BORON: BORANES IN ORGANIC SYNTHESIS

ANUAL SURVEY COVERING THE YEAR 1987

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CONTENTS

A.   INTRODUCTION

Boranes and borohydrides are used in thousands of reactions each year. The regiospecificity and stereospecificity of many borane reagents have become increasingly important in the syntheses of complex molecules. This area of research has evolved in sophistication to the stage where several classes of chiral molecules are now easily synthesized in optically pure form. This review focuses on reports concerning new synthetic methodology and/or reagents and not on the routine use of boranes and borohydrides.

B.   BORANE REAGENTS

1.   Hydroborating Agents

a. BH_3

Hydroboration reactions are used regularly in hydrogenation and anti-Markovnikov hydration sequences. A few of the more interesting examples are covered in this review. Most hydroborations are performed in ether solvents at 0°C although one group investigated the use of a laser to induce a reaction between BH_3 and alkenes.[1] In an attempt to confer thermoplastic properties on natural rubber, Perera, Elix and Bradbury used diborane to introduce a nonallylic hydroxyl group[2]. The authors expected only secondary alcohol groups but the presence of both secondary and tertiary alcohols was confirmed.
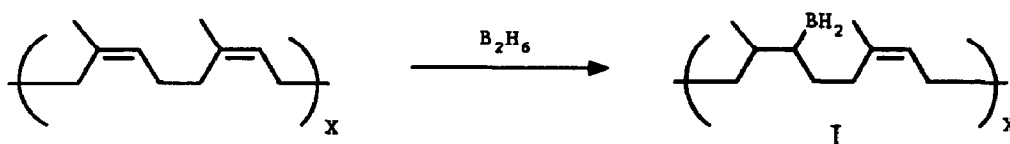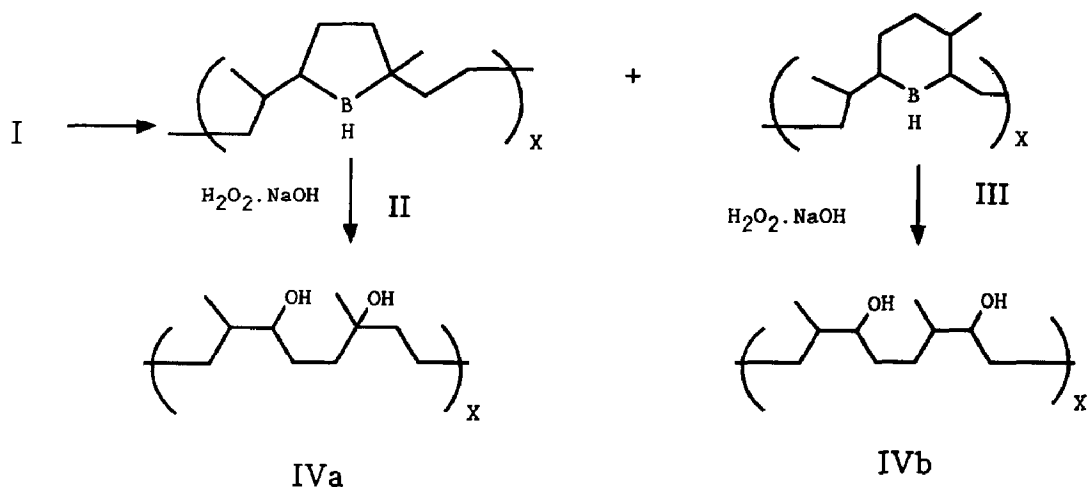
A review describing the use of borane-methylsulfide, 9-borabicyclo[3.3.1]nonane, dicyclohexylborane, and disiamylborane for the hydroboration of several types of heterocyclic olefins has appeared[3]. The review highlights versatile routes for synthesizing both racemic and optically active heterocyclic compounds.

A new entry to tricyclo[5,2,1,0^{4,10}]decane-2,5,8-trione was recently achieved via the hydroboration of the corresponding alkene[4].
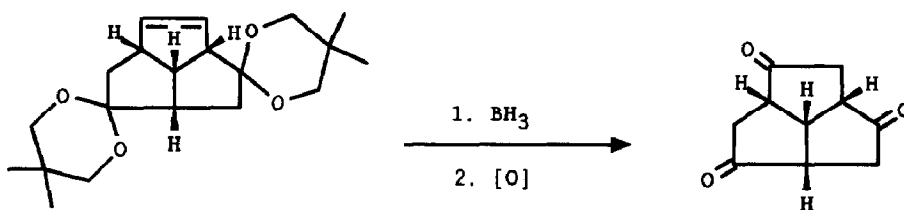
Brown, Goralski and Singaram synthesized 2-(dialkylamino)-boronic esters and acids via hydroboration of enamines with BMS[5]. The study included several enamines and covered the importance of side reactions such as protonolysis and elimination reactions which are highly dependent on the structure of the enamines. The boronic acids can be readily converted to the corresponding aminoalcohols via oxidation with trimethylamine N-oxide.

enamine
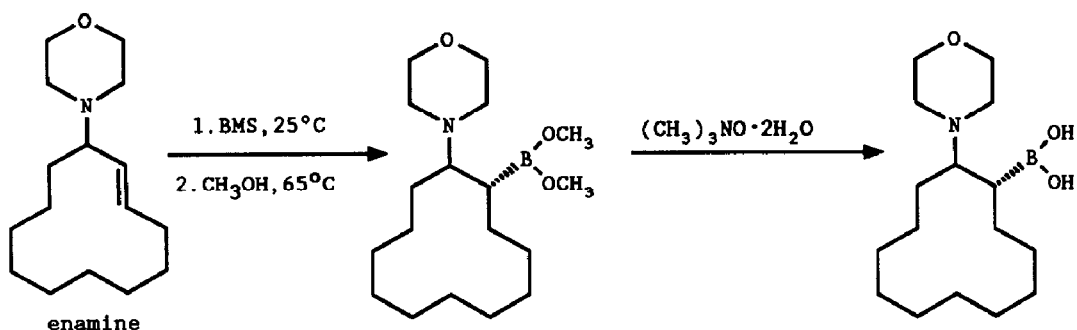
Kafka and his colleagues hydroborated a series of amine-substituted styrenes and piperidine derivatives. After oxidation, the expected hydroxyamines were obtained[6,7].

Fraser-Reid and his coworkers investigated the hydroboration of exo-methylene groups in carbohydrate systems with a view to determining the optimum conditions for obtaining axially-orientated -CH$_2$OH groups[8]. Treatment of C-methylene hexopyranosides, with BH$_3$ produced 40% of the axial product.
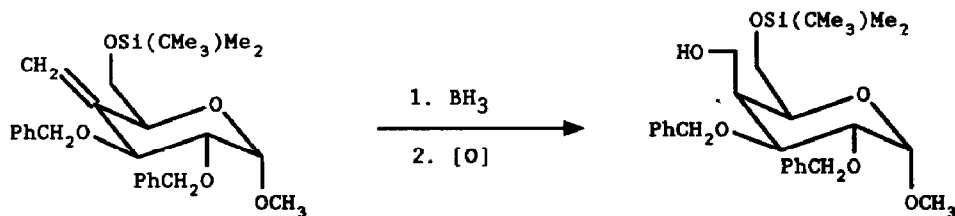
Rao, Mysorekar, and Yadav reported an efficient route to 1,3-diols involving a highly regioselective allylic oxidation of an olefin using tert-butyl hydroperoxide (TBHP) and selenium dioxide (SeO$_2$), followed by a hydroboration/oxidation sequence[9].
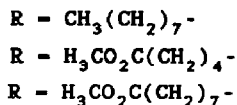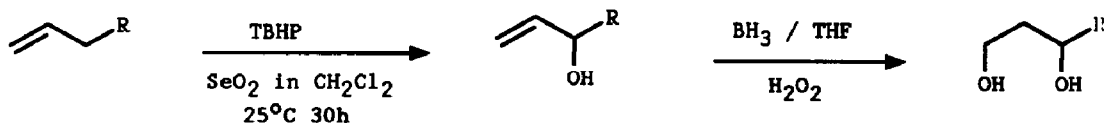
R - CH$_3$(CH$_2$)$_7$-
R - H$_3$CO$_2$C(CH$_2$)$_4$-
R - H$_3$CO$_2$C(CH$_2$)$_7$-

b.   RBH$_2$

Srebnic, Cole, and Brown reported the preparation and use of methylborane, a remarkably unhindered monoalkylborane[10]. It can be used in a controlled sequential hydroboration. MeBH$_2$, the simplest of the monoalkylboranes, possesses extraordinary hydroboration characteristics in THF. In this solvent, MeBH$_2$ is capable of monohydroborating the usual classes of alkenes, hindered and unhindered, to provide simple alkylmethylboranes, RMeBH. The addition of a second equivalent of another alkene to the alkylmethylborane formed initially, produced the sequential hydroboration product, RR'MeB. In all cases there is no evidence of an immediate redistribution in the products.
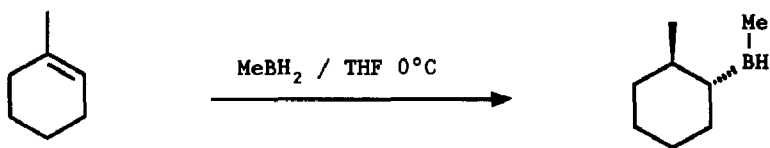
Brown, Vara, Gupta and Bakshi utilized monopino- campheylborane (IpcBH$_2$) to prepare _trans_-2-phenylcyclopentyl and _trans_-2-phenylcyclohexylboronates of very high enantiomeric purities[11]. The authors where able to correct the reported values
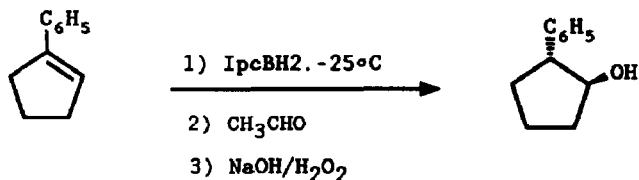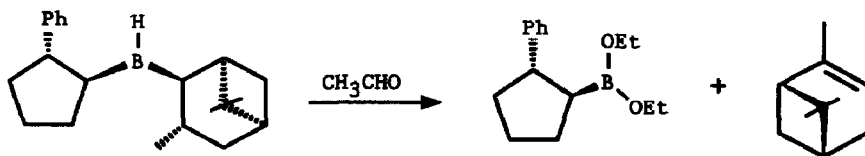
of trans-2-phenylcyclopentanol and trans-2-phenylcyclohexanol.

Yamamoto and his co-workers carried out a series of hydroborations in which monoalkylboranes were prepared in situ by reaction of boronic acids with dichloroaluminum hydride. Other organoborane reagents were also examined as sources of the borane moiety[12].

Bolton, Gates, and Jones report the preparation of monochloroborane and monobromoborane via the reaction of borane with a variety of halogenated precursors[13]. Triphenylmethyl-halides were the most effective reagents for preparing the haloboranes. The reaction of chloroborane with 1-pentene yielded dipentylchloroborane in 89% yield.

c. R_2BH

The most exciting use for dialkylboranes involves the transfer of chirality from chiral boranes to prochiral substrates. Masamune briefly reviewed this area of synthesis[14].

Soderquist and Negron used the interconversion of methoxyboranes and boron hydrides to generate 9-BBN in reaction sequences[15].
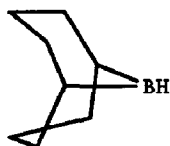
9-BBN

9-BBN was used as a precursor in a number of synthetic transformations that appear later in this review. Investigators have also utilized it to hydroborate heteroatom systems including methylenephosphine moieties[16] and carbon-tungsten multiple bonds[17].

Harada, Hayashiya, Wada, Iwaake and Oku[18] used 9-BBN in the

preparation of chiral spiroketals which are a prerequisite in the study of enantioselective functionalization of prochiral diols.

1) 9-BBN, THF
2) NaOH\H$_2$O$_2$
3) KH, BnBr, THF
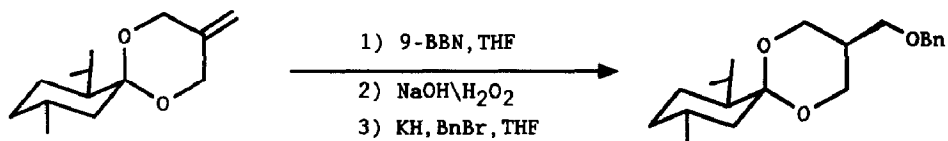
Zweifel and Leong utilized disiamylborane to convert silylated enynes to unsaturated carboxylic acids[19].

