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BORON: BORANES IN ORGANIC SYNTHESIS

ANNUAL SURVEY COVERING THE YEAR 1988

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A. INTRODUCTION

Organoboranes have become one of the most significant classes of organometallics used in organic synthesis. Numerous studies have established that organoboranes transfer an alkyl group to elements of synthetic interest with complete maintenance of stereochemical integrity. The boranes are also used in thousands of hydroborations and reductions each year. This review focuses on reports concerning new methodology and/or new reagents and not on the routine use of boranes and borohydrides.

B. BORANE REAGENTS

1. Hydroborating agents

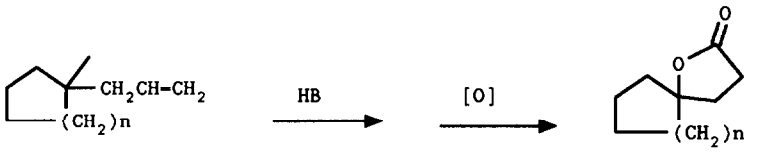
The asymmetric hydroboration-oxidation sequence has been developed as one of the methodologies for obtaining regio- and stereochemically defined alcohols; several exciting new reagents are described in this section.

a. BH_3

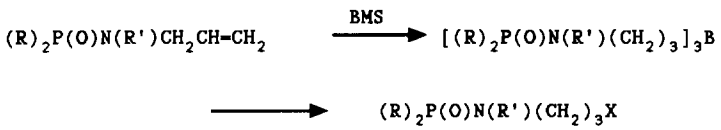
Borane solutions in THF (BH_3.THF) or dimethyl sulfide (BMS) are routinely utilized for hydroborations. Montury and coworkers report that the hydroboration of trimethylsilyl derivatives of olefinic amines provides a convenient route to aminoboronic acids[1].

Wu, Kakuzo and Yoshio carried out hydroborations of alkenes and alkadienes by generating borane *in situ* from sodium borohydride and zirconium salts in the presence of crown ethers[2].

The synthesis of γ-lactones by hydroboration-oxidation of homoallylic alcohols was reported by Nguyen, Mavrov and Chrelashvili[3].



Benmaarouf, Baboulene, Speziale and Lattes describe the synthesis of γ-halogenopropyl phosphoramidates by hydroboration-halogenation of N-phosphorylated allylamines; the use of allyl

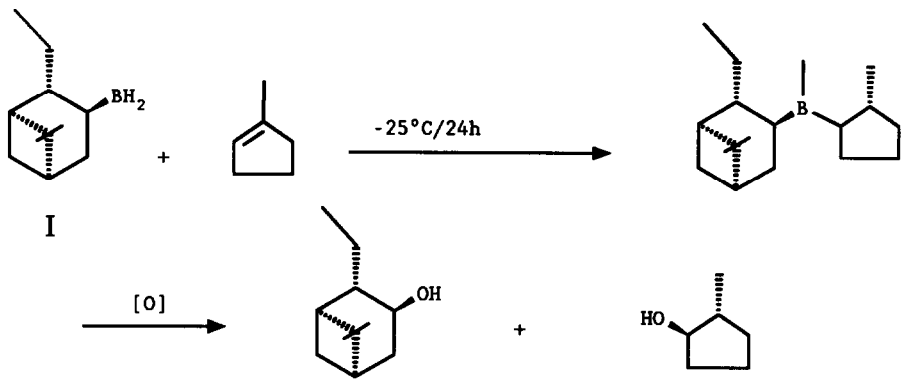


R-alkoxy R'-alkyl,aryl X-Br,I

phosphoramidates lead to a good regioselectivity in the addition of the boron atom to the terminal carbon atom of the allyl structure[4].

b. RBH_2

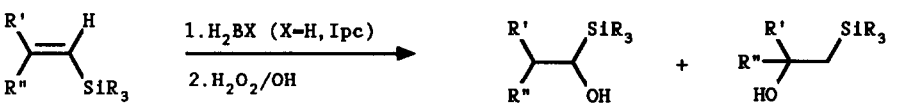
The functionalities available through hydroboration of alkenes with subsequent modification of the resulting organoboranes are extensive. Hydroboration of prochiral olefins with chiral hydroborating agents such as $IpcBH_2$ proceed with remarkable asymmetric induction, making this reaction a most valuable one for asymmetric organic synthesis. Brown and his coworkers prepared and used mono(2-ethylapoisopinocampheyl)borane ($EapBH_2$), I, as a chiral hydroborating agent for *trans* and trisubstituted olefins[5]. The data supported the postulation that



increasing the steric bulk at the 2-position of pinene would lead to a favorable increment in the optical induction.

Soderquist, Hwang-Lee and Barnes determined the single X-ray structure of a monoisopinocampheylborane-N,N,N',N'-tetramethylethylenediamine (TMEDA) complex (2:1). On the basis of this x-ray structure, the selectivity of the reagent in hydroboration reactions was explained[6].

Soderquist and his coworkers also studied the asymmetric hydroboration of various vinylsilanes with monoisopinocampheylborane ($IpcBH_2$). They found β-substitution on the vinylsilane gives monomeric dialkylborane adducts in which the boryl group is α to the silicon[7].



when R'-R"-H the yield is 57 + 43
when R'-R"-CH_3 the yield is 98 + 2
R = Me or Et

Brown and his coworkers used monoisopinocampheylborane ($IpcBH_2$) in asymmetric hydroborations of a series of 1-heteroarylcycloalkenes to synthesize *trans*-2-heteroarylcycloalkyl boronates (and derived alcohols) of very high enantiomeric purity[8].

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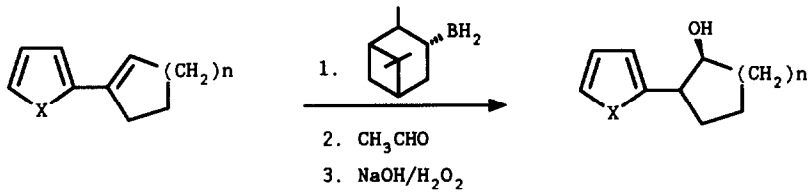
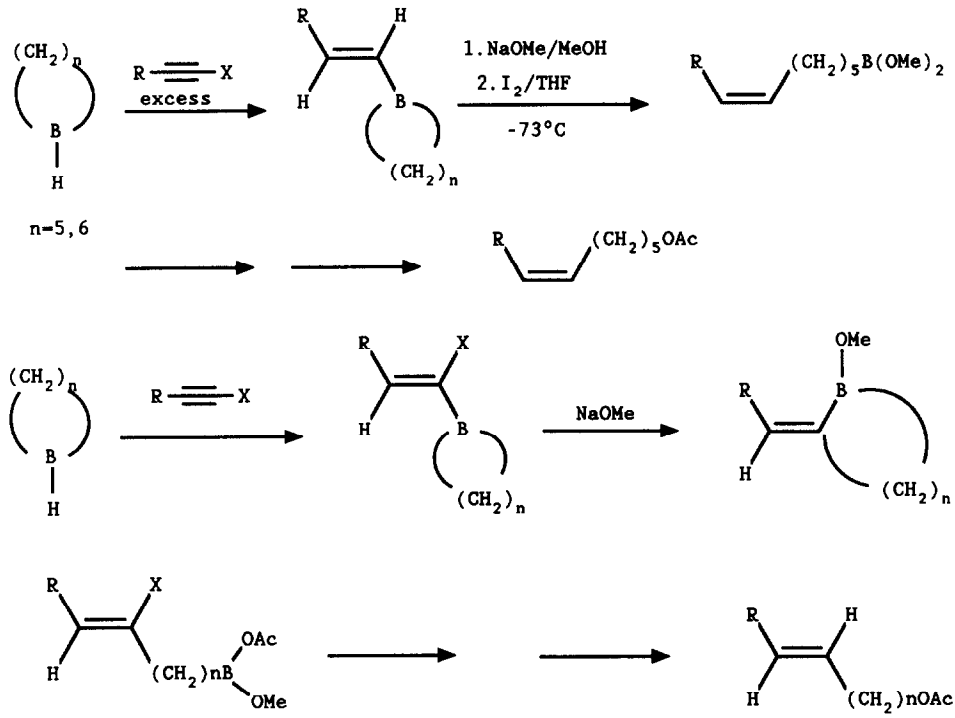
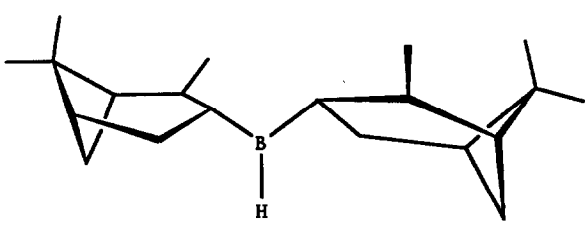


c. R_2BH

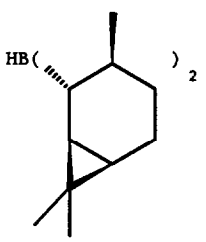
Brown and his coworkers successfully utilized readily available borinane and borepane for the stereospecific syntheses of (Z)- and (E)-6- and -7-alken-1-ols[9]. Peterson and Stepanian



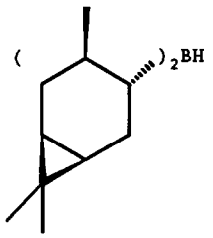
used crystalline diisopinocampheylborane to hydroborate several bulky vinyl ethers; low enantiomeric excesses were achieved[10].



Brown, Prasad and Zaidlewicz prepared the new hydroborating agents 2- and 4-dicaranylboranes (II and III). The reagents readily hydroborate prochiral *cis* disubstituted olefins to yield the corresponding dialkylboranes which, on oxidation, produce chiral alcohols of opposite absolute configuration in good to excellent ee[11]. Brown and Joshi describe an improved method for the

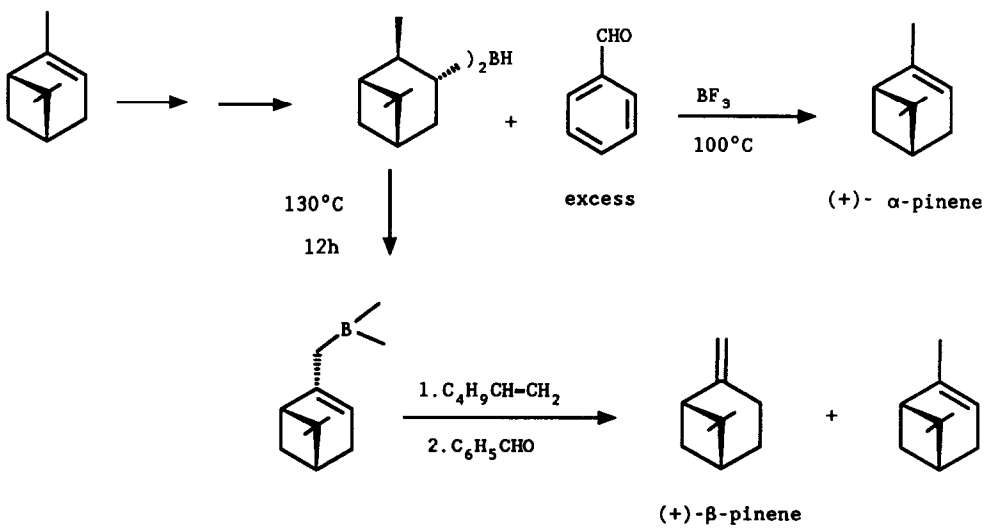


II



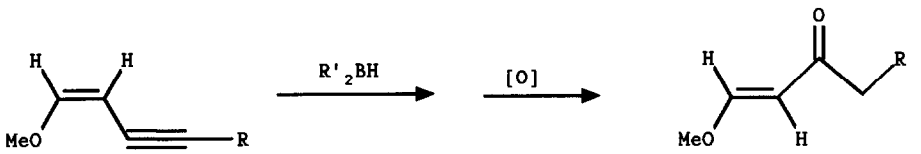
III

preparation of optically pure diisopinocampheylborane (Ipc_2BH) from commercially available (+) and (-)-α-pinene. Ipc_2BH can also be used for the preparation of optically pure (+)-α-pinene, as well as the relatively rare (+)-β-pinene[12].



