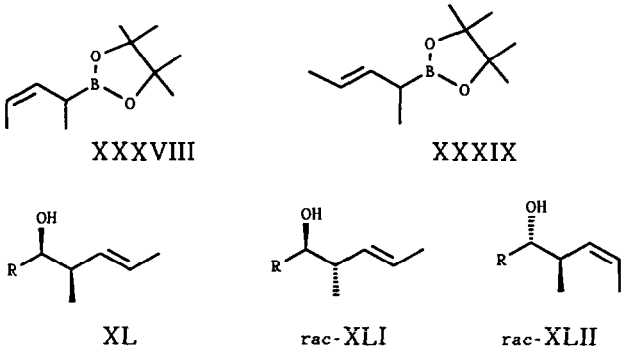


The two homochiral 2-(but-2-en-2-yloxy)-1,3,2-dioxaborolanes and RCHO are the starting materials for the synthesis of the regio- and diastereoselective enantiomerically enriched products [139]. It should be noted that the two transition states are pseudo-conformers,



that is to say they have the same *cis* relative configurations at the incipient stereogenic centers, and hence they will afford the same *syn*-ketol.

Both *Z*- and *E*-pentenylborates can be obtained by reaction of the pentenyl Grignard reaction with different borates. The *Z*-pentylboronates (**XXXVIII**) add to aldehydes diastereoselectively to produce pure *syn*-homoalylyl alcohol (**XL**). The corresponding addition of the *E*-pentylboronate (**XXXIX**) leads to a mixture of *anti*-homoallyl alcohols *E*-(**XLI**), *Z*-(**XLII**) [140].



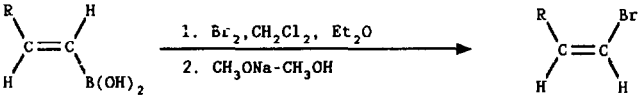
XXXVIII XXXIX

XL rac-XLI rac-XLII

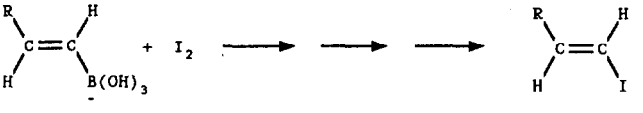
4. Carbon–heteroatom

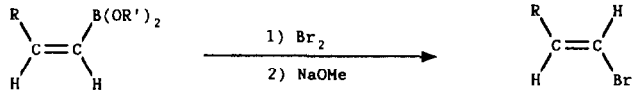
4.1. Group VII

Brown and his group described, a convenient stereospecific synthesis of (*Z*)-1-bromo-1-alkenes from 1-alkynes *via* (*E*)-1-alkenylborane derivatives with bromine [141].

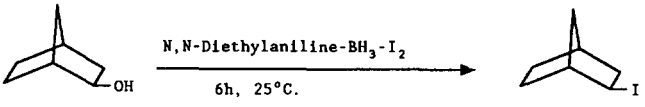


Brown also described a stereospecific synthesis of (*E*)-1-halo-1-alkenes from 1-alkynes [142]. Pure (*Z*)-alkenylboronic esters (from 1-bromo-1-alkynes) reacted with iodine in the presence of a base at 0°C giving the corresponding (*Z*)-1-iodo-1-alkenes. On the other hand, addition of bromine at −25°C to these esters, followed by treatment with sodium methoxide, resulted in the formation of the corresponding (*E*)-1-bromo-1-alkenes. Isolation of the (*Z*)-1-alkenylboronic ester was unnecessary.

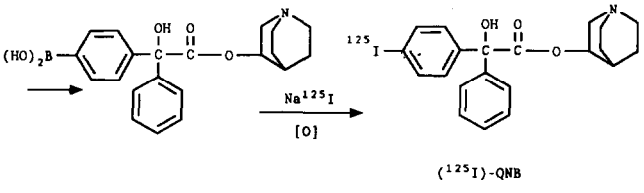




Periasamy and Reddy describe a simple procedure for iodination of alcohols and reductive iodination of carbonyl compounds using *N*,*N*-diethylaniline–borane–I_2 system [143].

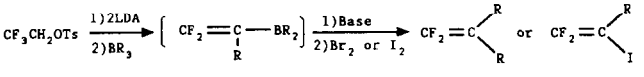


Kabalka and his group synthesized iodine-125 labeled 3-quinuclidinyl 4′-iodobenzilate, a compound that exhibits a high affinity for muscarinic receptors making it a candidate for use as a radiopharmaceutical. The title compound was prepared *via* the reaction of the corresponding boronic acid with sodium [^{125}I]iodide in the presence of a mild oxidant [144].

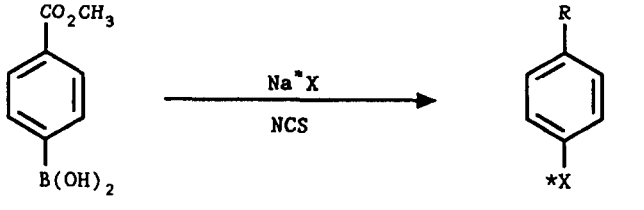


Kabalka and Varma reviewed the synthesis of radiolabeled compounds *via* organometallic intermediates [145].