1. H$_3$C-CH-CH $\Big)_2$ BH (with H$_3$C, CH$_3$ substituents)

2. [O]
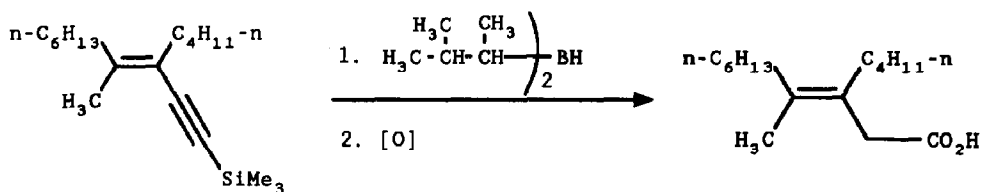
Endo-V (R=vinyl) was purified by Inoue[20] using 9-BBN to hydroborate the crude V (R=vinyl) to afford mainly V (R=CH$_2$CH$_2$OH). Iodo ether cyclization converts only endo-V (R=CH$_2$CH$_2$OH) to iodo ether VI which on reduction, elimination of iodine and dehydration gives pure endo V (R=vinyl)

V   VI
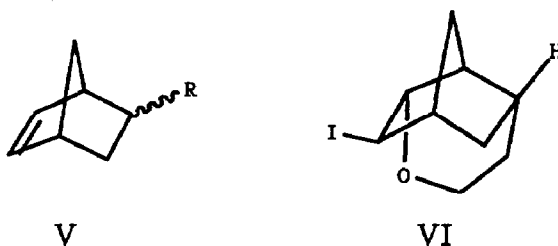
Bubnov, Gurskii and Grandberg reported an interesting

preparation of 3,5-dimethylenecyclohexene which involves the
dehydroboration of 3-borabicyclo[3.3.1]non-6-enes[21.]   Maennig and
Noeth prepared catecholborane, VIII, from VII[22].   The authors then
used the catecholborane in alkene and alkyne hydroborations[23].

VII   VIII
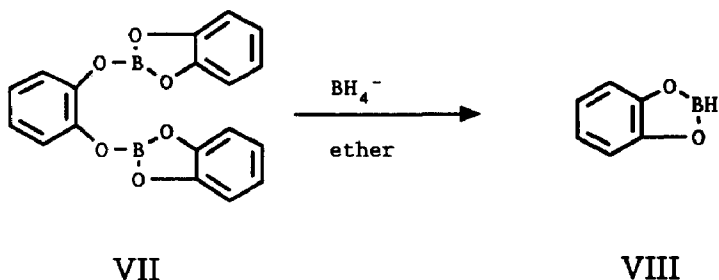
Bir and Kaufmann synthesized a number of mono- and
diisopinocamphenylhaloboranes and described their ability to act
as chiral catalysts in asymmetric Diels-Alder reactions[24].

1b 90:10

2b 80:20

1b X-Br

1c X-F

2a X-Cl

2b X-Br
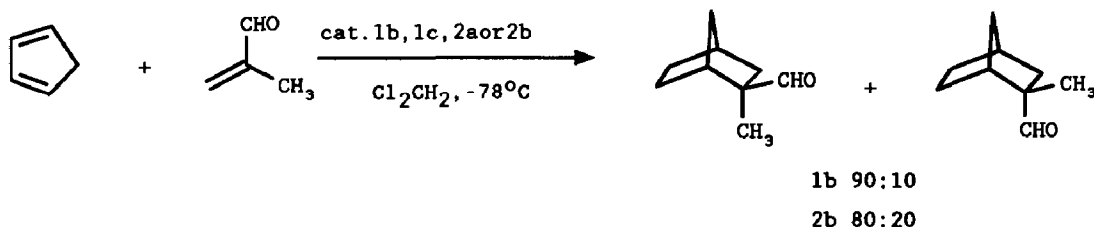
d. R_3B

Aoyama and his group report a most interesting hydroboration
method[25].   They find that (tetraphenylporphyrinato)-
rhodium(III)chloride catalyzes the hydroboration/oxidation of
alkenes when they are mixed with sodium borohydride in the
presence of air!   Basically, they achieve a one-step
anti-Markovnikov hydration reaction.   Although the yields are not
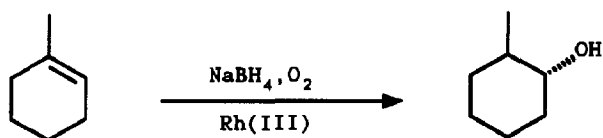
very high based on borohydride(~15%), the procedure offers an
unusually mild method for carrying out the hydroboration/oxidation
sequence. The essential role of the rhodium porphyrin is that of
a two-electron donor.

2. Reducing Agents

a. BH_3

Borane and its complexes, are used extensively for reducing
carbonyl compounds and related unsaturated systems. Martin,
Gonzaliez-Vila, and Almendros report that diborane can even be
used to reduce humic and fulvic acids[26]. Marquet, Gantry, and
Bory[27] prepared a proline derivative, X, by the reaction of IX
with diborane or its complexes.

$$HO_2CCHRCHR'CH(NHX)CO_2Y \quad \xrightarrow{BH_3\text{-}SMe_2/THF}$$

IX   X   78%
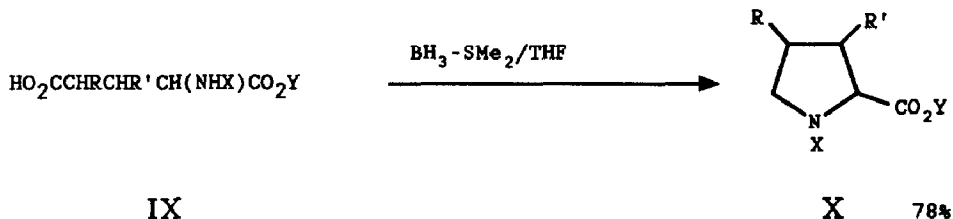
X - a common protecting group (Me_3CO_2C)
Y - (aryl) alkyl ($PhCH_2$)
R - H, F, Cl, alkyl
R' - H, alkyl

The most intriguing use of a borane reagent was contained in
a report by O'Connor and his coworkers[28] who utilized isotopically
labeled borane and borohydride reagents to prepare chiral methyl
groups. The syntheses were developed during their investigation

of the stereochemistry of the protolytic cleavage of rhenium-carbon bonds at both the metal and carbon centers.

Koester, Tsay, and Synoradzki[29] investigated the reduction of phenylphosphine oxide with organoboranes and reported the crystal structures of the resulting zwitterionic boron-phosphorus complexes. Kabalka and Varma reviewed the synthesis and selective reduction of conjugated nitroalkenes[30].
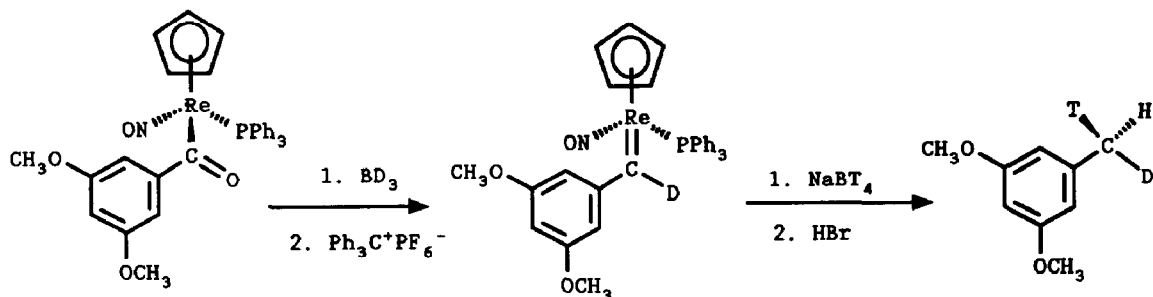
b. RBH_2

Reductions involving monosubstituted boranes were dominated by studies in which chiral ethanolamine derivatives were utilized. The area was briefly reviewed by Itsuno[31]. He and his coworkers reported that chiral ethanolamine could be incorporated into polystyrene. The chiral polymeric reducing agent can contain up to 33 mole percent of the ethanolamine derivative. The reagents are effective; as an example, acetophenone o-methyloxime was reduced to optically active 1-phenylethylamine in 99% ee[32]!
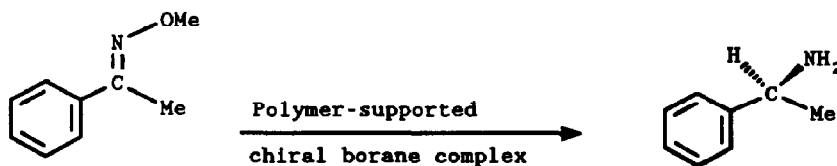
Itsuno also investigated the use of simple, optically active amino

alcohol-borane complexes in the enantioselective reduction of acetophenone oxime derivatives[33]. Norepinephrine was the amino alcohol used in a study involving the asymmetric reduction of ketones[34]. Enantomeric excesses approached 62% for this reagent.

Mandal and his coworkers report that an alkoxyborane complex formed via reaction of $BH_3.SMe_2$ and optically pure (2S,2S)-(+)-2-amino-3-methoxy-1-phenyl-1-propanol can be used to prepare chiral ketones in 30-65% enantiomeric excess. The reagent was not characterized but one boron-hydride bond reacts per borane molecule. The complex can also be used to induce chirality in prochiral alkenes in 8-37% enantiomeric excess[35].
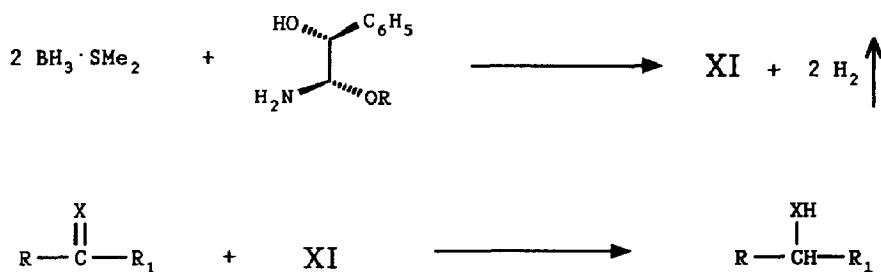
Cis-exo- and endo-aminohydroxybornanes were investigated in asymmetric reductions with mixed results[36]. Other investigators

utilized a proline derivative as the chiral auxiliary to achieve the asymmetric reduction of ketones[37]. Corey and his coworkers investigated the use of chiral oxazaborilidines as catalysts in

the enantioselective reduction of ketones by borane. A catalytic amount of (S)-(-)-2-(diphenylhydroxymethyl)-pyrrolidine, XII, and XIII were the most effective agents. For example, the presence of 0.1 equivalents of XIII results in the formation of (R)-1-phenylethanol from acetophenone in 97% e.e.[38].

XII   XIII
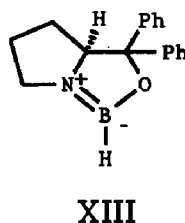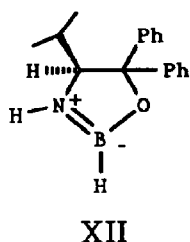
c.   R$_2$BH

Disubstituted borane derivatives have proven to be extremely versatile agents for chemoselective and sterioselective reductions. Brown and his coworkers carried out an evaluation of the relative effectiveness of twenty borane reagents for the asymmetric reductions of different classes of ketones[39]. The various ketones were organized into ten distinct classes. However, direct comparison of the relative effectiveness of these twenty reagents for individual classes of ketones proved difficult because of the wide variation in the individual ketones used to test each reagent. Thus one representative ketone was selected from each of the 10 different classes. Then, six of the more promising reagents were selected: B-isopinocampheyl-9-borabicyclo-[3.3.1]nonane in THF; diisopinocampheylchloroborane; a mixed reagent consisting of two equivalents of BH$_3$ with (S)-(-)-2-amino-3-methyl-1,1-diphenylbutan-1-ol; NB-Enantride; K-Glucoride; and Binal-H. These six reagents were reacted with the ten selected standard ketones. On the basis of the results

obtained for the six reagents and the ten selected ketones, preferred reagents are suggested for the asymmetric reduction of individual classes of ketones. This article is essential reading for those interested in the borane reducing agents.