Zweifel and his coworkers used the chemo- and regioselective hydroboration of (Z)-methoxyenynes with dialkylboranes to

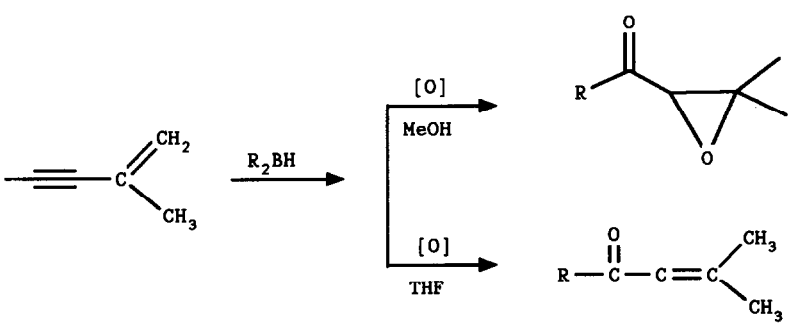
synthesize the valuable (E)-methoxyenones[13]. Interestingly the expected (Z)-methoxyenone products initially formed isomerized to the thermodynamically more stable (E)-isomers under the reaction condition.



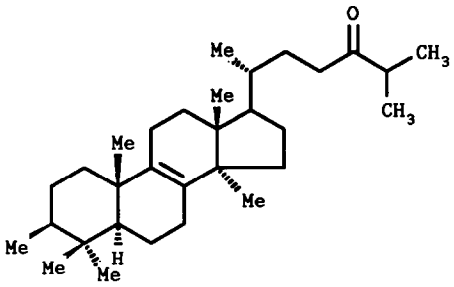
R'= cyclohexyl, 1,2-dimethyl propyl

For the synthesis of functionalized hydrocarbon polymers, Chung, Raate, Berluche and Schulz selectively hydroborated 1,2-polybutadienes in the presence of the 1,4-moieties[14]. Chung also prepared α-olefin polymers and copolymers from borane monomers obtained from monohydroboration of 1,7-octadiene with 9-borobicyclo[3.3.1]nonane in THF[15].

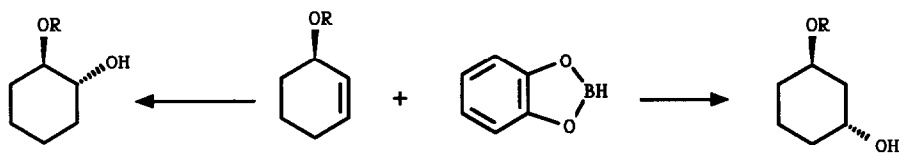
Zweifel and Shoup prepared α,β-unsaturated ketones and α,β-epoxy ketones via the hydroboration of 1-halo-3-alken-1-ynes[16].



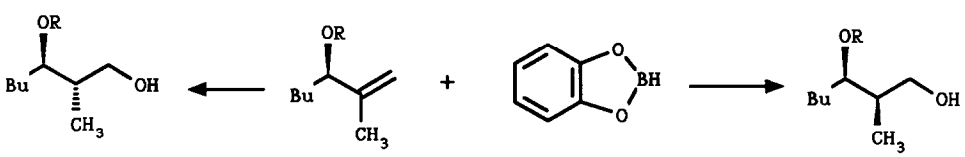
Parish, Honda, Chitrakorn and Taylor used a selective hydroboration of the C(24) double bond in lanosterol, followed by oxidation of the C-B bond, to prepare lanost-8-en-3β-ol-24-one (24-ketolanosterol)[17].



Evans, Fu and Hoveyda reported an extensive investigation of the rhodium-catalyzed hydroboration process. Wilkinson's catalyst [$Rh(PPh_3)_3Cl$] possesses better regio- and diastereoselective properties than [$Rh(nbd)(diphos\text{-}4)]BF_4$[18]. The stereochemical consequences of the catalyzed and uncatalyzed catecholborane hydroboration processes are different. Burgess and Ohlmeyer used

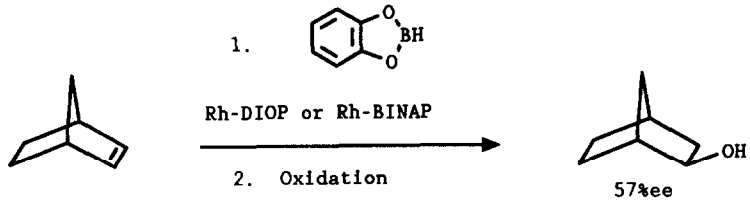


Uncatalyzed >80% Catalyzed >80%



Uncatalyzed >80% Catalyzed >80%

a homochiral rhodium-phosphene complex (DIOP or BINAP) for the enantioselective hydroboration of alkenes by catecholborane[19]. The optical purity of the norborneol was inversely related to the reaction temperature.

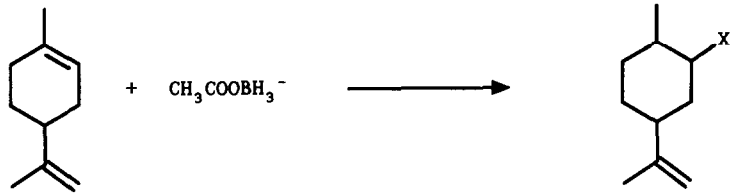


(1R,2R)-exo-norborneol

DIOP = 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane.
BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl.

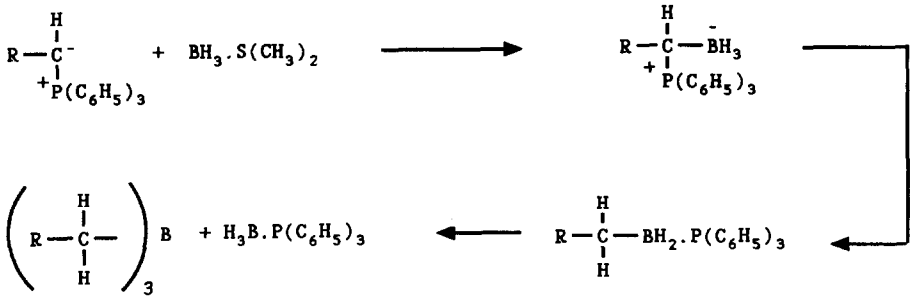
d. R_3BH^-

Gautam, Singh and Dhillon used acetoxyborohydride for the regioselective hydroboration of dienes to afford products, after oxidation or iodination, derived exclusively from the more substituted double bond[20].



X= OH or I

Bestmann and his group report that triphenylphosphonium ylides add borane to form alkylidenetriphenylphosphoraneboranes which rearrange on heating to give the triphenylphosphane-monoalkylborane adducts. The adducts can participate in hydroboration reactions[21].

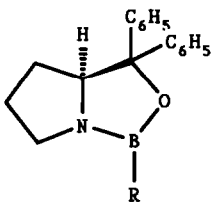


R = H, CH_3

2. Reducing agents

a. BH_3

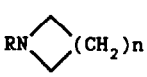
Corey and his coworkers described the preparation of a chiral oxazaborolidine (IV) which they utilized as a catalyst in the borane reduction of α-chloroacetophenone to (S)-(+)-α-(chloromethyl) benzenemethanol in 97% yield and 96.5%ee. The chloro alcohol was used to prepare (S)-(-)-phenyloxirane in 96% yield[22].



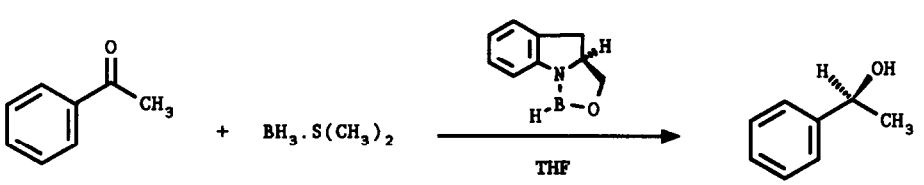
R= H or CH_3

IV

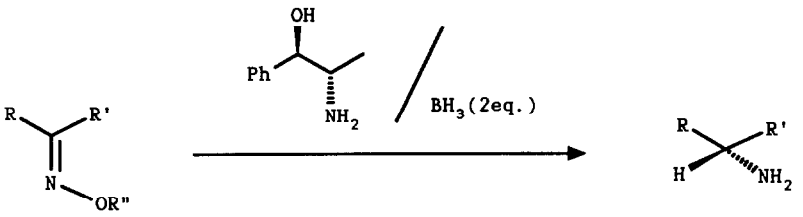
Choi and his coworkers studied the exeptionally slow reduction of phenylmalonic acid by borane-THF, they concluded that a relatively stable cyclic intermediate formed initially. From this intermediate a second intermediate was formed, by α-hydrogen abstraction, which is resistant to further reduction[23]. Venuti and Ort used borane-methyl sulfide in THF for the reductive cyclization of ω-ester alkylamides providing a convenient synthesis of N-substituted cyclic amines[24]. Youn, Lee and Pak



reduced prochiral ketones with borane-methyl sulfide (BMS) in the presence of chiral oxazaborolidine to afford the corresponding secondary alcohols in moderate to high (46-97%) optical yields. They found the optimum ratio of ketone:catalyst:BMS to be 1:1:2[25].

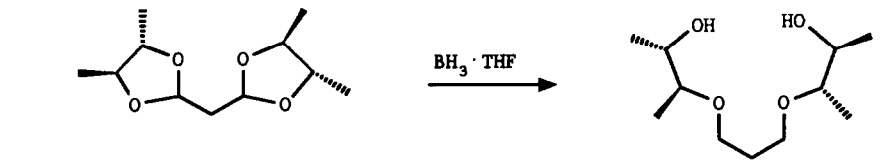


Sakito, Suzukamo and Yoneyoshi used (-)-norphedrine and 2 eq. of BH_3 as a chiral reducing agent for ketoxime ethers. They obtained (S) and (R) amines in up to 92% ee and established that the preferred absolute configuration of the amine was dependent on the geometry of the oxime ether[26].

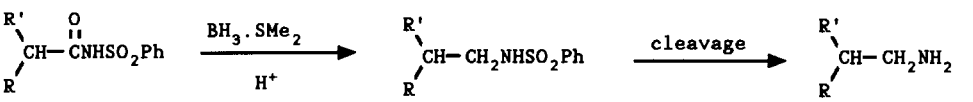


R = Ph, R' = p-tolyl-CH_2, R" = Me

Interest in the synthesis of highly substituted crown ethers prompted Gutierrez and his coworkers to develop a convenient synthesis of substituted polyether diols (crown ether precursors), by the selective reductive cleavage of C-O bonds in bis(cyclic acetals) [or bis(cyclic hemithioacetals)] by borane or monochloroborane[27]. Belletire and Fry describe a useful approach



to primary amines. Reduction of acylsulfonamides to sulfonamides by borane, when coupled to standard sulfonamide cleavage procedures, provides a general route to primary amines[28].



R=H, CH_3

R'-$CH_3(CH_2)_5$, $C_6H_5CH_2$, $(3,4,5\text{-}OCH_3)C_6H_2CH_2$, $(CH_3)_2CH$, C_6H_5O, CH_3, H.