Ichikawa, Sonoda and Kobayashi described the novel syntheses of symmetrically disubstituted 1,1-difluro-1-alkenes and 1,1-difluoro-2-iodo-1-alkenes *via* the reaction of 2,2-difluoroalkenylboranes with halogens in the presence of base [146].



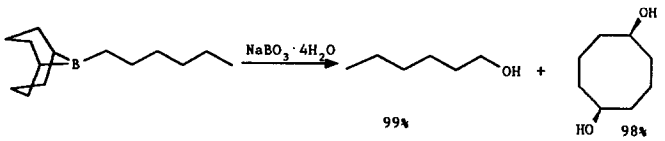
Wilbur, Hylarides and Fritzberg studied the reaction of organometallic compounds with astatine-211 for application to protein labeling [147].

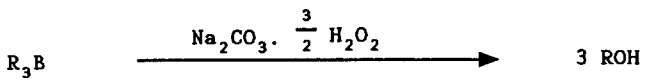


*X = astatine-211

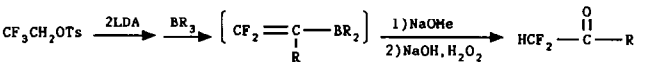
4.2. Group VI

Kabalka and his group reported that sodium perborate is a mild and convenient reagent for efficiently oxidizing organoboranes [148]. Kabalka and his group also used sodium percarbonate to oxidize organoboranes. The yields of the alcohols are the same as those obtained using the standard oxidation procedure [149].



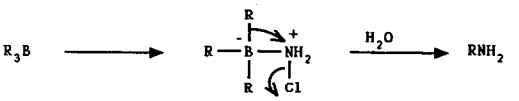


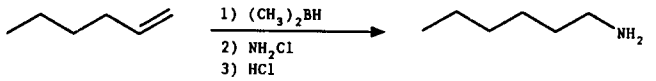
Ichikawa, Sonoda and Kobayashi synthesized difluoromethyl ketones by oxidation of 2,2-difluroalkenylboranes [150].



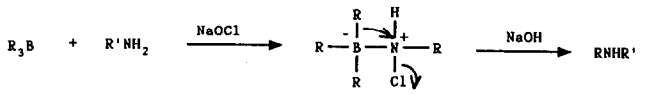
4.3. Group V

Kabalka and his group studied the preparation of isomerically pure alkylamines *via* the reaction of dimethylalkylboranes with chloramine. Dimethylborane was used to hydroborate alkenes regiospecifically. The resultant dimethylalkylboranes react with ammonium hydroxide and sodium hypochlorite to yield isomerically pure alkylamines [151].

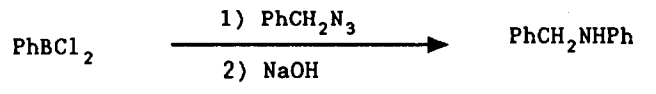


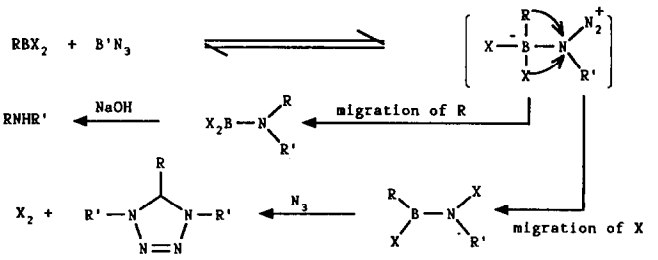


Kabalka and his group also prepared dialkylamines *via* the reaction of trialkylboranes with alkylamines in the presence of sodium hypochlorite. The reaction presumably proceeds *via* an anionotropic rearrangement of the organoboate complex formed by the organoborane and the N-chloroalkylamine generated *in situ* [152].



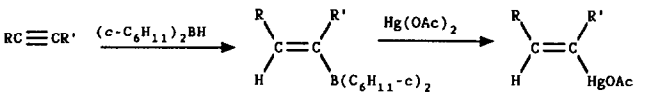
Carboni, Vaultier, Courgeon and Carrie describe the reaction of orbanoboranes with azides followed by hydrolysis to give secondary amines. When dibromoboranes were used, a competitive migration of the alkyl group and bromine occurred leading to the simultaneous formation of a teraazaboroline and the expected secondry amine. A mechanism accounting for these results was proposed [153].

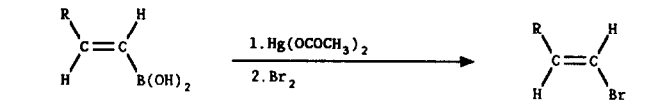




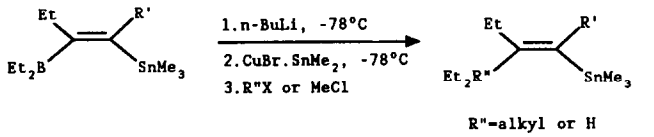
4.4. Metallation from B → M

Brown and his group studied the mercuration of 2-alkenyl-1,3,2-benzodioxaboroles and boronic acids; they report a convenient stereospecific procedure for the conversion of alkynes into (*E*)-1-halo-1-alkenes *via* mercuric salts [154]. They concluded that the procedure represents the first general, one-pot stereoselective synthesis of (*E*)-1-bromo-1-alkenes from (*E*)-1-alkenylboronic acids.