Yoon, Brown and their coworkers carried out a synthetic study of the direct reduction of carboxylic acids to the corresponding aldehydes with thexylchloroborane-methyl sulfide under practical conditions (CH_2Cl_2, room temperature). The reaction is quite general, and the yields of aldehydes are very good, almost quantitative in the aliphatic series; many readily reducible functional groups tolerate the reaction conditions[40]. Cha, Kim and
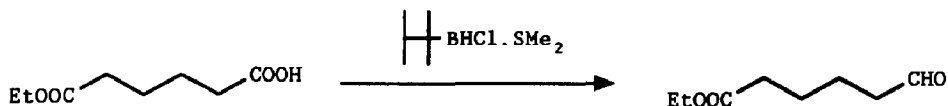
Lee investigated the use of thexylbromoborane for reducing carboxylic acids to aldehydes[41]. The results parallel those obtained using thexylchloroborane.

Dialkoxyboranes and diacyloxyboranes are also used in selective reductions. A new reagent formed by reaction of 1,2:5,6-di-O-isopropylidine-α-D-glucofuranose with BH_3 has been described[42]. Only modest yields of chiral products were obtained; however, a more effective agent was developed using 9-BBN and is discussed in section B2e.
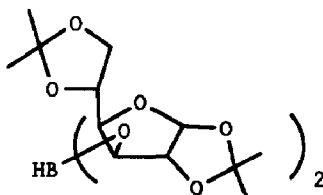
Catecholborane is a dialkoxyreagent which has proven popular in the past. This year it was reported that catecholboranes reduce methylene derivatives of phenylphosphines[16].

Choi and his coworkers[43] discovered that α-hydrogen abstraction can compete with reduction of carboxylic acid derivatives in stabilized systems. Thus, the reduction of phenylmalonic acid with BH_3 led to the predominant formation of the hydrogen abstraction product, XIV, rather than the desired product, XV. Hydrogen abstraction reactions could be minimized by

XIV   **XV**
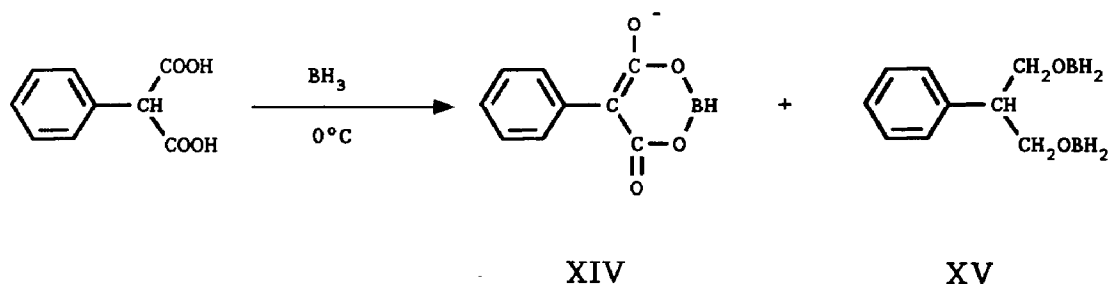
carrying out the reaction at -20°C with excess BH_3.

d. R_3B

Trialkylboranes such as Alpine-borane are often used in asymmetric reductions of prochiral ketones. Hanzawa, Kawagoe and Kobayashi reduced a series of fluoroalkyl alkynyl ketones enantioselectively using (S)-Alpine-borane[44]. The asymmetric reduction of prochiral ketones was also a recent thesis topic[45]. Chen, Gunderson, Hardtmann, Prasad, Repic and Shopro developed a novel method for the in situ generation of alkoxydialkylboranes which they then used in the selective preparation of 1,3-syn-diols[46].
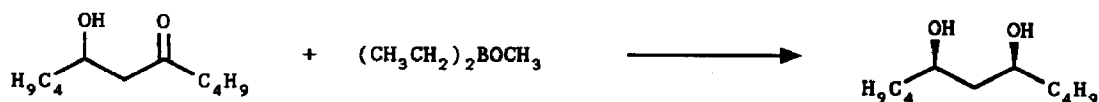
e. R_4B^-

Simple borohydride reagents provide a convenient and operationally simple method for reducing aldehydes and ketones. However the use of complex borohydrides often offers much greater stereochemical and regiochemical control. Ookawa and Soai developed an asymmetric synthesis of optically active threo- and erythro-pyrolidinylbenzyl alcohols via the arylation of (S)-proline followed by a highly diastereoselective reduction with K-selectride[47].
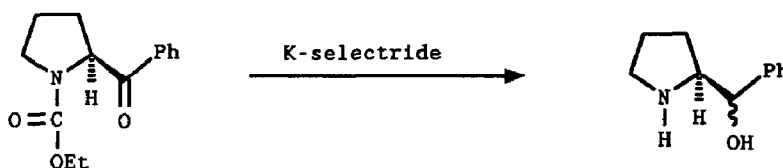
Kabalka and his coworkers discovered an unprecedented Grignard-like addition of trialkylborane to nitroso groups in a study of the reaction of superhydride to nitroalkenes[48]. Brown,
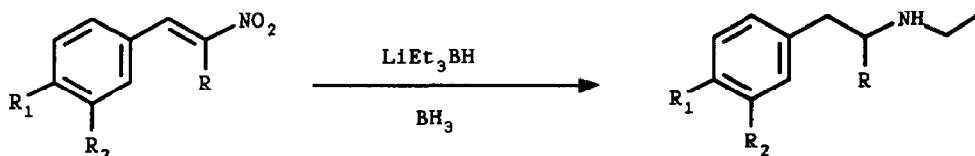
Ranaishenvi and Racherla synthesized dialkylborohydride reagents via the reaction of trialkylboranes with LiAlH$_4$[49]. These reagents serve as a source of "masked" dialkylborane and provide access to reagents which cannot be obtained via direct hydroboration.
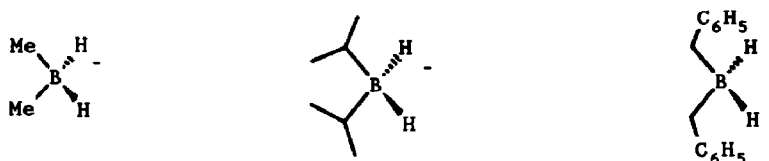
Cha, Kim, Oh and Kim reported that 9-boratabicyclo[3.3.1]-nonane reduced boron esters of carboxylic acids to aldehydes in excellent yields[50]. The reagent was also utilized by Hutchins and
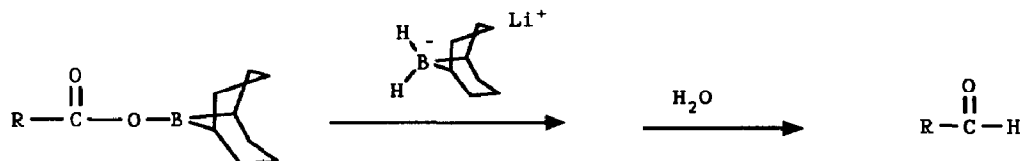
his coworkers to carry out the enantiomeric reduction of phosphinylamines[51]. They found the reagent to be more effective than alternative hydride reagents such as bi-2-naphthol-LiAlH$_4$.

Alkoxyborohydride derivatives are among the most promising asymmetric reducing agents currently being examined. Cho and his coworkers have continued to investigate the use of K-Glucoride (1,2:5,6-di-O-isopropylidene-α-D-glucofuranose) a reagent which he and Brown reported in 1986. Cho reports that the reagent reduces prochiral α,β-acetylenic ketones in 90% yield with up to 87% enantiomeric excess[52]. Prochiral aliphatic ketones were reduced in somewhat lower enantiomeric excess[53].

Chiral dialkoxymonoalkylborohydrides are also available. Brown, Cho and Park prepared chiral cyclic boronic esters using alkyl and/or diol moieties to impart chirality[54]. Chiral butanediols and 1,2;5,6-di-O-isopropylidene-D-mannitol are representative of the chiral alcohols whereas the monoisopinocampheyl group is an effective chiral alkyl group. Potassium 1,2;5,6-di-O-isopropylidene-D-mannitol thexylhydridoborate provides the best results. Acetophenone, for example, is reduced in 78% enantiomeric excess.
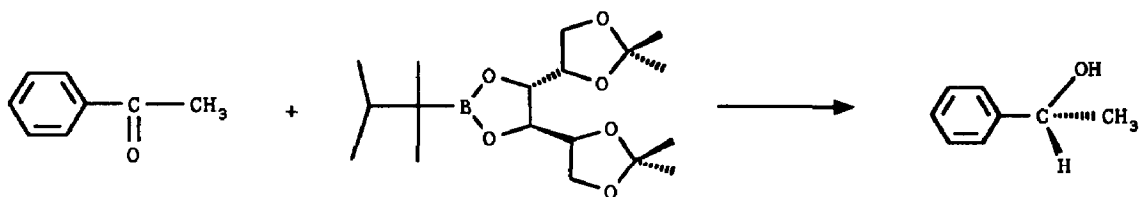
3. Mechanism and Theory

a. Theory

The electron deficient boranes have traditionally attracted the attention of theoreticians. This year is no exception. Schleyer and his coworkers carried out an ab initio investigation focussed on the existence of methylborylene[55]. Methylborylene, $CH_3-B:$, is a minimum on the potential energy surface. Although $CH_2=BH$ is 24.3 kcal/mol more stable (MP4/SDTQ/6-311G**//6-31G*), the 1,2-H shift barrier is indicated to be 25.0 kcal/mol. as higher levels of theory are not expected to reduce this value appreciably, it should be possible to observe methylborylene under appropriate experimental conditions. This contrasts with the carbene analogue $CH_3-CH:$, which is predicted to rearrange to ethylene without any appreciable barrier. Similarly, the boron-substituted singlet carbene $H_2B-CH:$, although stabilized by π-delocalization ($H_2B=CH^+$), is not indicated to be a stable species when electron correlation corrections are taken into consideration. Rearrangement into $CH_2=BH$, the simplest compound with a C=B double bond, is predicted to occur without activation. The entire triplet CBH_3 potential energy surface is indicated to lie above the singlet surface. The singlet triplet energy separation in BH (31.8 kcal/mol at the highest level of theory) is increased by 11.8 kcal/mol in CH_3B due to methyl substitution. The Schleyer group also studied the binary association complexes of borane and related hydrides[56]. Ab initio MO theory was used to study B_2H_6. Geometry optimization and vibrational analysis at the HF/6-31G* level indicate $H_2B--(H)_2--BH$ (D_2h) to be the most stable form. Inclusion of electron correlation corrections at the MP4/6-31G* level does not alter this conclusion. Other isomers were examined. The potential energy surfaces for the species are generally flat. Activation energies for isomer interconversion and H scrambling reactions are generally <10 kcal/mol^{-1}. There is

no activation energy for the dimerization of BH_3 at the correlated MP2/6-31G* level, although a small barrier is found on the HF/6-31G* surface. Enthalpy of complexation at 298K from separate BH_3 fragments, computed by using the HF/6-31G* harmonic frequencies and the MP4/6-31G* electronic energy for B_2H_6, is -36.0 kcal/mol^{-1}.

Schleyer, Streitweiser and their coworkers carried out an ab initio study focused on the structures and energies of main group metal formyl complexes. Formyl complexes, MCHO, of first- and second-row metals and metal hydrides (M = Li, BeH, BH_2, Na, MgH, AlH_2) were investigated by means of ab initio calculations (MP2/6-31+G*//6-31G* and lower levels). Both η^2 (i.e.,bridged) and η^1 coordination of the metals are found: the former is favored by larger electronegativity differences between the metal and the formyl carbon[57].

Pannell, Raghuveer, DelBene and Nathan investigated ion pairing in transition metal carbohydrates using ab initio calculations on BH_2COM systems[58]. Ab initio calculations provide an excellent model for the type of ion pairs that have been observed spectroscopically, and by X-ray crystal determination for various transition-metal carbonylate salts. Three stable ion pair structures have been identified: one involves the alkali metal bonded to the terminal O atom of the CO group with a linear COM_a linkage; the second has a direct alkali-metal-boron bond with essentially tetrahedral geometry around boron; and the third is a π-complex in which the alkali metal is bonded to the CO π-system orthogonal to the plane of the BH_2 group, i.e., stabilization requires an extended π-system involving the nonbonding electrons on B. A study on ion pairing with an (acyl)$BHCOM_a$ system reveals a chelate complex, as has been identified experimentally in related acyltransition-metal carbonylates. Calculated infrared stretching frequencies for the CO group in the various minimum

energy structures change from one structural form to the other in
a manner exactly paralleling those obtained experimentally for the
metal carbonylate ion pairs, e.g., $[BH_2CO]^-$, 2030 cm^{-1}, $[BH_2COLi]$,
1944 cm^{-1}, and $[LiBH_2CO]$, 2103 cm^{-1}. Addition of a water molecule
to the alkali-metal ion also causes changes in the CO stretching
frequencies that are consistent with experimental data for solvent
effects.