Green and his group used transition metal mediated homologation of BH_3.THF to prepare arachno-2-tungstametallaborane, $[WH_3(PMe_3)_3B_3H_8]$, in over 90% yield[29].

$$W_6(PMe_3)_3 + BH_3.THF \longrightarrow WH_3(PMe_3)_3B_3H_8$$

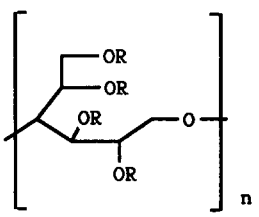
b. RBH_2

Schmidbaur, Wimmer, Reber and Mueller prepared the hydrotris (phosphonio)borate dication in several steps from bromoboranes[30].

$$BrBH_2.SMe_2 + R_3P \longrightarrow \cdots \longrightarrow \left[H_2B(Ph_2P)(PPh_2) \right]^+ Br^-$$

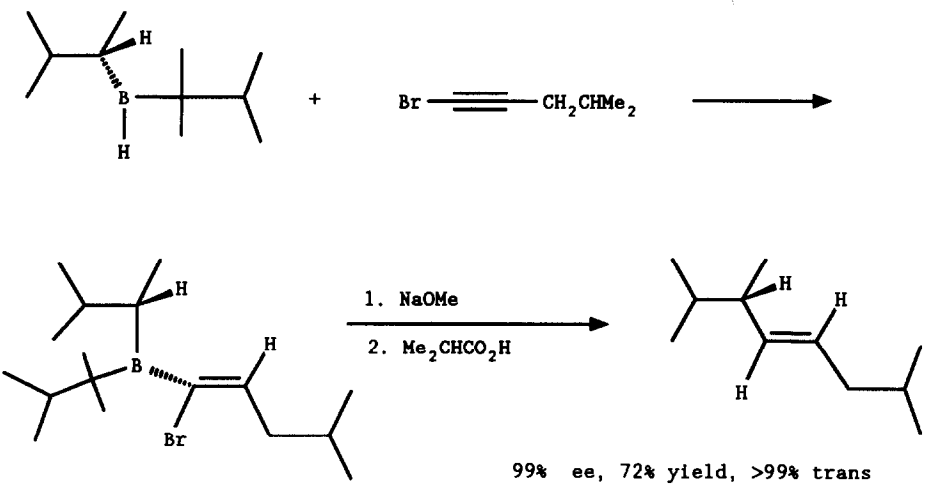
R = Me, Et

Dahlhoff, Imre and Koester used ethyldiboranes in the presence of 9-methanesulfonyloxy-9-borobicyclo[3.3.1]nonane for the regioselective reduction of cellulose to yield poly(1,4-anhydro-D-glucitols)[31].



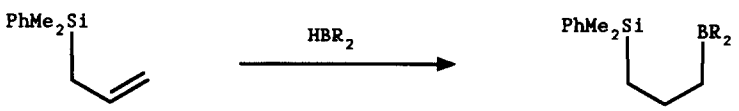
c. R_2BH

Brown, Bakshi and Singaram provided a simple procedure for the synthesis of various optically active monoalkylthexylboranes, which are valuable reagents for chiral synthesis. The synthetic potential of these monoalkylthexylboranes was demonstrated by carrying out reactions leading to the synthesis of optically active *trans*-olefins, *cis*-olefins, alkynes and ketones of very high enantiomeric purities[32].

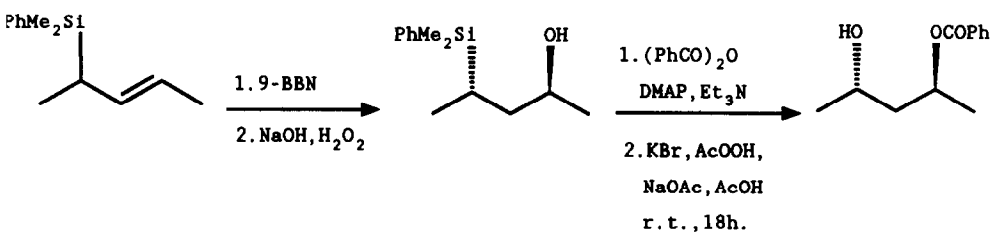


99% ee, 72% yield, >99% trans

Fleming and Lawrence found 9-BBN to be a highly selective hydroborating agent for most types of allylsilanes. The products have the metals (silicon and boron) in a 1,3 relationship and each be replaced by a hydroxy group independently of each other[33].



The authors later converted the products stereospecifically into 1,3-diols[34].



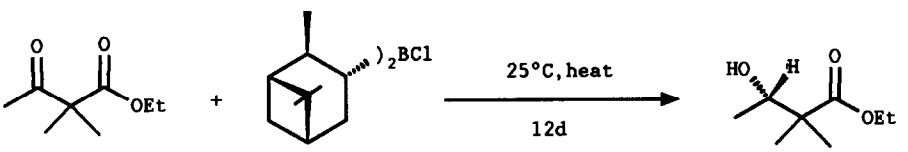
Cha, Lee, Yoon and Lee used 9-borabicyclo[3.3.1]nonane and thexylbromoborane-dimethyl sulfide to reduce Li or Na salts of carboxylic acid [e.g. $PrCO_2H$, Me_2ChCO_2H, cyclohexanecarboxylic acid, p-$ClC_6H_4CO_2H$ and p-$(HO_2C)_2C_6H_4$] to give the corresponding

aldehydes. Yields of aliphatic aldehydes (85-99%) were higher than those of the aromatic aldehydes (38-99%)[35].

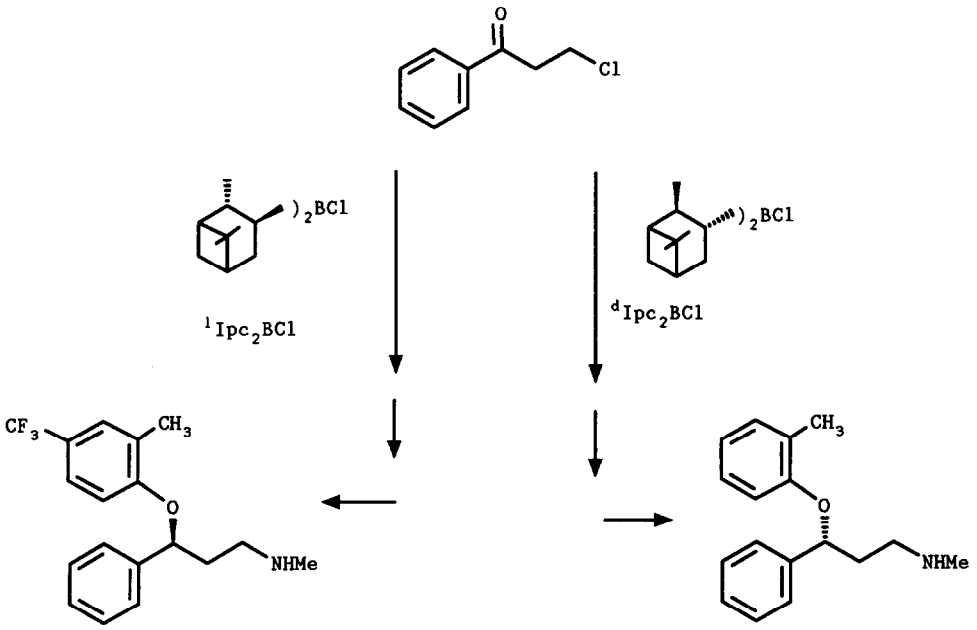
Cha, Oh, Lee, Yoon and Lee were able to directly transform carboxylic acids into aldehydes by stepwise treatment of acyloxy-9-borabicyclo[3.3.1]nonane with *tert*-butyllithium and 9-BBN[36]. The same authors also report the exceptionally facile reduction of carboxylic acid salts to aldehydes by 9-BBN in THF[37].

d. R_3B

Brown and his coworkers report that diisopinocamphylchloroborane is as an exceptionally efficient chiral reducing agent for a large variety of ketones. The reduction of simple dialkyl ketones yielded the corresponding alcohols with very low optical induction while arylalkyl ketones gave excellent asymmetric induction. The reagent reduces α-tertiary aliphatic ketones under neat conditions at room temperature[38].

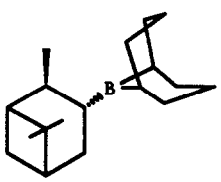


Brown, Srebnik and Ramachandran demonstrated that diisopinocampheylchloroborane, Ipc_2BCl, is an excellent chiral reducing reagent for haloarylalkyl ketones. The corresponding haloalcohols are generally obtained in >90% ee. The reagent provides for highly enantioselective syntheses of the antidepressant agents Tomoxetine,Fluoxetine and Nisoxetine[39].



Brown and his group report the enantioselective ring-cleavage of meso-epoxides with β-halodiisopinocampheylboranes (in particular the bromide and iodide which differentiate between the enantiotopic C-O bonds of meso-epoxides) to obtain optically active 1,2-halohydrins[40].

Flynn and Beight used S-Alpine Borane to reduce an α-keto

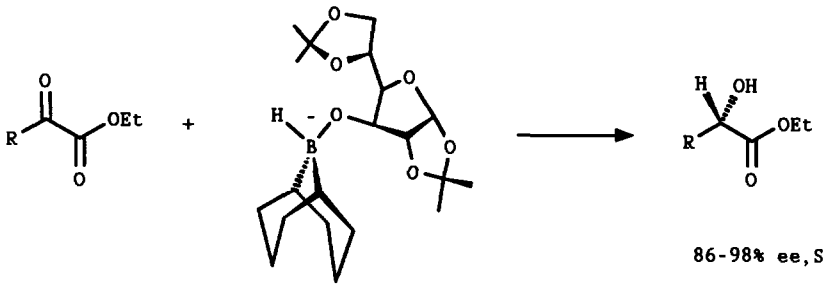


ester to produce ethyl (R)-2-hydroxy-4-phenylbutyrate. The latter is a useful intermediate in the synthesis of enzyme inhibitors[41].

e. R_4B^-

Brown and his coworkers provided a convenient and simple synthesis of a highly effective chiral borohydride reagent, K-glucoride. The reagent produces high optical inductions in the

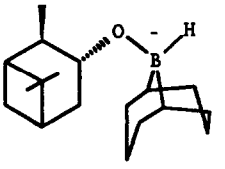
reductions of prochiral ketones, including hindered aliphatic ketones, alkyl arometic ketones and α-keto esters. Moreover, the



k-glucoride

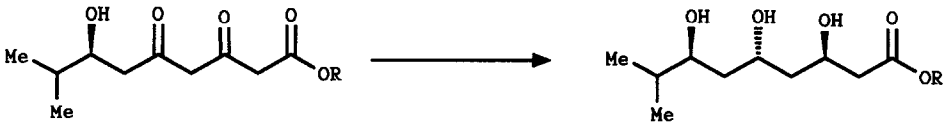
R = Me, Et, n-Pr, i-Pr, i-Bu, t-Bu, Ph or 1-naphthyl

directions of the asymmetric inductions are consistent: the reduction provides the corresponding alcohols enriched in the R enantiomers for both aliphatic and alkyl aromatic ketones. α-Hydroxy esters produce products enriched in the S enantiomers[42]. Cha, Lee, Yoon, Lee and Yoon also used the K-glucoride and another chiral potassium 9-BBN system in the reduction of (±)-1,2-epoxyalkanes to yield the (R)-2-alkanols in modest enantiomeric excess[43].