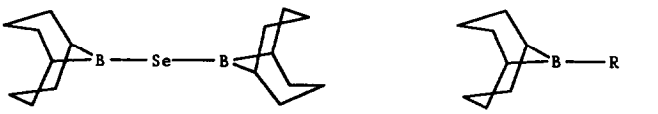




Wang and his coworkers prepared di- and trisubstituted alkenylstannanes by selective conversion of the dialkylboryl moiety to the alkenylcopper reagent followed by treatment with MeOH or alkyl halides. They also produced 2-(trimethylstannyl)-1,3-butadienes from conjugated terminal enynes [155].

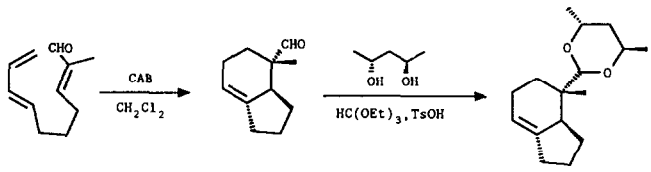


Koester, Seidel and Yalpani prepared bis(1,5-cyclooctanediylboryl)selenide quantitatively from bis-(9-borabicyclo[3.3.1]nonane), $(BBN)_2$ and Se in mesitylene at 150°C. The title compound reacts with aniline to give the BBN derivative (R = SeH, NHPh) [156].

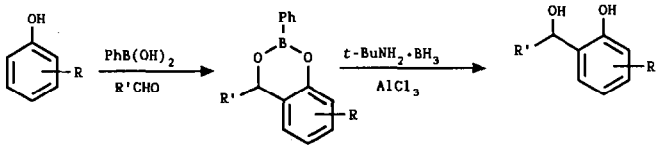


5. General synthetic methods

Yamamoto and his coworkers reported tht the intramolecular Diels–Alder reaction of 2-methyl-(*E*,*E*)-2,7,9-decatrienal catalyzed by a chiral acyloxyborane complex (CAB) proceeded with high stereo- and enantioselectivities [157].



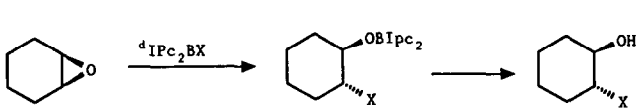
Lau and his coworkers reported *ortho*-specific alkylation of phenols *via* 1,3,2-benzodioxaborins. They reacted a phenol with an aldehyde in the presence of phenylboronic acid to produce the 1,3,2-benzodioxaborin. The latter was then reduced to the corresponding *ortho*-alkylphenol with tert-butylamineborane in the presence of aluminum chloride. Alternatively the dioxaborin, when reacted with an alkylthiol



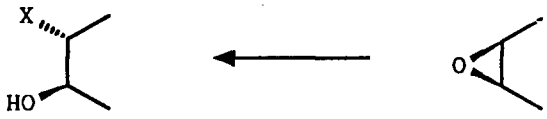
R' = H, C_6H_5, $CH_2C_6H_5$, $(CH_2)_4C_6H_5$

or an alcohol in the presence of an acid, gave the corresponding *ortho*-alkylthiomethyl or *ortho*-alkoxymethyl phenol [158].

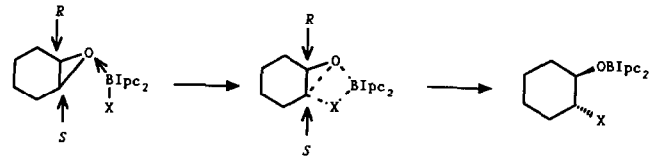
Brown and his associates reported an extensive study on enantioselective ring opening of *meso*-epoxides with β-halodiisopinocampheylboranes (Ipc_2BX).



1,2-Epoxycyclohex-4-ene is converted to the bromohydrin and iodohydrin in 84 and 91% ee. *cis*-2,3-Epoxybutane, *cis*-3,4-epoxyhexane and cyclopentene oxide were also studied. In general optical induction, increases in the order I > Br > Cl for any given epoxide. Thus *cis*-2,3-epoxybutan furnishes the corresponding chlorohydrin in 35% ee, the bromohydrin in 69% ee, and the iodohydrin in 78% ee.



In certain cases recrystallization provides essentially optically pure material. In all cases examined, $^dIpc_2BX$ (derived from (+)-α-pinene) provided (1*R*,2*R*) halohydrins in which the enantiotopic *S* C–O bond is cleaved. Ring cleavage is *anti*-periplanar, consistent with as S_N2 reaction pathway [159].



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