Boyd and Edgecombe calculated the bond critical points in the
electronic structures of the main group diatomic hydrides of
lithium through bromine[59]. As part of a systematic study of the
polarity of chemical bonds, the position of the bond critical
point, the charge diatomic at the bond critical point, the
Laplacian of the charge diatomic at the bond critical point, and
the molecular dipole moment of each molecule were calculated.
Particular attention was paid to the effect of bond length
elongation and contraction on the electronic properties.
Variation of the bond length reveals that with atoms of low
electronegativity, the bond critical point of AH tends to follow
atom A, whereas with atoms of high electronegativity, the bond
critical point tends to follow the hydrogen atom as the bond
lengthens. Some properties of the diatomic hydrides vary
monotonically within each row of the periodic table, while others
effect a classification according to the character of the bond.

Rowlands and Somasundram carried out a SCF investigation of
the H-bonded complex between HF and B_2H_6 at the (double
zeta)-polarization-bases-set level which revealed a structure in
qualitative agreement with existing experimental data, in which
the intermolecular bond is formed between a diborane terminal H
and the H in HF. Infrared frequencies and intensities, rotational
constants, and the dipole moment of the complex were calculated[60].

Diercksen, Gruener, Sabin and Oddershede performed second-
order polarization propagator calculations of the transition

moment as well as the radiative lifetime of the A1.PI. state of
BH. The electronic oscillator strength computed at the ground
state equilibrium is rather different from the band absorption
oscillator strength which demonstrates that theoretical electronic
oscillator strengths should not be expected to agree with
experimental determinated band oscillator strengths[61].

Braun, Rebane and Semakova performed refined calculations on
the dependence of the component of magnetic susceptibility and
polarizability of BH in the ground state on vibrational quantum
numbers from zero to seventeen. Averaged over vibrations, the
transverse magnetic susceptibility increases by a factor of 7.1,
and the longitudinal polarizability increases by a factor of 2.2.
There is an abrupt rise in the anomalous paramagnetic
susceptibility for vibrational excitation[62].

b.   Kinetics

A correlative study involving the relative rates of
hydroboration and oxymercuration for a series of alkenes[63], by
Nelson and her group, indicates similar steric requirements in the
transition states of the two reactions.

Davidovits and his coworkers examined the reaction rates of
boron atoms with the bromomethanes and bromofluoromethanes. In
the simplest reaction with these molecules, a single halogen atom
is extracted by the boron atom to form a boron monohalide. The
substitution of fluorine in those systems produced a notable
reduction on the reaction of the bromine site, while the fluorine
sites are assumed to be nonreactive[64].

c.   Spectroscopy

A variety of spectroscopic investigations were reported this
year. Kawaguchi, Kanamori and their coworkers detected the
gas-phase infrared spectrum of borane (BH_3) by diode laser

spectroscopy[65]. The BH_3 was produced by photolysis of B_2H_6 with an ArF excimer laser. Line assignments were made for the Q-branch; effects due to Coriolis perturbations were recognized. Dureg, Hizer and Odom investigated the infrared and Raman spectra of phosphorus complexes of borane-d_6[66]. The Raman (10-3500 cm^{-1}) and IR (50-3500 cm^{-1}) spectra of solid $EtMe_2P-BH_3$ and $EtMe_2P-BD_3$ were recorded. The Raman spectra of the liquid phase were recorded, and quality depolarization ratios obtained. Based on the fact that several bands were observed to disappear upon going from the liquid to the solid phase, the molecule exists as a mixture of the trans and gauche conformers with the trans conformer being the only one present in the solid phase. Employing Raman depolarization data, group frequencies, and isotopic shift data, the spectrum of the solid phases was interpreted on the basis of Cs symmetry for the trans conformer. The assignment is supported by a normal coordinate calculation which was carried out using a modified valence force field to obtain the frequencies of normal modes and the potential energy distribution. Odom and his coworkers also investigated difluoromethylphosphine borane complexes[67]. The Raman (10-3500 cm^{-1}) and IR (20-3500 cm^{-1}) spectra of $MePF_2BH_3$ and $MePF_2BD_3$ were recorded for the gaseous and solid states. The Raman spectrum of the liquid was recorded, and depolarization values obtained. All the fundamental modes, except the two internal rotations, were assigned using band contours, depolarization values, isotopic shifts, and group frequencies. A normal coordinate calculation was carried out using a modified valence force field to calculate the frequencies and the potential energy distributions.

Geanangel and Wendlandt detected a very unusual light emission using emission thermophotometry during the thermal decomposition of the ammonia-borane complex[68]. The emission probably has its origin in reactions involving the B-H bond.

Contreras and her coworkers carried out a boron-11 nuclear
magnetic resonance study of the reaction of borane-THF with
representative dithianes, diazolidines, Thiazolidines,
benzothiazolines and benzothiazoles[69]. The NMR not only allowed
observation of the borane adducts but provided evidence concerning
their stereochemistry.

Borane derivatives were also investigated by spectroscopic
techniques. Gerry, Jemson, Lewis-Bevan, MacLennan and Westwood
measured the high resolution infrared spectrum of
difluoroborane[70]. The type-B totally symmetrical stretching
fundamental .nu.2 (at approx. 1164 cm^{-1}) of HBF_2 was recorded.
Rotational and centrifugal distortion constants were evaluated for
$H_{10}BF_2$ and $H_{11}BF_2$, in both the ground and the twenty one levels.
The spectrum was regular, with no peturbations and no new
information on the position of the missing fundamental .nu.6.

Sugie, Takeo and Matsumura observed the microwave spectra of
five isotopic species of BH_2NH_2[71]. The rotational constants,
centrifugal distortion constants, and nuclear quadrupole coupling
constants of ^{11}B and ^{14}N were determined from the spectra. The
planarity and symmetry of the molecule were confirmed by the
measurements of inertia defects, dipole components and statistical
spin wt. due to the four H nuclei. The complete rs structure was
determined from the rotational constants and presented in the
manuscript.

Long and Hutchinson carried out a high pressure and low
temperature applied field Moessbauer effect study[72]. It revealed
that $Fe[HB(pz)_3]_2$ (pz = 1-pyrazolyl), which contains low-spin
Fe(II) from room temperature down to 4.2K, may be converted in
part to high-spin Fe(II) at pressures above approximately 40 kbar.
In contrast, $Fe[HB(3,4,5-(CH_3)_3pz)_3]_2$, which studies reveal
remains high-spin down to 1.7 K, may be converted to the low-spin
state at high pressure. Because of the weaker crystal field

potential of the substituted ligand in this compound, a pressure
of approximately 55 kbar is required to make the high-spin $^5T_{2g}$
state and low-spin $^1A_{1g}$ state equivalent in energy at room
temperature. In Fe[HB(3,5-(CH$_3$)$_2$pz)$_3$]$_2$ the intermediate crystal
field potential yields a spin crossover at low temperature (ca.
195 K), and in this case only 4 kbar is required to make the two
spin states equivalent in energy at room temperature. All three
compounds show a linear dependence of the isomer shift and
quadrupole interaction upon the applied pressure, and the
spin-state transitions are completely reversible.

Other studies include a report that the fluorescence
quenching of 2-naphthyl-substituted 1,3-diketo-boronates by
naphthalene is accompanied by exciplex emission[73]. Baban and
Roberts reported on an ESR study of dialkylsulfide-boryl
radicals[74].

Gianturco and Schneider reported on the possible dynamic
pathways which are likely to occur in collisional encounters
between BH(X1.σ.+) molecules and protons in the center-of-mass
energy range of a few eV. The DIM model is used to describe the
potential energy surfaces of the (BH$_2$)$^+$ system which are most
relevant at the considered energies. Possible processes include
inelastic scattering and charge-transfer events, which can be
different electronic states of BH$^+$, depending on the relative
orientations of colliding partners during encounters[75].


d.   Structure

The crystal structure of a number of boron derivatives are
beginning to be reported. Orvig, Rettig and Trotter reacted
diphenylborinic acid with 3-hydroxy-2-methyl-4-pyrone and reported
the crystal structure of the resultant product[76]. Structural and
spectroscopic data are consistent with weak binding of the oxygen
atoms to the boron.

Kliegel, Lauterbach, Rettig and Trotter determined the crystal structure of the 8-methyl-6,6-diphenyl-5,7-dioxa-
-8-azonia-6-borato-6,7-dihydro-5 H-benzocycloheptene[77]. The envelope-like conformation adopted by the 7-membered chelate ring places one B-Ph group above the plane of the fused-ring system facilitating a thermally-induced 1,4-migration of a B-Ph group to the nitrone carbon atom.

4.   Synthesis of Organoboranes

Organoboranes are generally prepared via hydroboration reactions[78]. However, not all boranes can be prepared in this fashion; aromatic, highly branched, and methyl derivatives are classic examples of groups which are attached to boron via alternative routes such as transmetallation reactions. Joworski and Shahanullah examined the exchange reaction of alkyl groups between Me_4Pb and Et_3B[79]. Exchange does not proceed when triethylborane is complexed with Lewis base. Yuan, Zheng and Zhang prepared tri(2-furylborane) via reaction of 2-furyllithium
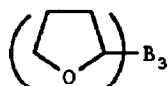

with (N,N-diethylamino)dichloroborane[80]. Nakadaira, Sato and Sakurai prepared 1-methyl-1-boracyclohepta-2,4,6-triene, the first C-unsubstituted borepin via metal-metal exchange of 1,1-dibutylstannepin with $MeBBr_2$[81].
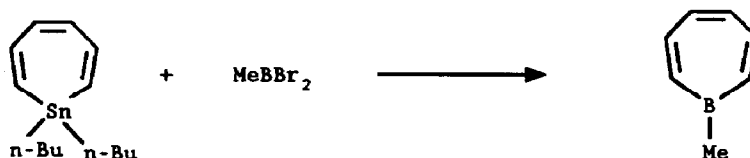

Schacht and Kaufmann synthesized benzoannulated boracycloalkenes via the flash vacuum pyrolysis of alkylated

arylalkylchloroboranes[82]. They also prepared benzoborole via an
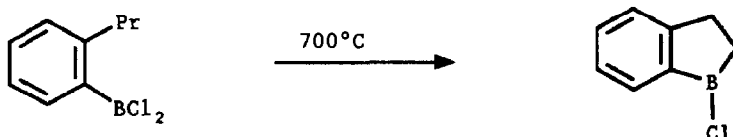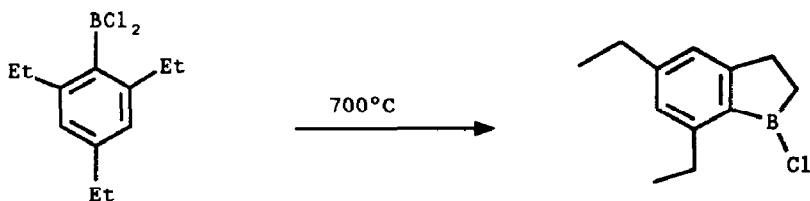
analogous route[83] by pyrolyzing a dichloroarylborane.

Eisch and his coworkers synthesized trimesitylborirene via
irradiation of an alkynylborane derivative[84]. The material
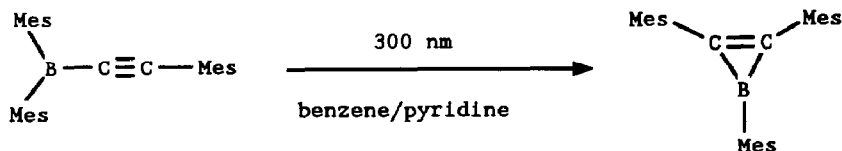

Mes - 2,4,6-trimethylphenyl

displays unusual chemical stability towards oxidation and
thermolysis, but does undergo protodeboronation with AcOH.
Furthermore, it can still form complexes with pyridines. By x-ray
crystallography, the borirene ring forms an equilateral triangular
array of atoms with separations of 1.42 angstroms; the identities
of the atoms in the ring are completely disordered. This change
from the expected C:C and B-C bond lengths strongly supports the
conclusion that the p-electrons of the borirene ring are highly
delocalized.