Evans, Chapman and Carreira used tetramethylammonium triacetoxyborohydride to reduce acyclic β-hydroxyketones with high anti diastereoselectivity. In every case that has been examined, good to excellent yields of diastereomerically homogeneous diols are obtained[44]. These reductions apparently proceed via a rate-determining, acid-promoted exchange of the substrate hydroxyl

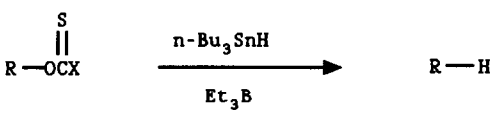
group for an acetate of the triacetoxyborohydride anion prior to the reduction step.



R = $(CH_2)_3Ph$

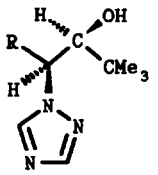
Cha and his coworkers used a new class of stereoselective reducing agents, potassium 9-alkyl-9-boratabicyclo[3.3.1]nonanes, and found potassium 9-t-butyl-9-boratabicyclo[3.3.1]nonane to be the most effective[45].

Oshima and his coworkers describe a facile reduction of dithiocarbonates with n-Bu_3SnH-Et_3B, providing an easy access to hydrocarbons from secondary alcohols[46].

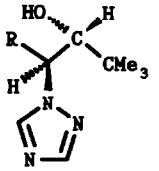


R = cyclododecyl X = SMe (93%)

Roesslein and Tamm report that the key step in the preparation of optically active 1,3-diols was the selective reduction of (R)-$RCH_2CH_2CH(OH)CH_2COMe$ by sequential treatment with Bu_3B-air and $NaBH_4$[47]. Thieme, Sauter and Reissenweber found the diastereoselectivity of the borohydride reduction of α-triazolyl ketones was altered by $TiCl_4$. In the absence of $TiCl_4$, the formation of diastereomers VI with OH and triazole groups syn to each other was preferred. While in the presence of $TiCl_4$ the diastereomer with OH and triazole groups anti was selectively formed[48].

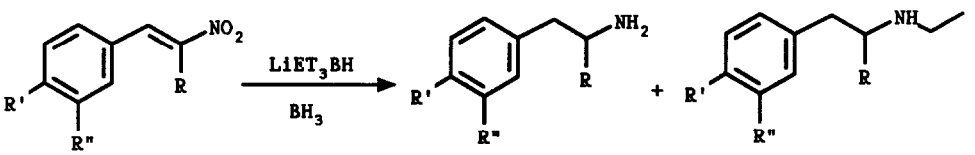


V

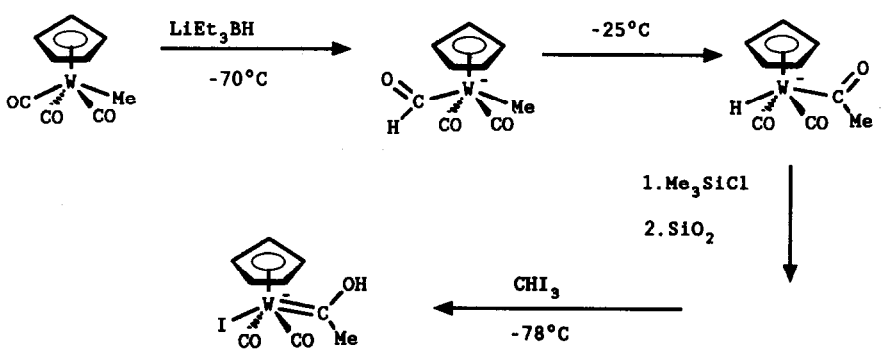


VI

Kabalka and his coworkers found that the reaction of $LiBHEt_3$ with nitroalkenes in the presence of borane results in the unexpected formation of N-ethylamine derivatives. Their evidence supports a reaction sequence involving the 1,2-addition of BEt_3 to a nitroso intermediate[49].



Gauntlett, Mann and Winter added $LiEt_3BH$ to $CpWMe(CO)_3$ to form *trans*-$[CpWMe(CHO)(CO)_2]^-$ and *trans*-$[CpWH(COMe)(CO)_2]^-$. The latter reacts with CHI_3; and the product was subsequently treated with Me_3SiCl and SiO_2 to yield carbenes[50].



Shimagaki, Suzuki, Nakata and Oishi also report a highly

syn-selective reduction of α-phenylthio-β-methoxy ketones with super-hydride[51].

3. Mechanism and Theory

a. Theory

Dewar and his coworkers parameterized AM1 for boron[52] and reported an extensive set of calculations for a variety of boron-containing compounds. Most of the results are better than those given by MNDO and related quantum mechanical treatments in which major problems are encountered in attempts to interpret the structures of the boron hydrides and carboranes. Ab initio Hartree-Fock methods fail, for example, to reproduce the heat of dimerization of borane to diborane unless a large basis set is used together with adequate allowance for electron correlation. The same situation holds generally true for reactions such as hydroboration. They find that AM1 procedure provides results comparable with those from high level ab initio methods at a very small fraction of the cost in computing time.

A theoretical study of the structure and stability of diborane was reported in which the geometry was optimized at the SCF level. The total energies and the dissociation energies were refined using Moeller-Plesset 3rd order perturbation theory[53].

Forcada, Moscardo and San-Fabian[54] performed MO-LCAO-SCF calculations to analyze the interaction of first row atoms and BH_3. Interaction energies of the predicted stable systems: $2BBH_3$, CBH_3, and $3OBH_3$ were calculated. Horn, Ahlrichs, and Koelmel also carried out SCF calculations on borane hydrides[55].

Paddon-Row and Wong performed an ab initio study on a borane radical.[56] The potential energy surface for the BH_4 radical has been investigated using ab initio MO theory. Stationary points were located at the UHF and UMP2 levels with the 6-31G(d) and 6-31G (df,p) basis sets, and characterized by

harmonic frequency calculations. Single-point calculations on the optimized structures were carried out at the UMP4 level using the 6-311G (df,p) basis set. BH_4 has only two stable structures, one of C2v (2B1) symmetry and the other of C3v (2A1) symmetry. The C2v structure is the global minimum, lying about 55 kJ mol-1 below the C3v structure. The C3v structure is predicted to have only fleeting existence, dissociating to BH_3 and H with neglibile activation energy. The C2v structure is predicted to be kinetically stable to dissociation at 77 K, in agreement with the ESR data for BH_4. However, it should rapidly dissocate to BH_3 and H above 250 K. Intramolecular hydrogen scrambling pathways in C2v BH_4 were also investigated. Two such processes were identified: homochiral scrambling (H exchange with retention of configuration at B), and heterochiral scrambling (H exchange proceeding with inversion of configuration at B). The activation energy for heterochiral scrambling is greater than that required for competing dissociation of C2v BH_4 into BH_3 and H; consequently, this scrambling mechanism is not predicted to be observed. In principle, the homochiral mechanism could be observable, but would be too slow to be detected by ESR.

The ESR spectra of the phosphine- or phosphite-ligated radicals derived from arylboranes show that there is a substantial conjugative delocalization of the unpaired electron from B onto the aromatic rings, although this delocalization is less extensive than in comparable benzylic carbon-centered radicals. The results of ab initio MO calculations support the proposal that hyperconjugative delocalization onto the P ligand competes with conjugative delocalization onto the ring in the complexed arylboryl radicals. The ESR spectra of the amine-arylboryl radicals were too weak to detect. The ligated arylboryl radicals are less reactive and more selective in

bromine atom abstraction than homoleptic ligated alkylboryl radicals, presumably because the former are appreciably stabilized by conjugative delocalization of the unpaired electron onto the aromatic rings[57].

Pius and Chandresekhar carried out ab initio MO calculations designed to obtain the structures and relative isomer energies of organometallic radical anions[58]. Comparison with results for the corresponding neutral molecules indicates a dramatic reduction in the energy gap between classical and H-shifted isomers on addition of an electron. However, the classical isomers of the radical anions generally represent the preferred form. Organoborane radical anions are thus the most likely systems to adopt distonic structures with the formal charge and radical centers on different atoms. Further separation of the charge and the radical sites through homologation is predicted to be ineffective in stabilizing the distonic structures.

Bowie and his coworkers utilized a combination of deuterium labeling and ab initio studies to investigate bismethyleneborane $[B(CH_2)_2]^-$ and trismethyleneborane $[B(CH_2)_3]^-$ anions.[59] Their results confirm the stability of the bismethylene borane anion and indicate a structure similar to that of allene, in accord with classical theory. The trismethyleneborane anion is unstable with respect to the isomeric methylene cycloborapropane anion and is thus analogous in behaviour to the isoelectronic trimethylenemethane.

b. Spectroscopy

Ruscic, Mayhew, and Berkowitz carried out a photoionization study on borane and diborane.[60] The photoion yield curves of $B_2H_n^+$ (n = 2-6) and NH_n^+ (n = 2-3) from B_2H_6,

as well as BH_n^+ (n = 1-3) from BH_3 were obtained. The combination of appearance potential measurements for BH3+ (B_2H_6) and BH_3^+ (BH_3) yields a poor upper limit for the ΔH of dimerization, 52.7 kcal/mol for BH_3 at 0°K while the combination of BH_2^+ (B_2H_6) and BH_2^+ (BH_3) provides a better upper limit (46.6 ± 0.6 kcal/mol) for this quantity. However, the threshold for BH^+ (BH_3), combined with auxiliary data, provides the best current experimental value, (34.3-39.1 ± 2 kcal/mol). This experimental value is in good agreement with a recent ab initio calculation, and is arrived at by using the best current estimate of ΔH_f (B_2H_6). The ionization potential of BH_3, and the atomization energy of BH_3 obtained experimentally are in excellent agreement with other ab initio calculations.

Yan and Fang reported the differentiation of stereoisomeric monosaccharides as n-butaneboronate derivatives by fast atom bombardment mass spectrometry[61]. The stereoselective reaction of 11 monosaccharides (D-ribose, D-lyxose, D-xylose, L-arabinose, L-rhamnnose, L-fucose, D-glucose, D-mannose, D-galactose, D-fructose, L-sorbose) with butaneboronic acid was studied by fast atom bombardment mass spectrometry (FAB MS). Characteristic mass spectra of the derivatized monosaccharides showed some differences which could be used in the differentiation of the stereoisomers in FAB MS. This reaction was effected by the orientation of OH groups and the favored configuration (furanose or pyranose) of monosaccharides; 1-hydroxyl groups also participated in the reaction if the 2- and 3-OH groups were in the trans-positions.

Brown, Cragg, Miller and Smith used carbon-13 NMR to determine the activation parameters for the restricted rotation about the boron-nitrogen bond.[62]

Wrackmeyer authored a review of boron-11 chemical shifts,

nuclear spin-spin coupling, and substituent effects[63].

c. Structures

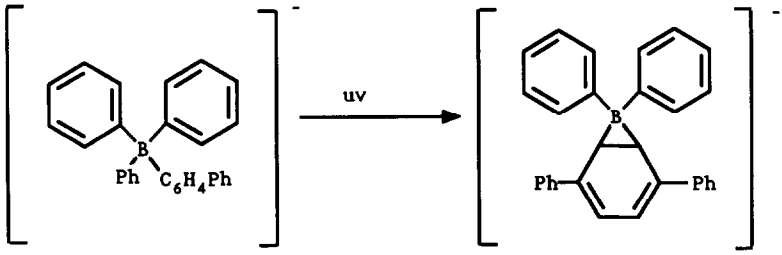
Cullen, Rettig, Trotter, and Wickenheiser reported the crystal structure of (3-benzoyl-(+)-camphorato)diphenylboron. The crystals are triclinic.[64] The unit-cell contains two crystallographically independent molecules, related to one another in the crystal lattice by a pseudo-inversion center; they have the same configurations but different conformations.