## C.   CARBON-CARBON BOND FORMATION

1.   Homologation

Formation of C-C bonds provides the foundation of organic synthesis.   Organoboranes can be used effectively to construct larger carbon frameworks from functionally substituted fragments. One significant aspect involves the use of chiral borane reagents in asymmetric syntheses, an area which was recently reviewed[85].
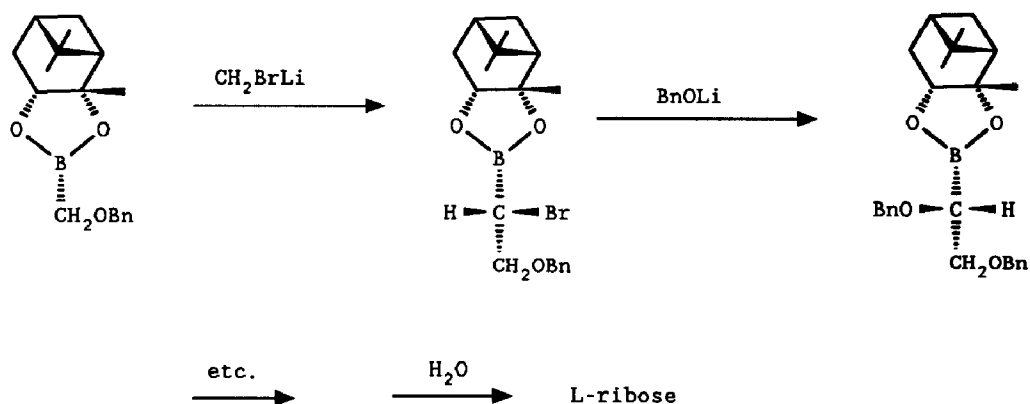
The simplest homologation reaction of organoboranes involve one-carbon moieties such as carbon monoxide or cyanide ion. Kabalka and his coworkers utilized the reaction of carbon-13 labeled cyanide ion to prepare carbon-13 labeled phenanthrene derivative[86].   An alternative ketone synthesis utilizes
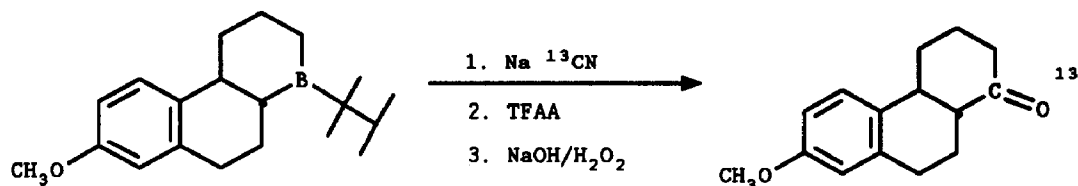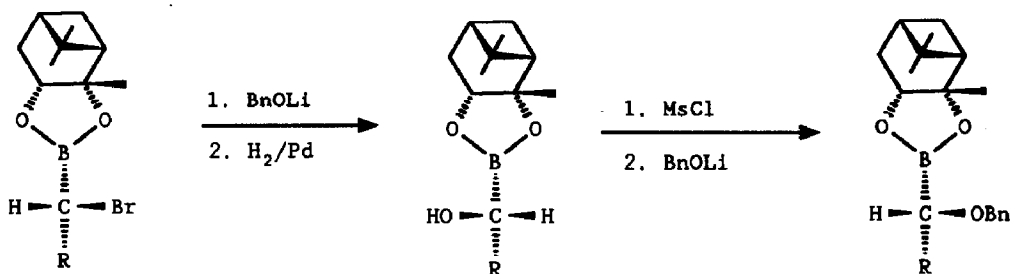

dichloromethyl methyl ether (DCME) as the homologation reagent. Brown and his coworkers utilized the DCME reaction to prepare chiral acyclic ketones of exceptionally high enantiomeric excess using chiral borinic esters[87].
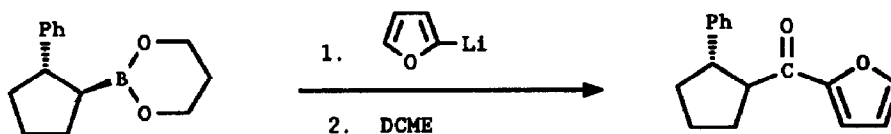

Matteson continues to develop the use of chiral α-haloboronic esters in organic syntheses.   Matteson and Peterson reported a synthesis of L-(+)-ribose using a chiral α-bromoboronic ester[88].

$$\xrightarrow{\text{CH}_2\text{BrLi}}$$

$$\xrightarrow{\text{BnOLi}}$$

H — C — Br

CH₂OBn → H $-$ C $-$ Br / CH₂OBn

BnO $-$ C $-$ H / CH₂OBn

$$\xrightarrow{\text{etc.}} \xrightarrow{\text{H}_2\text{O}} \text{L-ribose}$$

Matteson and Kandil also developed a method to invert chiral centers adjacent to boron atoms. This allows assembly of adjacent chiral centers with one of them having its absolute configuration opposite to that directed by the pinanediol boronic ester group[89]. These results also provide unequivocal direct proof of inversion in nucleophilic displacement at the α-carbon of a boronic ester.

$$\xrightarrow[\text{2. H}_2/\text{Pd}]{\text{1. BnOLi}}$$

$$\xrightarrow[\text{2. BnOLi}]{\text{1. MsCl}}$$

H — C — Br / R

HO — C — H / R

H — C — OBn / R

Matteson and Beedle utilized boronic esters in a directed chiral synthesis of amino acids[90]. Conversion of (S)-pinanediol (1S)-1-haloalkylboronates (R= Me_2CH, $PhCH_2OCH_2$, $Me_3CO_2CCH_2CH_2$) to (1R)-1-azido boronates, homologation with $LiCHCl_2$ to 1-chloro-2-azido boronates, oxidation with $NaClO_2$ to the α-azido acids, and catalytic hydrogenation yielded L-amino acids in 92-96% enantiomeric excess.
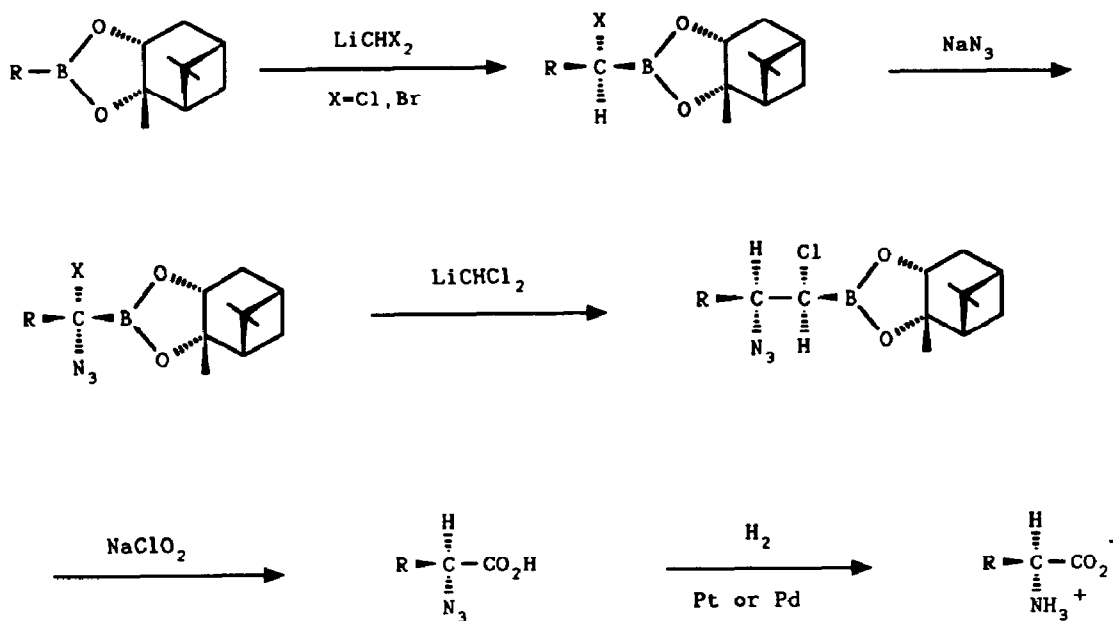
Ohta and coworkers were able to ethylate pyrazines using alkylmetals such as triethylaluminum and triethylborane[91].
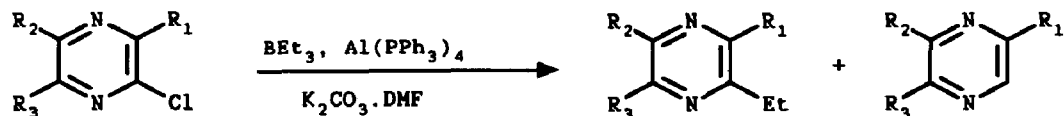
Pelter, Buss and Colclough utilized the boron-Wittig reaction in the stereoselective synthesis of (E)- and (Z)-alkenes via an erythro-intermediate which can be trapped by trimethylsilylation or trifluoroacetylation[92].
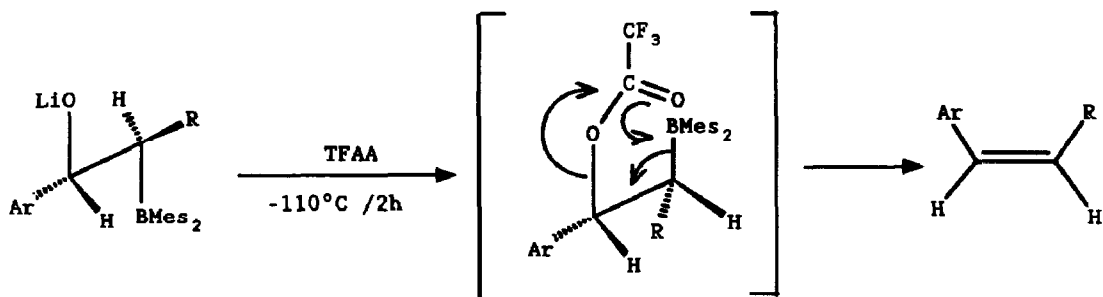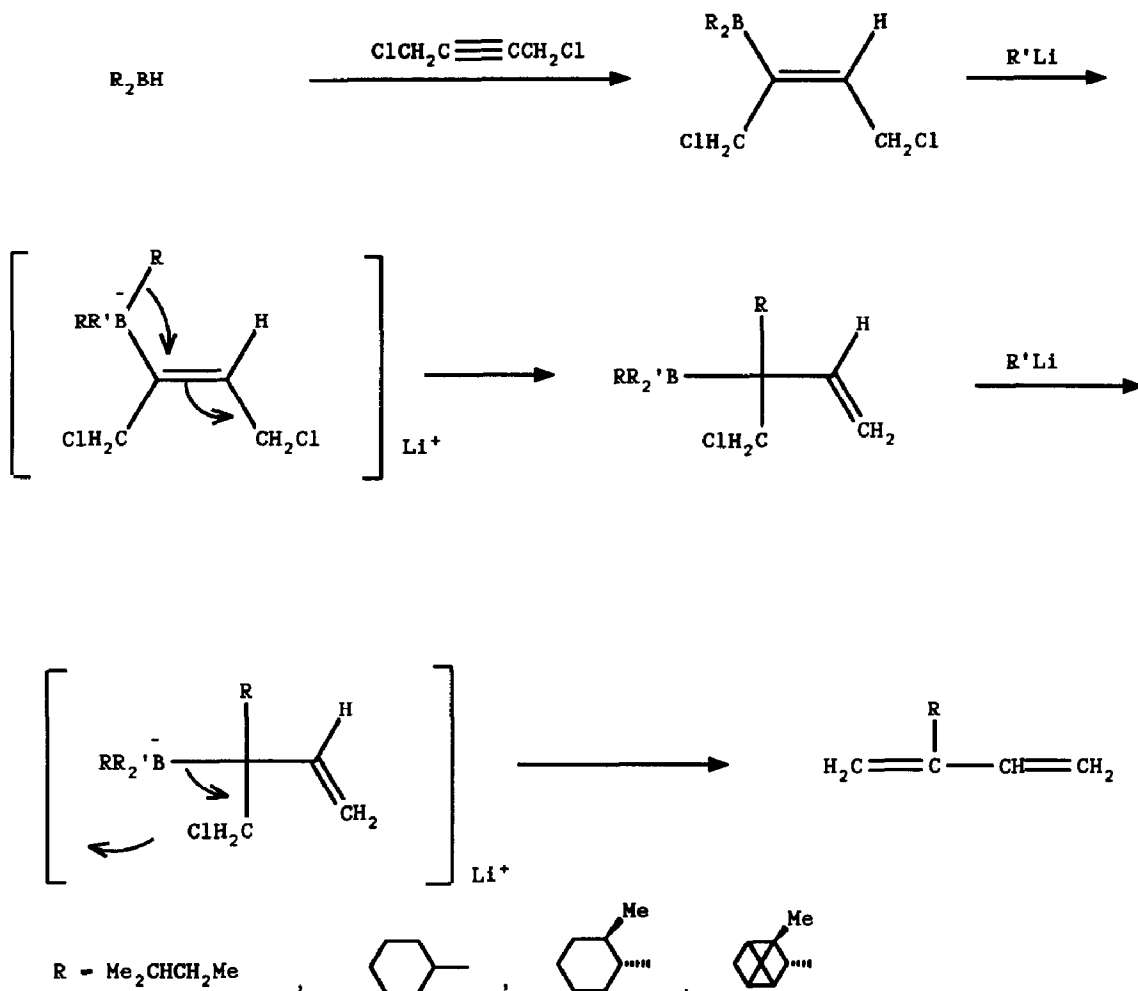
2. Alkenyl- and Arylborates

Alkenyl- and Arylborates undergo a wide variety of anionotropic rearrangement reactions in which organic moieties migrate from the electron-rich boron atom to a neighboring electron-deficient carbon atom. The electron deficiency which induces the migration can be created in a variety of ways, the simplest of which is the presence of an electronegative halogen atom, another popular method involves transition metal catalyzed coupling reactions. Terashima, Oda, Ishikura and Kraatz synthesized a series of 4-substituted isoquinolines utilizing the palladium catalyzed cross-coupling reaction of organic halides with 4-borylisoquinolines[37].
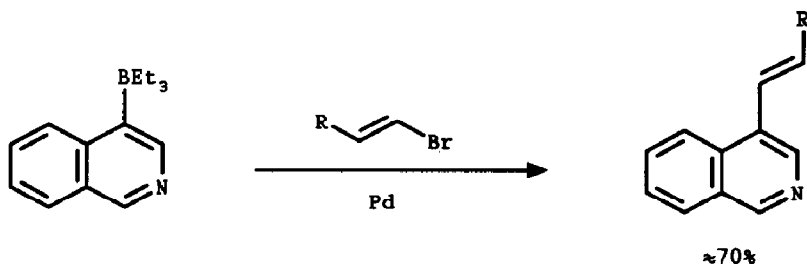

In a Chemical Letters article, the authors describe an organic synthesis using haloboration reactions to prepare 1,2-disubstituted ethenes[93].
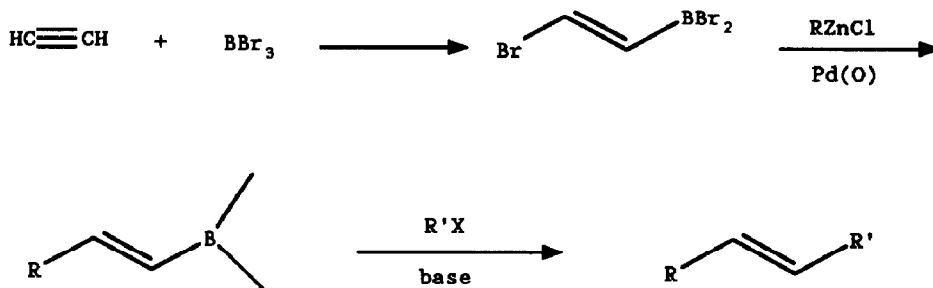

Arase and Hoshi describe the syntheses of 2-alkyl-1,3-butadienes from internal alkenes and 1,4-dichloro-2-butyne via anionotropic rearrangment of dialkyl(1,4-dichloro-2-buten-2-yl)--boranes[94].

R_2BH →[$ClCH_2C\equiv CCH_2Cl$]

(structure with R_2B, H, ClH_2C, CH_2Cl) →[$R'Li$]

(bracketed intermediate)

$$R \quad \text{—} \quad RR'B^- \quad H \quad ClH_2C \quad CH_2Cl \quad \Big]\ Li^+$$

→ $RR_2'B$—(structure with R, H, ClH_2C, CH_2) →[$R'Li$]

(bracketed intermediate with $RR_2'B^-$, R, H, ClH_2C, CH_2, Li$^+$)

→ $H_2C=C(R)-CH=CH_2$

$R = Me_2CHCH_2Me$, (cyclohexyl) , (methylcyclohexyl, Me) , (bicyclic, Me)

Negishi, Merrill, Abramovitch and Campbell discussed
the factors affecting the di/mono substitution ratios of
alkylation and allylation of lithium arylborates. Factors which
promote polarization or ionization of alkylating agents favor
disubstitution. While alkylation with Et_2SO_4 gave very low yields
of the disubstituted products[95].
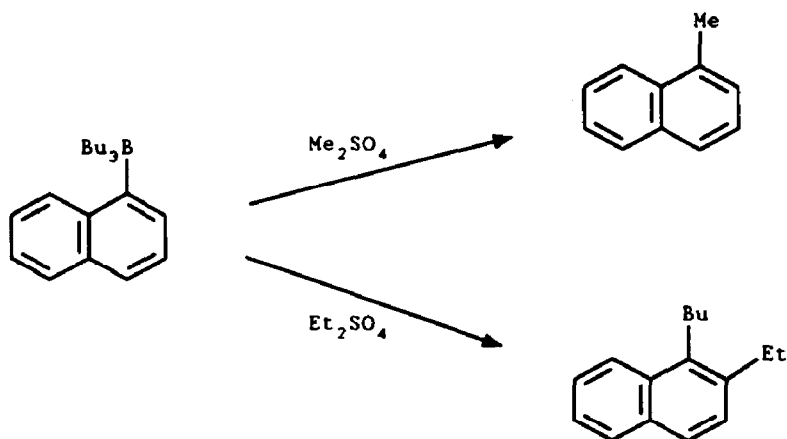
Ishikura, Oda, Kamada and Terashima prepared alkyl quinolines from alkylquinolylborates[96].
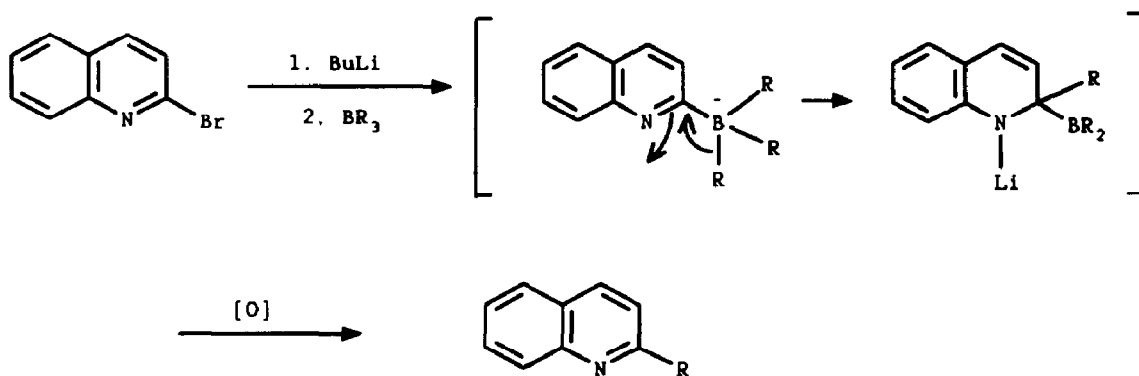

Hoffman and his coworkers used the Diels-Alder reaction of 1,3-dienylboronates as a new route to functionalized carbocycles. The dienylboronates add to aldehydes in a highly sterioselective fashion, establishing the relative configuration at up to four steriogenic centers[97].
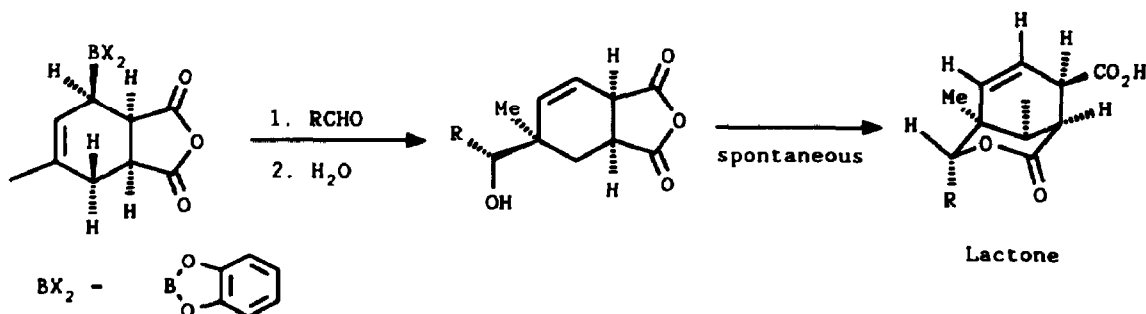
Carpita, Neri and Rossi, synthesized analogs of naturally-occuring (2E,6E,8E)-N-(2-methylpropyl)-2,6,8-hexadecatriene-10-ynamide, using boron for a Pd-catalyzed C-C bond-formation[98]. Bumagin, Ponomarev and Beletskaya investigated the influence of the organic moiety on the yields of the palladium catalyzed coupling reactions between organoborates and aryl iodides[99]. Stavenuiter, Hamzink and others studied the cross-coupling of phenylboronic acid with heterocyclic aromatic halides[100].
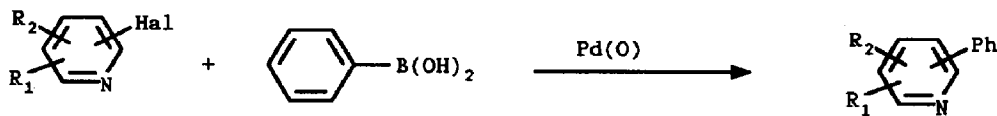
Kishi and his coworkers investigated the Suzuki diene synthesis and found that the rate was dramatically enhanced by using thallium hydroxide as the base instead of potassium hydroxide[101].


X- Ac   Z- Si(Me)$_2$(t-Bu)
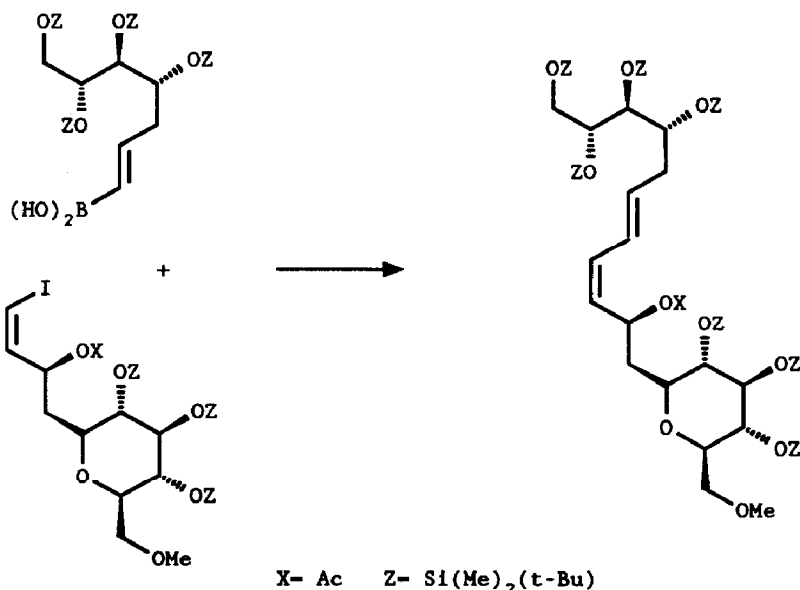
Satoh, Miyaura and Suzuki studied the palladium catalyzed cross- coupling reaction of (1-ethoxy-1-alken-2-yl)boranes with ortho-functionalized iodoarenes[102].
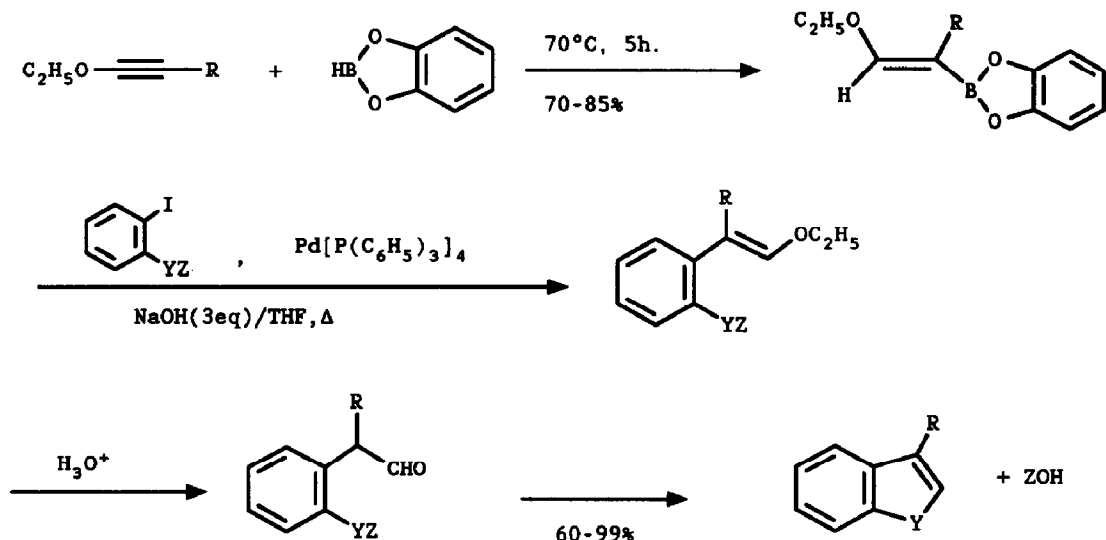

R- CH_3, n-C_6H_{13}.