Noeth and his coworkers also used crystallography to determine the ring strain of 1, 3, 2, 4, -diphosphadiborabicyclo[1.1,0]butanes[65] and azaphosphadiboretidine[66]. Whereas Iijama, Hakamata, Nishikawa, and Shibata utilized both electron-diffraction and microwave spectroscopy to determine the molecular structure of the trimethylphosphine-borane adduct.[67]

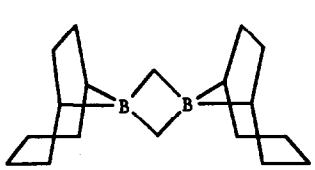
Kirwan and Roberts studied the hydrogen atom transfer to alkenes from aminyl-borane radicals. The process was highly exothermic and the H atom transferred was originally attached to boron[68].

4. Synthesis

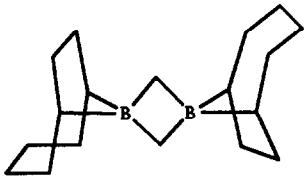
The perturbation of electronic and structural properties caused by replacement of a carbon by a boron atom is a topic of expanding theoretical and experimental interest. Wilkey and Schuster reported the first isolation and characterization of a boratanocaradiene: 2,5,7,7-Tetraphenyl-7-boratabicyclo[4.1.0]-hepta-2,4-diene a blood-red solid[69]. The material was formed via UV irradiation of (*p*-biphenylyl)triphenyl borate which is easily prepared by reaction of biphenylyllithium with triphenylborane.



Yalpani, Boese and Koester synthesized syn- and anti-bis(9-borobicyclo[4.2.1]nonane)from the [3.2.1]derivative and quinuclidine in hydrocarbon solvents at 150°C[70]. Tokles and

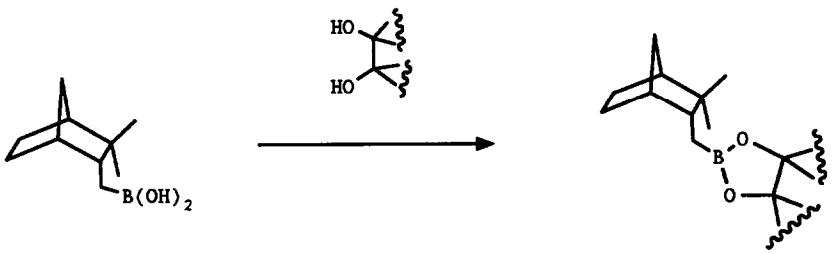


syn

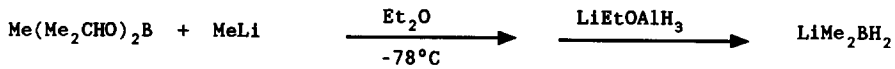


anti

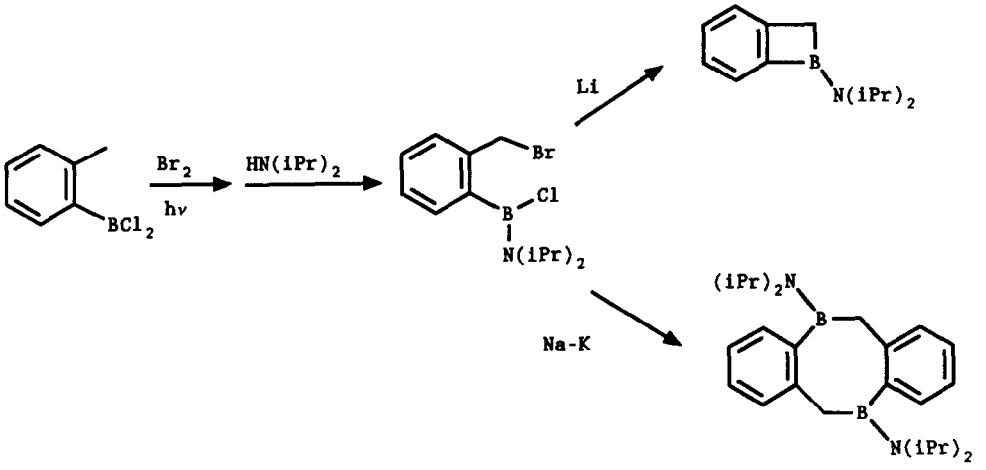
Snyder prepared camphanylboronic acid and reported its use as a chiral derivatizing agent for 1,2-diols for inducing nonequivalence in the ^{13}C-NMR spectrum. Boronate esters of hindered diols can be prepared in quantitative yield[71].



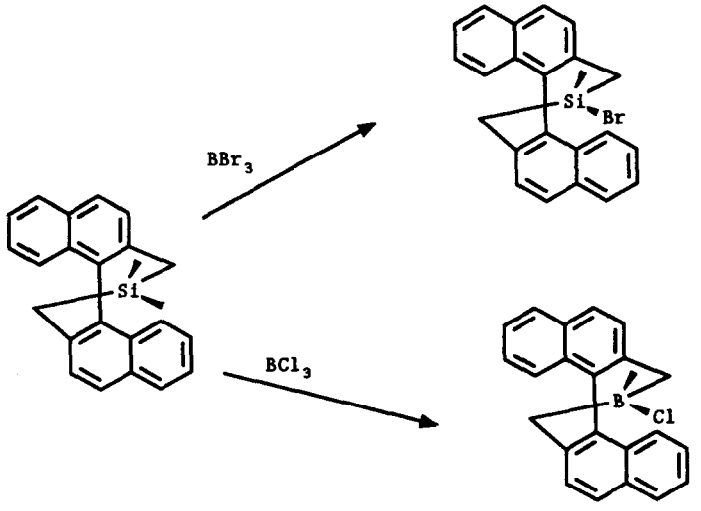
Brown synthesized lithium dimethylborohydride from a lower alkyl boronate and an alkyllithium[72].



Schacht and Kaufmann prepared the dihydrobenzoborate and its dimer tetrahydrodibenzo[b,f][1,5]diborocine from alkali metal mediated 1,4-cyclization[73].

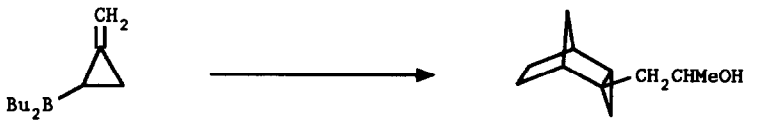


Kaufmann and his coworkers published the first asymmetric synthesis of a β-binaphthyl borane, silane and stannane. The reaction of the silane compounds with boron tribromide led exclusivly to a halogen-methyl exchange reaction. While the reaction of the stannane compound with trichloroborane led predominantly to the formation of the chlorodihydroborepine[74].

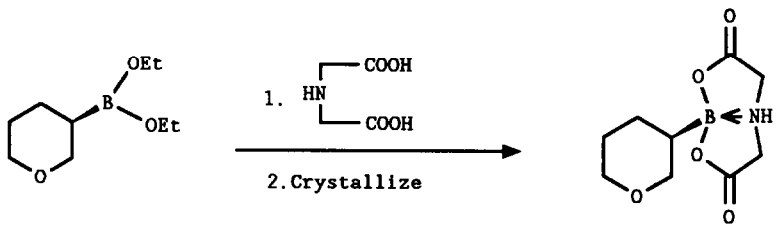


Dibutyl(methylenecyclopropyl)borane was prepared in 74% by treating 2-methylenecyclopropyllithium with $BuB(OMe)_2$ followed by

treatment with $EtO.BF_3$. The title compound was treated with AcH followed with 1,3-cyclopentadiene to yield the adduct[75].



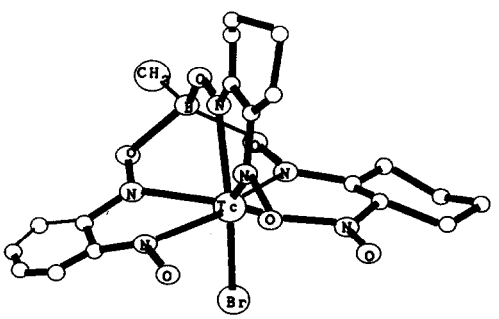
Brown and Gupta presented an extensive study to demonstrate the utility of chelates derived from borinic and boronic acids and selected amino acids to achieve excellent upgrading of the optical purities of the original borinates and boronates. Boronates were prepared via reaction of 3,4-dihydropyran with diisopinocampheylborane from (+)-α-pinene followed by treatment with acetaldehyde. The iminodiacetic acid converts the boronate into a crystalline chelate. Recrystallization upgrades the adduct



83% e.e. >99% e.e.

to >99% e.e. Treatment of the crystalline adducts with dilute HCl, followed by oxidation gives (+)-3-hydroxytetrahydropyran of >99% e.e.[76].

A new boronic acid adduct of technetium dioxime (BATO) was prepared by reacting $NH_4^{+}{}^{99m}TcO_4^{-}$ with dimethylglyoxime, boronic acids, and $SnCl_2$[77]. BATO is an effective myocardial perfusion imaging agent.



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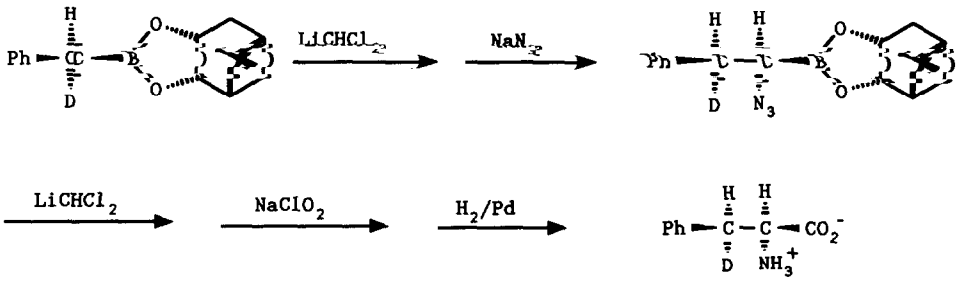
C. CARBON-CARBON BOND FORMATION

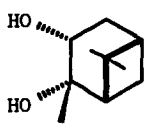
1. Homologation

Matteson published a review of asymmetric syntheses with boronic esters[78]. Brown and Singaram reviewed the development of general procedures for synthesis of pure enantiomers via chiral organoboranes[79].

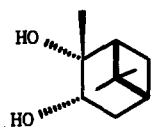
Matteson and his group used boronic esters in the chiral synthesis of (2S,3S)-phenylalanine-3-2H[80].



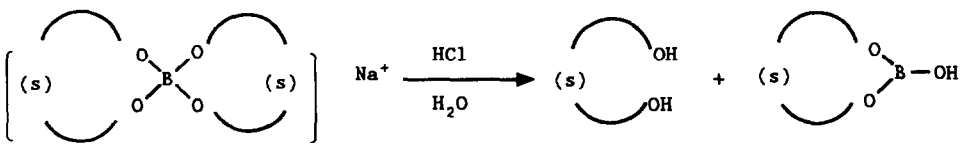
Brown and Rangaishenvi developed a practical procedure for the recovery of pinanediol from boronate esters and markedly extended the applicability of the Matteson asymmetric synthesis[81].



(S)pinanediol



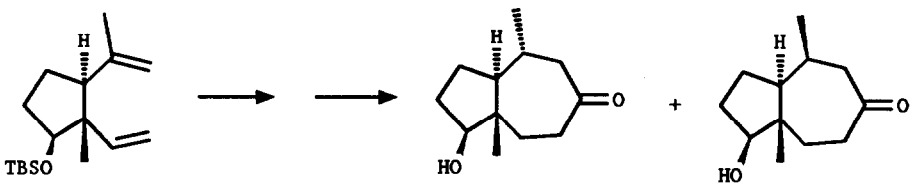
(R)pinanediol



Mixtures were eluted over a column of Amberlite IRA-743 resin; pinanediol was recovered quantitatively.