YZ- NH_2, NHAc, OCH_3, CH_3.

Ishiyama, Miyaura and Suzuki studied the stereoselective syntheses of conjugated 1-(phenylthio)-1,3-alkadienes and -1,3,5-alkatrienes through the palladium-catalysed cross-coupling reaction of (E)- or (Z)-1-alkenylboronates with (E)- or (Z)-2-bromo-1-(phenylthio)-1-alkenes[103]. Cheng and Snieckus
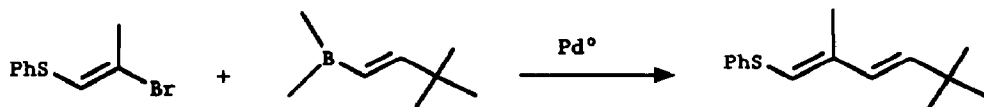
discussed the synthetic connections to the aromatic directed metalation reaction for the construction of polyphenyls[104].
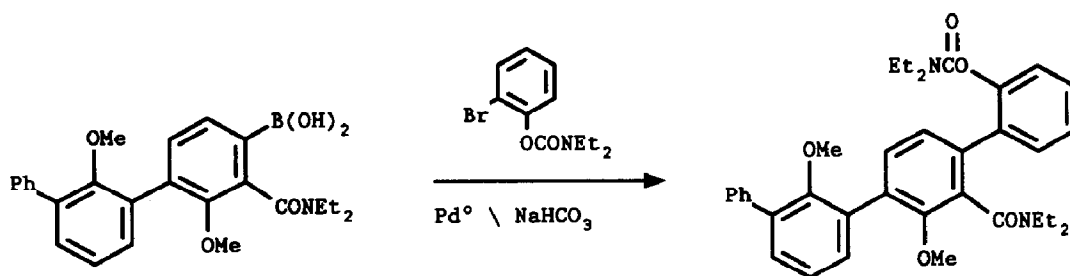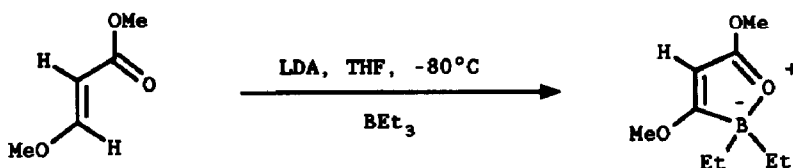
Zweifel, Hahn and Shoup investigated the regio- and diastereoselective conversion of 3-borolenes, into substituted homoallylic alcohols[105].
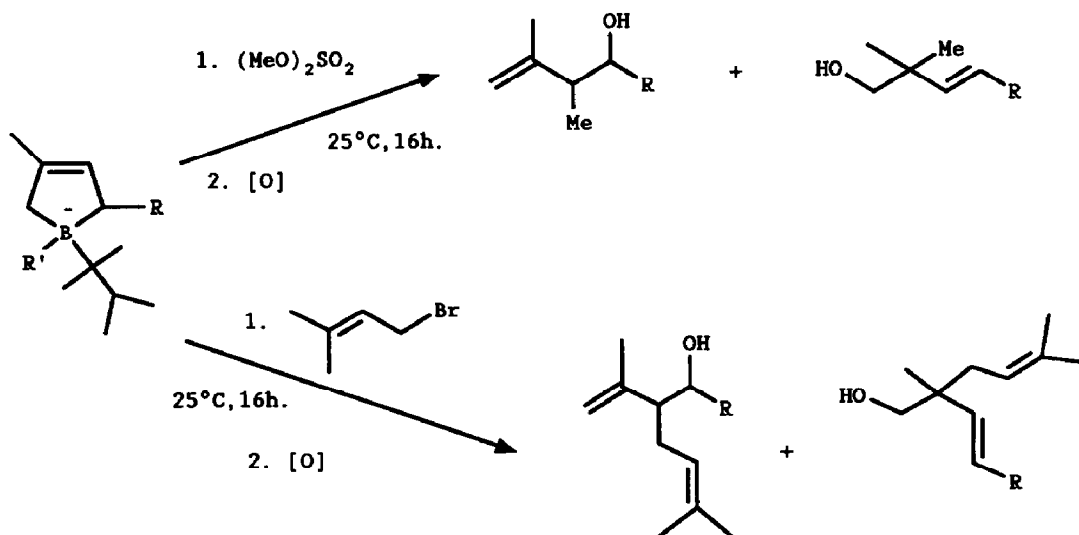

R- n-hexyl, cyclopentyl, cyclohexyl.

Vinyl carbanions were utilized in the synthesis of 1,2-oxaborole betaines by Barua, Evertz, Huttner and Schmidt[106].

Bihlmayer, Kersch and Wrackmeyer synthesized a new butadiene derivative from B-ethyl-9-borabicyclo[3.3.1]nonane and 1-propynylstannane. Attempts to oligomerize the propenyl stannane by organoboration with trimethylborane lead to a hexatriene derivative[107].
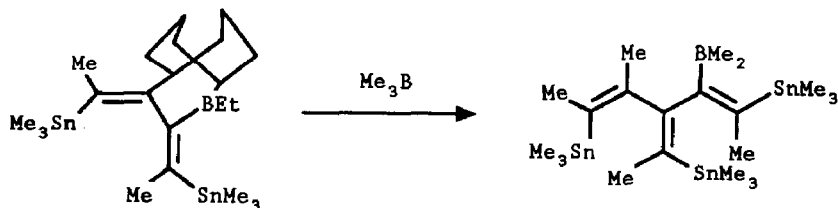
Schmid, Vehreschild-Yzermann and Boese synthesized a diazastannaborolidine and diazadiborolidine[108].
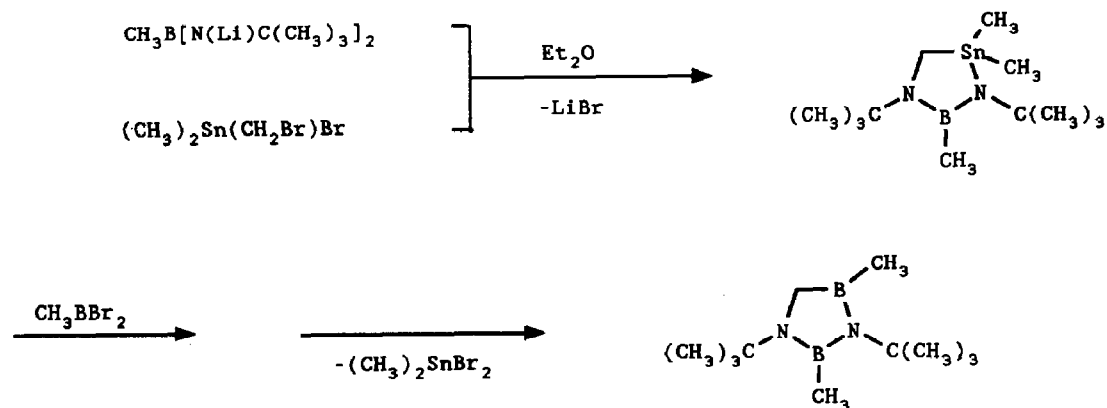
Wrackmeyer and Abu-Orabi reported the smooth rearrangement of (E)-2-stannyl-1-boryl-1-alkene to its (Z)-isomer on ultra violet irradiation[109]. The authors also prepared tricyclic heterocycles

E-isomer
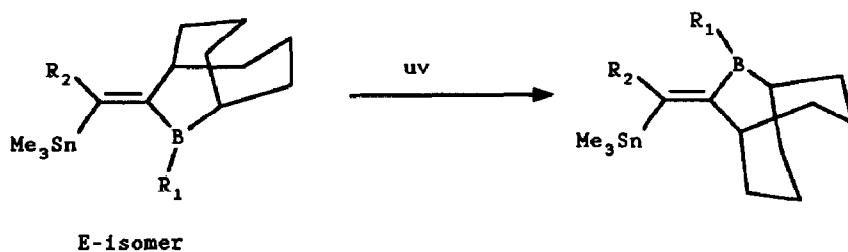
containing a stannacyclopentadiene using the reaction of
diethynyldimethylstannane with B-alkyl-9-borabicyclo-
[3.3.1]nonanes[110]. Brown and Srebnik prepared
organyl-1-alkynylborinic esters in high purity via the addition of
a lithioacetyllide to a borinic ester[111].

3.   Alkynylborate

Wang and his coworkers used lithium 1-alkynyltrialkylborates
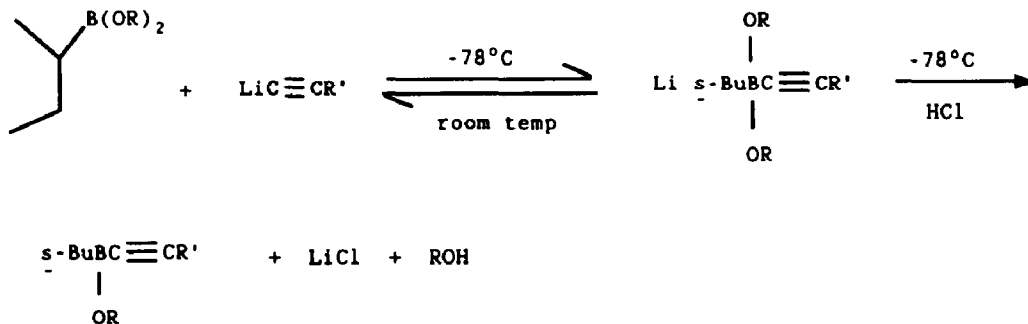in the synthesis of allylsilanes and β-(trimethylsilyl) ketones.
Electrophilic attack on the alkynylborate induced migration of an
allyl group from the boron atom to the adjacent acetylenic carbon
atom[112]. Wang and Dhumrongvaraporn also used the
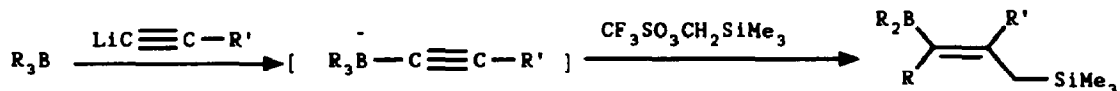
tris[(trimethylsilyl)methyl]borane for the preparation of
allylsilanes[113].
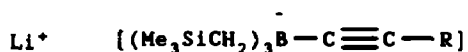
Hoshi, Masuda and Arase used alkenylboranes in the synthesis
of 2-__tert__-alkyl-1,3-butadienes and 2-(alkylthio)-1,3-butadienes
from 1,4-dichloro-2-butyne[114]. Koester, Seidel, Boese and
Wrackmeyer prepared several N-substituted 4,5-diethyl-2,5-
dihydro-2,2,3-trimethyl-1,2,5-azasilaboroles[115].
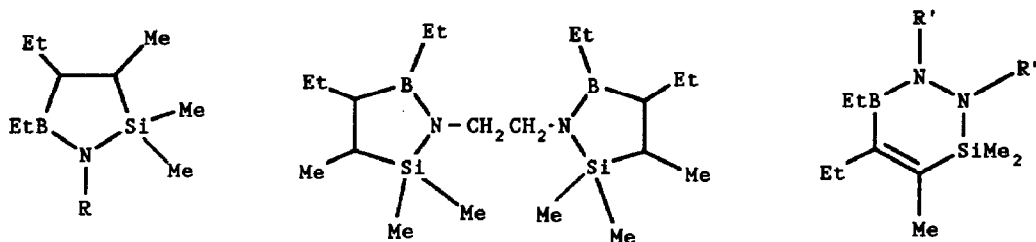
4. Propargyl- and allylboranes

Bubnov reviewed the construction of cyclic, cage, and acyclic organoboron systems through the use of allylboranes[116]. Bubnov, Gurskii and Pershin used 1,1-bis[(dipropylboryl)methyl]- ethylene XVI as a new reagent for allylboration[117].
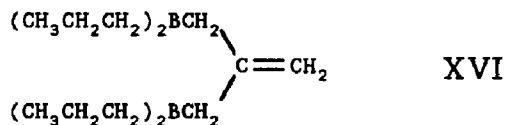
Brown and his coworkers prepared β-allyldiisopinocamphenyl-boranes XVII and XVIII from (+)-α-pinene. These reagents are the most highly diastereoselective allylboranes reported[118]. Brown
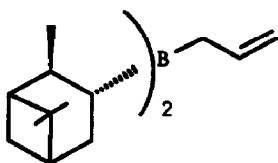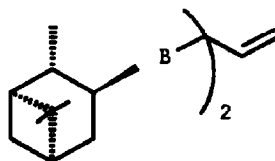
XVII   XVIII

and his coworkers used the diastereofacial selectivity of (E)- and (Z)-crotyldiisopinocampheylboranes in their reaction with chiral aldehydes[119].
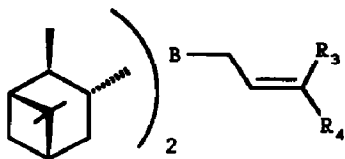
R_3- H, CH_3

R_4- CH_3, H
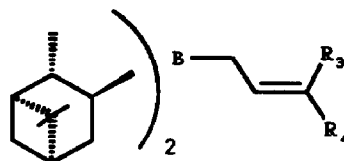
Hoffman and Endesfelder used crotylboronates XIX to diastereoselectively prepare oximes[120]. Roush and his coworkers

XIX
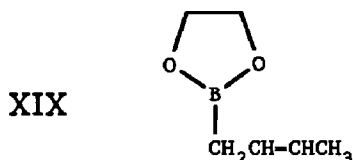
synthesized several modified crotyl- and allylboronates XX-XXII,which were used to stereoselectivly construct 1,3-dimethyl-2-hydroxy stereochemical relationships[121].