Brown and his coworkers reported the first synthesis of boracyclanes in the strained medium ring range. Ring enlargement of boracyclanes via sequential one-carbon homologation was utilized[82]; the homologation of B-methoxyboracyclanes with *in situ* generated (chloromethyl)lithium, $LiCH_2Cl$, proceeds smoothly to furnish the next higher homolog.

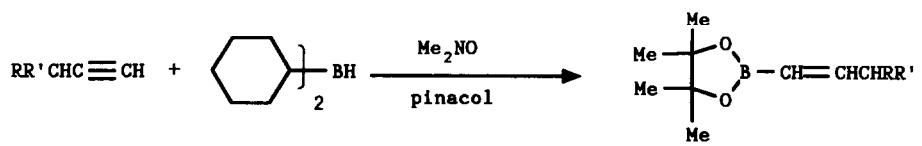
Welch and Bryson used boron annulation to synthesize pseudogualanolide sesquiterpene lactones[83]. They hydroborated the siloxy-diene with thexylborane, followed by cyanidation, to give the hydroazulone as a 70:30 mixture. Stepwise annulation using monohalothexylboranes provided the same mixture following cyanidation, with a slight reduction in yield.



70 : 30

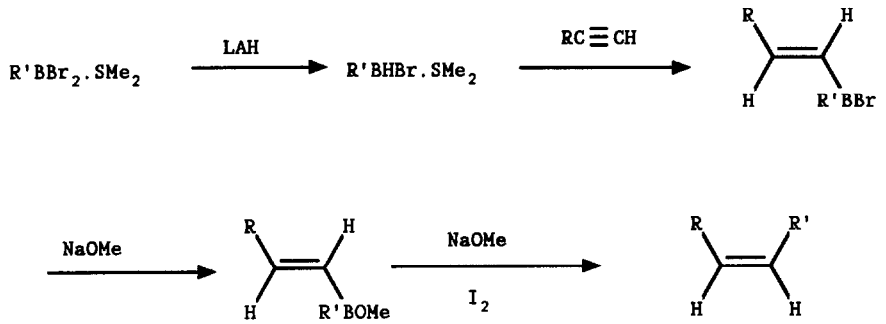
2. Alkenylborate and Arylborate

Hoffmann and Dresely prepared 3-substituted (E)-1-alkenylboronic esters using an oxidative procedure[84].

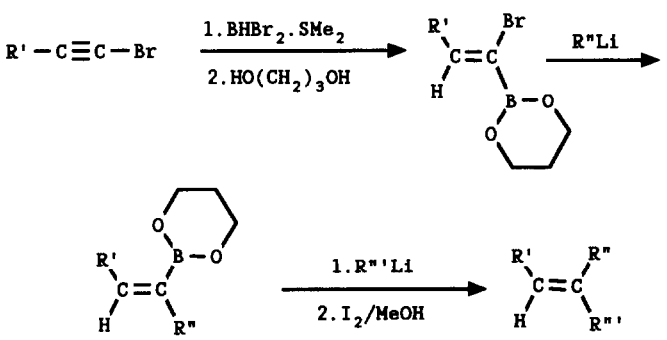


(R=$PhCH_2O$, $PhCH_2S$, Me_2CSiMe_2O, PhS, R'-H; R=PhS, Me_3SiO, PhSe, R'-Me)

Brown and his group presented a detailed discussion on the general stereospecific synthesis of (Z)- and (E)-disubstituted alkenes via organoboranes. They developed new methods to prepare (Z)-disubstituted alkenes using dialkylmonohalo- and monoalkyldibromoborane reagents, thus extending the scope and applicability of Zweifel's original synthesis. Monoalkyldibromoborane proved to be the most effective reagent[85].

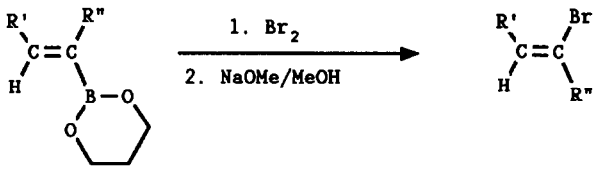


Brown, Bhat and Narayan developed a practical general procedure for the preparation of trisubstituted olefins containing three different alkyl substituents of varying stereochemistry. The

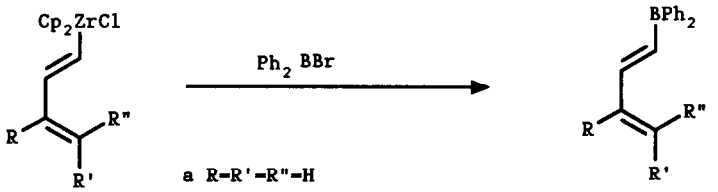


procedure is useful for introducing organic groups not available via hydroboration[86]. The authors also described a highly stereo- and regioselective conversion of [E]- into [Z]-2-(1-substituted-1-alkenyl)-1,3,2-dioxaborinanes. Replacement

of the boron moiety with bromine proceeds with complete inversion[87]. Fryzuk, Bates and Stone describe the stereoselective

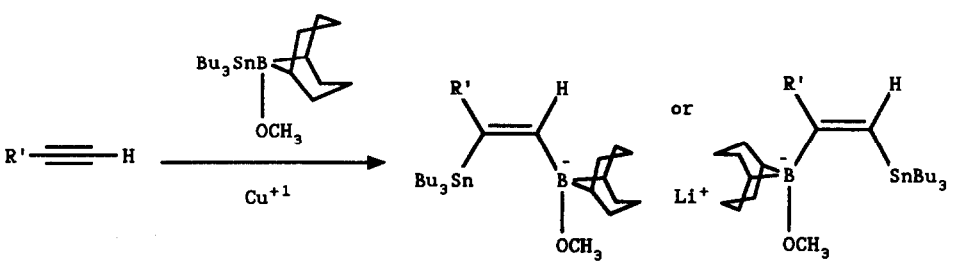


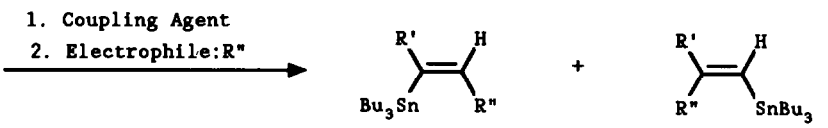
preparation of 1,3-dienylboranes via a transfer process from zirconium. They report the reaction proceeds smoothly and in excellent yields.[88]



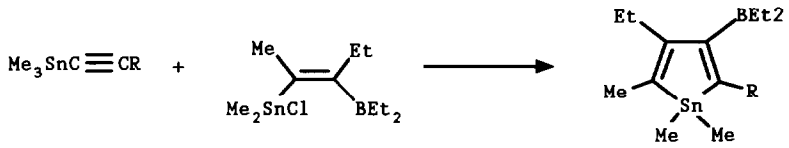
a R=R'=R"=H
b R=R"=H, R'=OMe
c R=R'=H, R"=OMe
d R=R'=-$(CH_2)_4$-, R"=H

Sharma and Oehlschlager used the copper(I) catalyzed addition of the 9-borabicycloborate complex to 1-alkynes in the regioselective synthesis and cross coupling reaction of 1,2-borostannyl-1-alkenes. Coupling via organopalladium or organocuprate with a variety of electrophiles proceeds exclusively at the vinyl boron bond.[89]



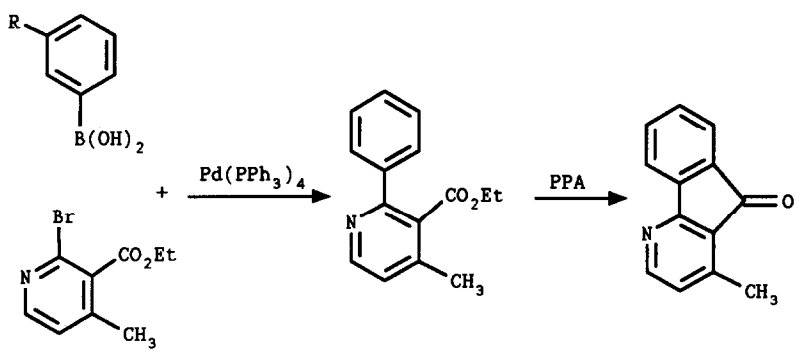


Kerschl and Wrackmeyer studied the exchange reaction between (E)-2-dimethyl(chloro)stannyl-3-diethylboryl-2-butene and various trimethyl(organyl)stannanes. If the organyl group R is Ph, C_5H_5, 2-thienyl or 3-thienyl, the exchange process is accompanied by numerous side reactions. However, if the organyl group is an alkynyl group, the elimination of Me_3SnCl leads to a new stannacyclopentadiene carrying different substituents[90].



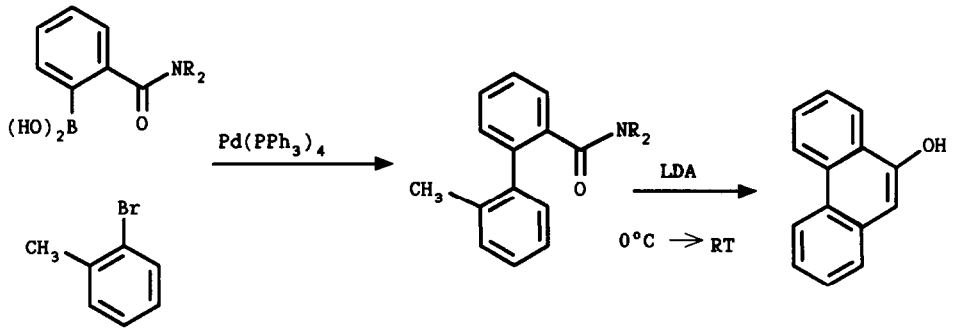
R=-t-Bu, $-SiMe_3$, $-SnMe_3$

Snieckus and his coworkers used the Pd(0)-catalyzed cross coupling reaction of arylboronic acids with a bromonicotinate ester to synthesize the azafluorenone alkaloids.[91]

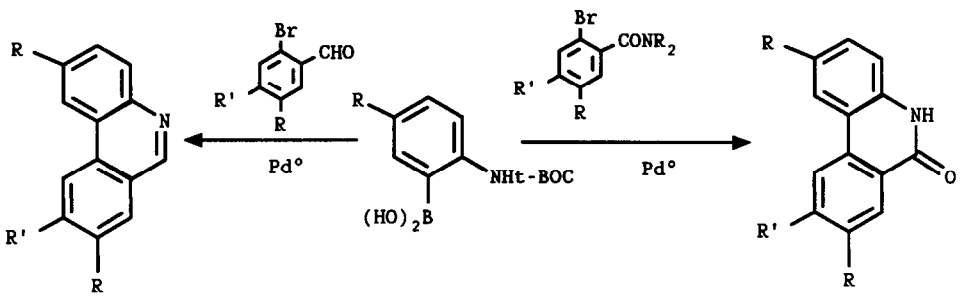


R = H, OCH_3

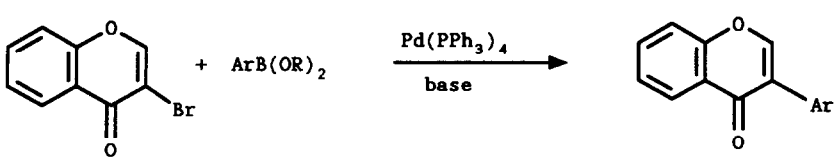
Snieckus also used benzamide o-boronic acids for a general directed metalation-based cross coupling synthesis of phenanthrols, which in turn lead to the synthesis of a variety of substituted phenanthrenes.[92]



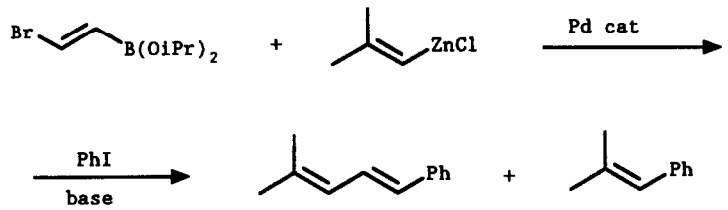
Siddiqui and Snieckus used o-N-t-BOC arylboronic acids in a concise general route to phenanthridines and phenanthridinones based on directed ortho metalation and cross coupling tactics[93].



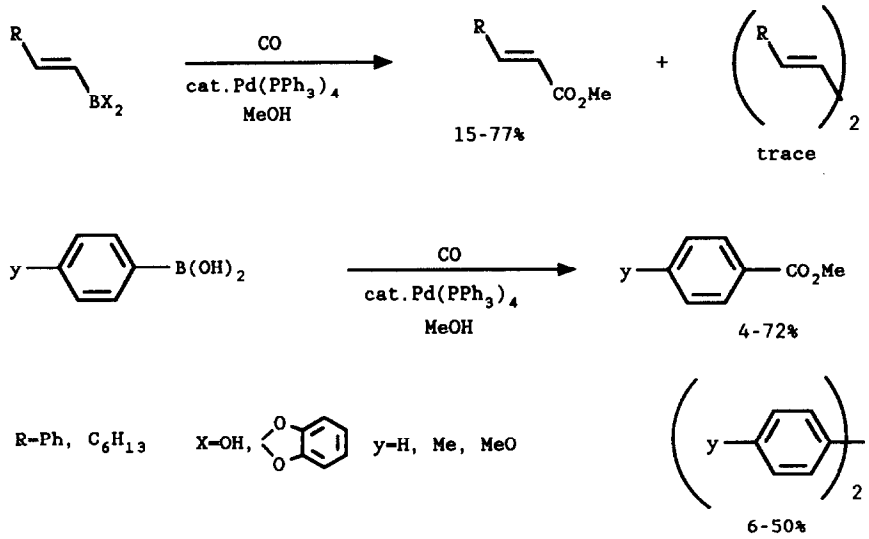
Hoshino and his group describe a novel synthesis of isoflavones by the palladium-catalyzed cross-coupling reaction of 3-bromochromones with arylboronic acids or their esters. The optimum conditions for carrying out the reaction were studied and the best yield of isoflavone can be obtained by using aqueous Na_2CO_3 as the base[94].



Suzuki and his coworkers prepared (E)-(2-bromoethenyl)-diisopropoxyborane, a new building block for (E)-olefins[95].

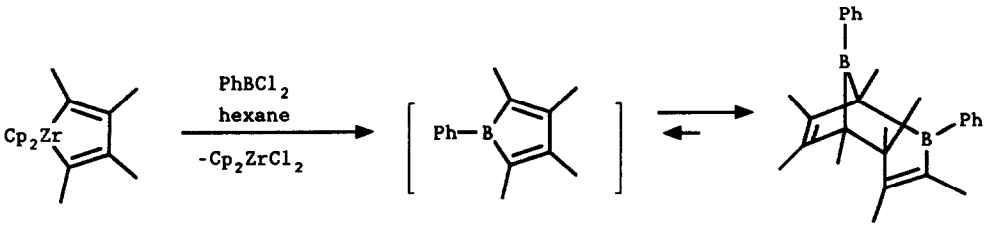


Uemura and his coworkers used catalytic amounts of $Pd(PPh_3)_4$ in the reaction of alkenyl- and aryl- borates or boronic acids with carbon monoxide in methanol at 25°C to give the corresponding methyl carboxylates and ketones in moderate yields[96].

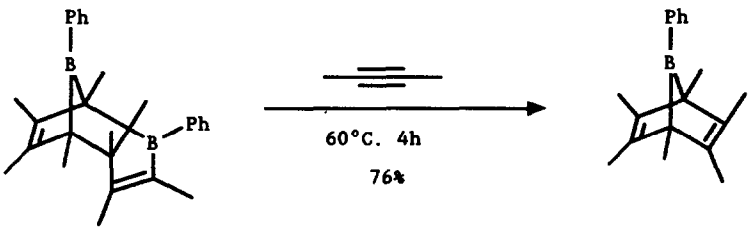


Norio and Suzuki reviewed the general and convenient methods for the stereo- and regioselective synthesis of conjugated alkanes, alkynes, arylated alkenes and heterobiaryls[97].

Fagan, Burns and Calabrese reported the preparation of a Diels-Alder dimer, 1-phenyl-2,3,4,5-tetramethylborole, using metallacycle transfer from zirconium reagents. They heated the

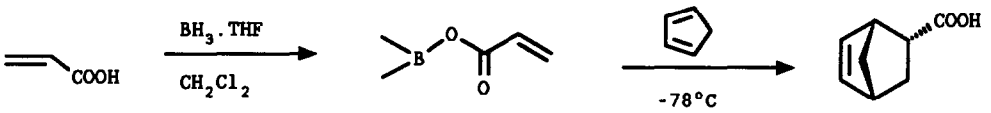


dimer with 2-butyne in toluene to yield the Diels-Alder adduct, proving the existence of the borole intermediate[98]. The reaction



of the dimer with unactivated alkenes generated the expected Diels-Alder adducts in high to moderate yields.

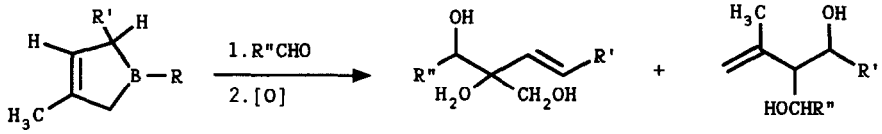
Yamamoto and his coworkers describe the reactivity of acyloxyboranes and their usefulness in organic synthesis. The Diels-Alder reaction of the acyloxyborane intermediate gave bicyclic carboxylic acid.[99]



3. Propargyl- and Allylboranes

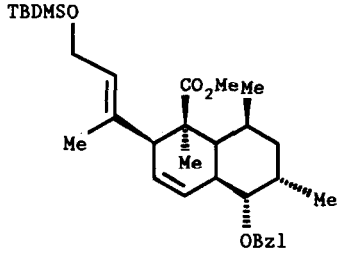
Hoffmann reviewed the addition of chiral α-heterosubstituted allyl(crotyl)boronates to aldehydes; reactions in which the chirality is transferred to the new stereocenter[100].

Zweifel and Shoup developed a diastereoselective synthesis of (E)-alkene-1,3-diols via the reaction of 3-borolenes with aldehydes. The ratio of the diols varies from 99:1 to 53:47; the percentage of diol VI increases as R' decreases in size[101].

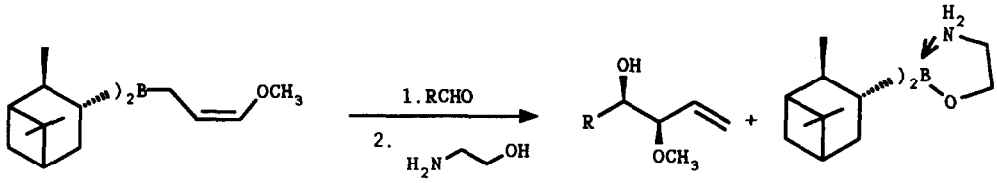


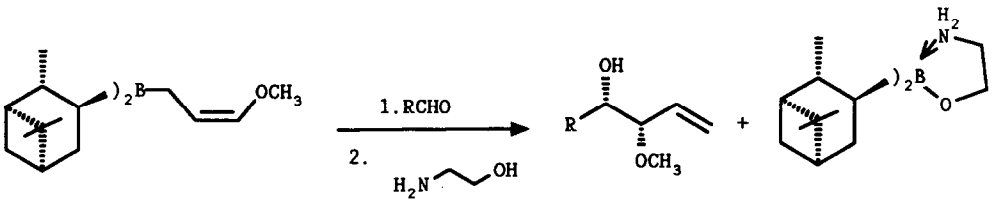
V VI

An exceptionally stereoselective synthesis of the octahydronaphthalene subunit of kijanolide and tetronolide has been accomplished by a sequence in which all seven stereocenters are introduced via reaction of acyclic substrates. (R,R)-Tartrate crotylboronate and dienyl boronic acid were used in two of the steps[102].



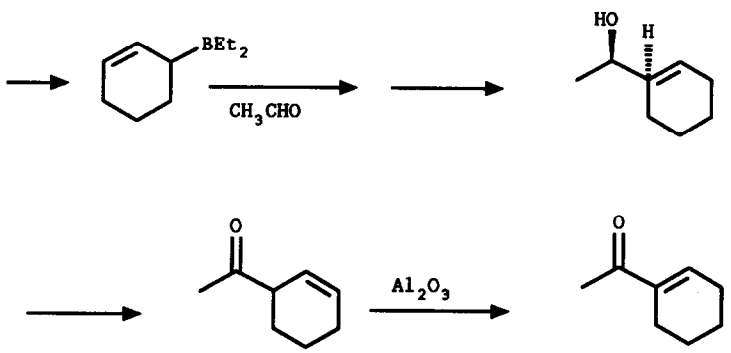
Brown, Jadhav and Bhat used the highly diastereoselective and enantioselective addition of [(Z)-γ-alkoxyallyl]diisopino-campheylboranes to aldehydes in chiral syntheses. The authors achieved >99% diastereoselectivity and 95% enantioselectivity[103].



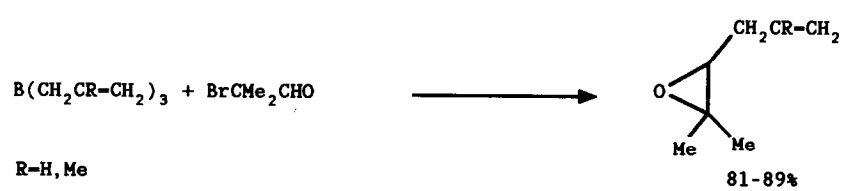


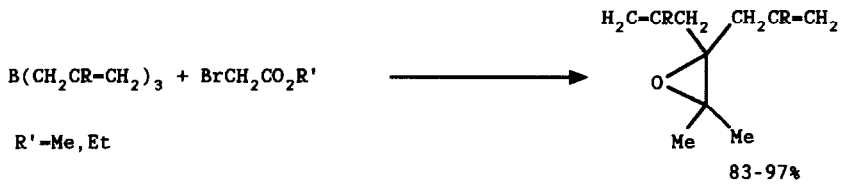
Chiral synthesis via organoboranes was further explored in a highly diastereoselective and enantioselective addition of [(Z)-γ-alkoxyallyl]diisopinocampheylboranes to aldehydes[104].

Paetzold, Kiesgen, Von Plotho and Schwan report an application of Mikhailov's allylboration to iminoboranes, the latter undergoes a thermal intramolecular reaction to form azadiboracyclohexanes [105]. Zaidlewicz reported the transformation of olefins into homoallylic alcohols, β,γ-unsaturated ketones and α,β-unsaturated ketones via allylic diethylboranes[106].