XX   XXI   XXII
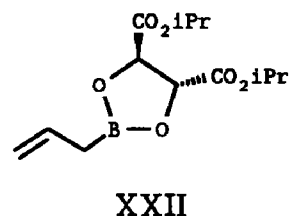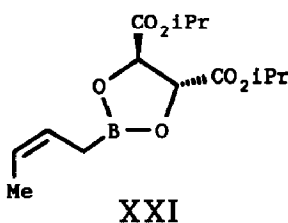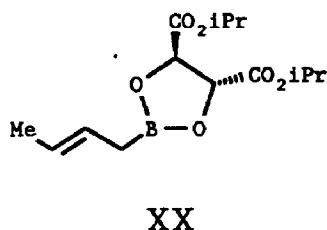
Roush and Palkowitz used the modified allylic boronates, XX and XXII, in an efficient, highly stereoselective synthesis of the C(19)-C(29) segment of Rifamycin S.[122]. Hoffmann, Matternich and Lanz used the (Z)- and (E)-alkoxyallylboronates, XXIII, to synthesize the arabino, ribo, and lyxo 2,6-dideoxy-L-hexose[123].

XXIII
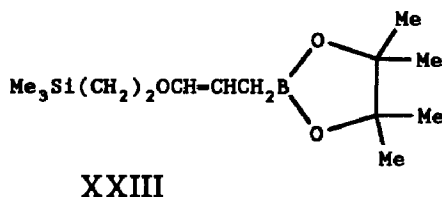
Bubnov and Zheludeva prepared the allylborane with an exocyclic double bond, XXIV, for use in the syntheses of vinylcyclane derivatives[124]. Ota and Terashima studied the

XXIV

$$CHCH_2BR_2$$
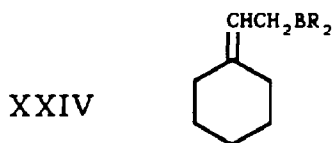
reaction of various lithium tributylheteroarylborates with allylic bromides in the presence of copper(I) cyanide to regioselectively allylate at the heteroaryl ring[125].

5.   Enol Borinates

Hooz and his coworkers prepared several Mannich Bases and Cross-Aldol products using Enol Borinates[126]. Hoffmann, Ditrich

$$\overset{+}{Me_2N} = \overset{-}{CH_2}I$$

$$R - \underset{OB(R^1)_2}{\overset{|}{C}} = CH_2$$

$$R^1COCH_2CH_2NMe_2$$

$$R^1COCH_2C(OSiMe_3)R^2R^3$$

$$\underset{\underset{O}{\overset{||}{C}}}{R^2} {R^3}$$
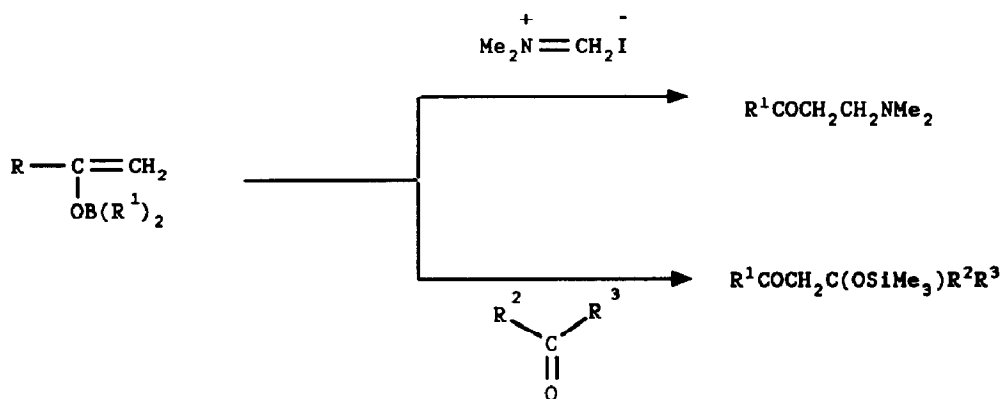
and Froech prepared stable (E)- and (Z)-enolborinates and reacted them with aldehydes in a sterioconvergent reaction leading to syn-aldols[127]. Paterson and his coworkers studied the Aldol condensation of chiral ethyl ketones with boron enolate, the simple dialkylboron (Z)-enolate of chiral ketone XXV was found to show high sterioselectivity in the formation of the all-syn aldol adduct XXVI[128].

L$_2$BOTf

Et$_3$N

XXV

Me H

O—BL$_2$

R$_2$

H

O

H

O

R$_2$ R$_1$

HO O OTBS
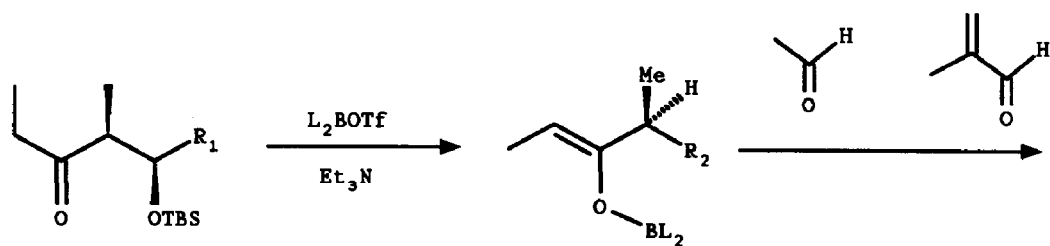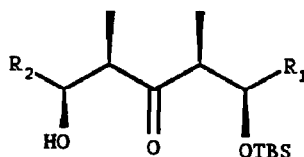
XXVI

R$_1$- MeC-CH$_2$

R$_2$- Me

BL$_2$- 9-BBN or ^{n}Bu$_2$B

D. CARBON-HETEROATOM

1. Group VI

Pelter and Rowlands converted furans to butenolides via oxidation of their boron derivatives with m-chloroperbenzoic acid[129].

R O BX$_2$

1. [O]

2. H$_2$O

R O O

and/or

R O O
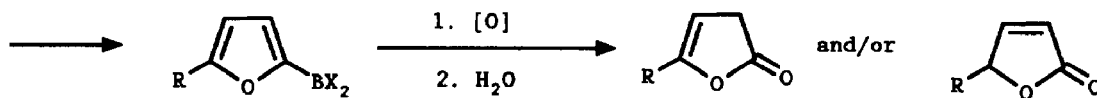
R- Ph, substituted Ph, PhCH$_2$, octyl.

Kim and Kim converted carboxylic acids and esters directly into (S),(S')-diphenyl acetals and phenyl sulfides using thexyl(phenylthio)borane[130].

BHSC$_6$H$_5$ $\xrightarrow[\text{R.T.} \quad \text{CH}_2\text{Cl}_2]{\text{BBr}_3 \cdot \text{SMe}_3}$

$\xrightarrow{\text{RCOOH}}$

$\xrightarrow{\text{RCOOR'} \quad + \quad \text{ZnI}_2}$ RCH$_2$SC$_6$H$_5$
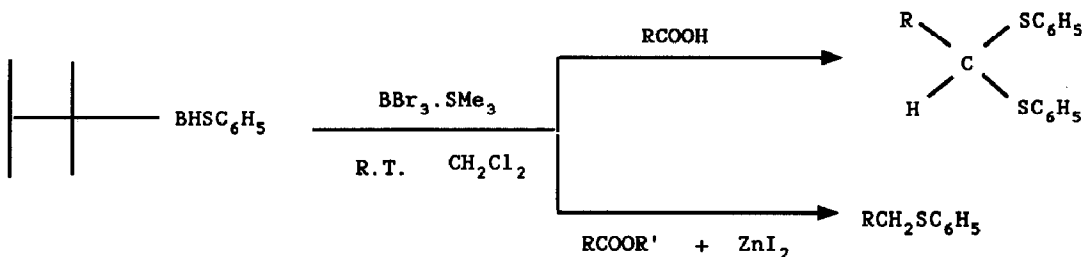
2. Group V

Kabalka and his coworkers reacted trialkylboranes with sodium azide in the presence of aqueous acid to yield primary amines. The reaction presumably proceeds via the anionotropic rearrangement of an organoborate complex[131].

R$_3$B $\xrightarrow{\text{HN}_3}$ $\xrightarrow{}$ $\xrightarrow{}$

$\downarrow$ H$_2$O

RNH$_2$
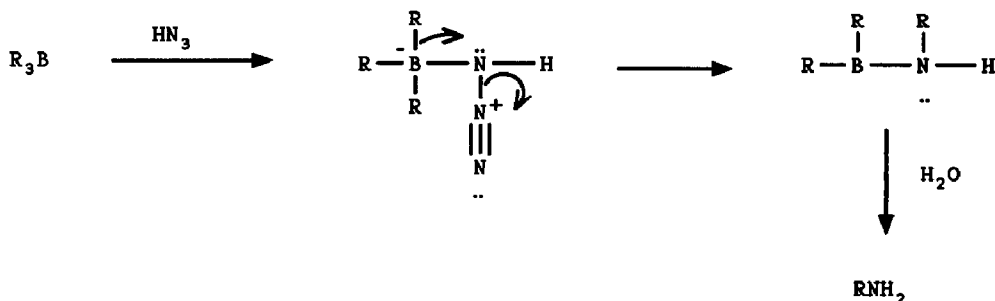
Brown and his coworkers reported an efficient procedure for converting alkenes to amines. They utilize dimethylborane to hydroborate alkenes; the resultent dimethylalkylboranes are then reacted with chloramine or hydroxylamine O-sulfonic acid to produce the desired alkylamines[132].

+ LiMe$_2$BH$_2$ $\xrightarrow[\text{EE}]{\text{Me}_3\text{SiCl}}$ $\xrightarrow{}$ NH$_2$
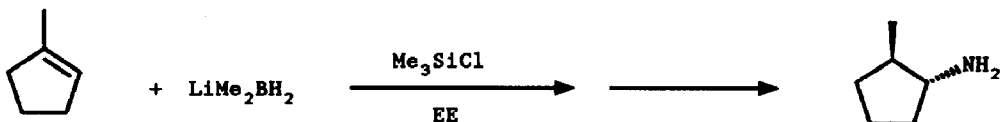
E. Hydroboration-Oxidation /Hydroboration-Protonation

Mori, Kitahara, Takagi and Katsuta prepared monoesters which

on hydroboration/oxidation gave cyclopentanols such as XXVII which are synthetic intermediates for fragrance compounds[133].
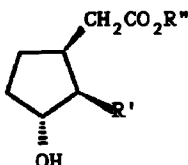
XXVII

Umeno and Tomomi Prepared phenols via arylboronic and borinic acids[134].

Taba, Koester and Dahlhoff prepared octa-O-(diethylboryl)-sucrose, which reacts with ethylboron reagents to give various mixtures of ethyl boranediylsucroses. The O-diethylboryl groups were selectivly removed with acetylacetone[135].

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