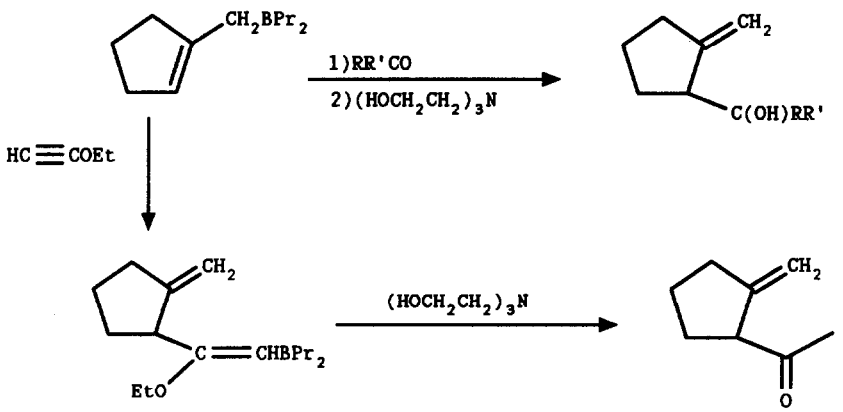


Bubnov, Zykov and Donskaya developed a synthesis of 2-allyl- and 2,2-diallyloxiranes via allylboration of α-halocarbonyl compounds[107].





Bubnov and Lavrinovich describe a novel method for the synthesis of 2-substituted methylenecycloalkanes based on allylboronation of carbonyl compounds and alkoxyacetylenes[108].



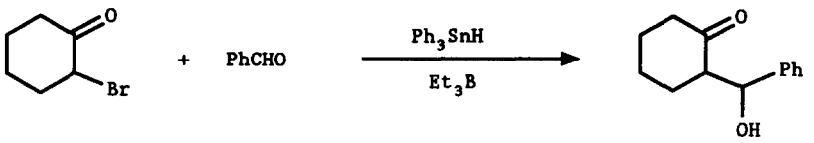
R=H, R'=H, Me, 2-furyl; R=Me, R"=Me, CH=CH_2

Hoffmann, Dresely and Hildebrandt report that the diasterioselectivity of the reaction of chiral (E)-(α-chlorocrotyl)boronates with chiral aldehydes depends on whether the asymmetric induction of the reagent and the substrate cooperate (matched pair) or whether they are opposed (mismatched pair)[109]. Hoffmann, Dresely and Lanz also describe the stereoselectivity in the syntheses of homoallyl alcohols utilizing (Z)-(α-chlorocrotyl)boronate[110].

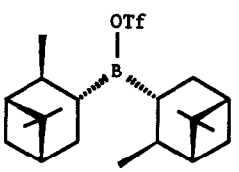
4. Enol Borinates

Nozaki, Oshima and Utimoto describe a facile synthetic route

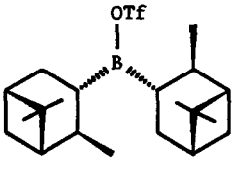
involving boron enolates using a triethylborane mediated Reformatskii type reaction[111].



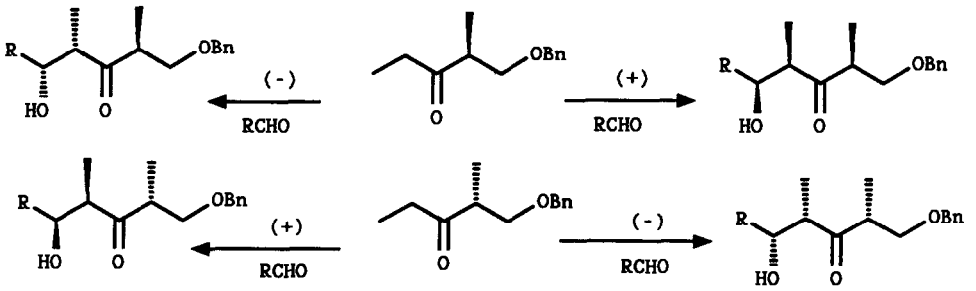
Brown and his group made a comparative study of dialkylboron chlorides and triflates for the enolization of ketones. They also studied the controlled stereospecific synthesis of (E)- and (Z)-enol borinates[112]. Paterson and Lister describe the aldol condensations of chiral ethyl ketones prepared by chiral boron reagents[113].



$(-)$-$(Ipc)_2BOTf$



$(+)$-$(Ipc)_2BOTf$



Roush reviewed asymmetric intramolecular Michael reactions[114] and novel routes to steroids using transannular Diels-Alder reactions of macrocyclic trienes[115]. Houk and his coworkers studied the transition states for the reaction of acetaldehyde boron enolates . They found the transition states of the reaction

of the boron enolate of acetaldehyde and of the (Z)- and (E)-enol borinates of propionaldehyde with HCHO were remarkably similar[116].

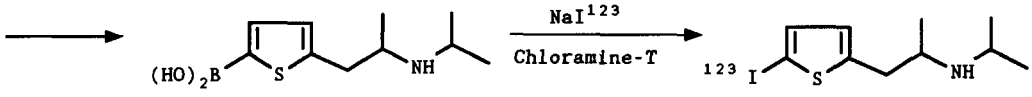
5. Boroadamantanes

Bubnov, Gurskii and Geiderikh prepared 3-dimethylamino-2-oxa-1-boraadamantane, a new heterocycle[117].

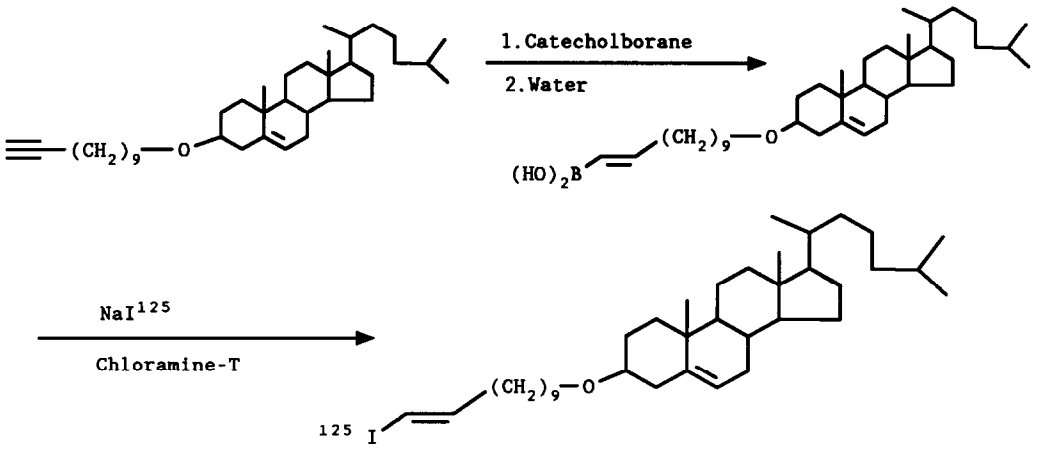
D. CARBON-HETEROATOM BOND FORMATION

1. Group VII

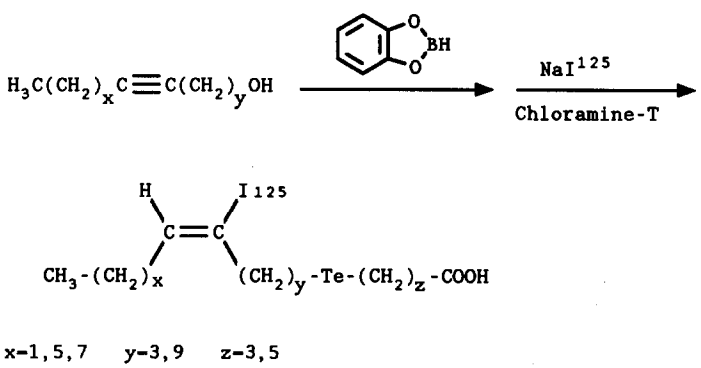
Marks synthesized N-isopropyl 2-(2-aminopropyl)-5-iodothiophene, a thienylamphetamine derivative, via borane chemistry. The title compound is a potential substitute for the labeled N-isopropyl *p*-iodoamphetamine used in PET and SPECT for brain imaging[118].



Kabalka and his group used catecholborane in the synthesis of iodine-125 labeled ω-[^{125}I]iodoundecenyl cholesteryl ether[119].

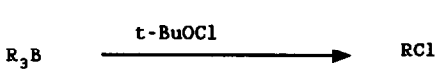


Catecholborane was also used in the synthesis of a new radiohalogenated alkenyl tellurium fatty acid[120]. Radiolabeled long-chain unsaturated fatty acids have diagnostic value as radiopharmaceutical tools in myocardial imaging.

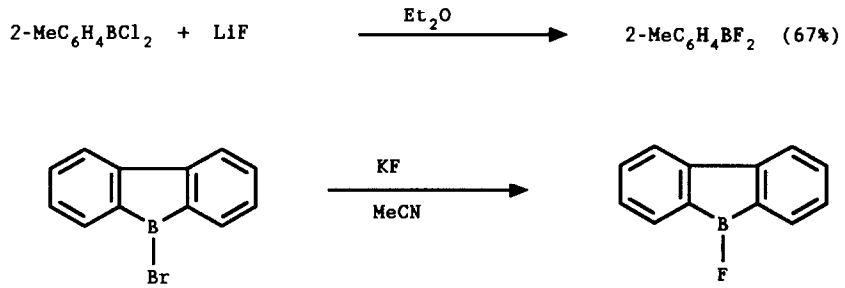


x-1,5,7 y-3,9 z-3,5

Nelson and Soundararajan studied the chlorinolysis of trialkylboranes. They found dichloramine-T to be the most effective chlorinating agent, producing good yields with high stereoselectivity[121].

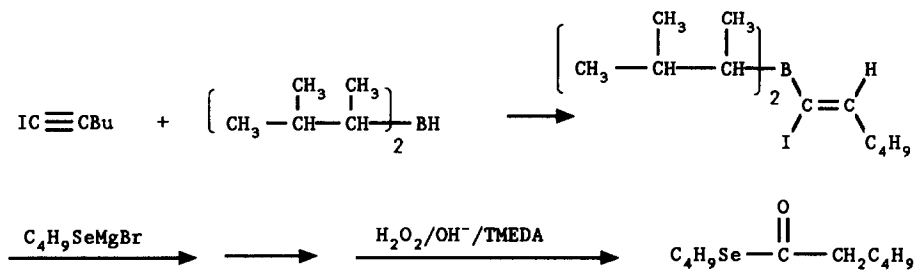


Kaufmann and his coworkers developed a general, simple and efficient way to synthesize fluoroorganoboranes[122].

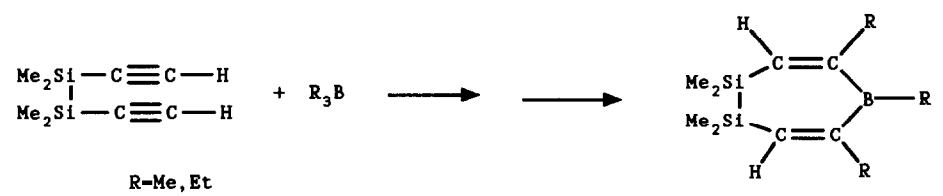


2. Group VI

Arase and his coworkers synthesized Se-alkyl alkaneselenoates via (1-iodo-1-alkenyl)dialkylboranes in moderate yields[123].

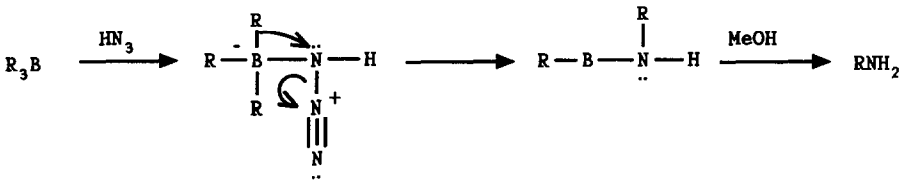


Wrackmeyer described the synthesis of 1,2-dihydro-1,2,5-disilaborepines and 1,2-dihydro-1,2-disilafulvenes via organoboration and hydroboration/organoboration[124].



3. Group V

Kabalka and his group describe a facile method for the preparation of primary amines using trimethylsilyl azide and trialkylboranes in a neutral protic solvent[125].



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