BORON: BORANES IN ORGANIC SYNTHESIS

ANNUAL SURVEY COVERING THE YEAR 1986

George W. Kabalka and Laila H.M. Guindi

Department of Chemistry
University of Tennessee
Knoxville, TN 37996-1600 (USA)

CONTENTS

A. INTRODUCTION

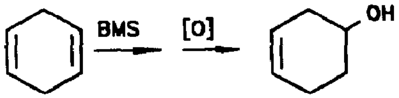
Organoboranes continue to play an expanding role in organic synthesis. The boranes are used in thousands of hydroborations and reductions each year. This review focuses on reports concerning new methodology and/or reagents and not on the routine use of boranes and borohydrides. Traditionally Professor H. C. Brown's group has led the way in developing new technology. This year is no exception. It is heartening to note, however, that many other familiar names and a few new names appear regularly in the reference section. This is further evidence of the growing importance of boranes in synthesis, there is every reason to believe that the growth rate will continue to increase for the foreseeable future. The format of this year's review has not been changed; as always, the classifications can be somewhat arbitrary but, presumably, logical.

B. BORANE REAGENTS

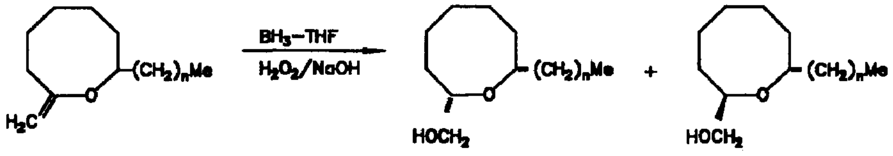
1. Hydroborating Agents

a. BH_3

Hydroboration reactions are regularly used in hydrogenation and anti-Markovnikov hydration sequences. Brown and Bhat[1] carried out a detailed study involving the hydroboration of cyclic dienes using stoichiometric amounts of the popular hydroborating agents. 1,4-Cyclohexadiene and 1,3-cyclohexadiene undergo monohydroboration with BMS, 9-BBN, Sia_2BH whereas the 1,5-cyclooctadiene and 1,3-cyclooctadiene give the dihydroboration products, predominantly, with all reagents studied (BMS, 9-BBN, Sia_2BH, $Br_2BH.SMe_2$ and Br_2BH.)

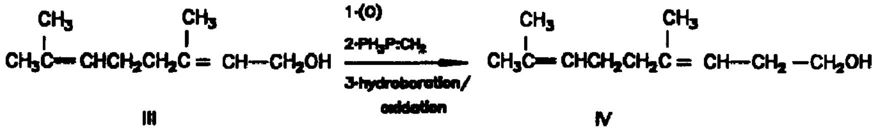


Carling and Holmes[2] hydroborated a substituted enol ether containing an exocyclic double bond and observed that the syn isomer formed preferentially (I:II ~ 15:1).



I II

Leopold[3] prepared homogeraniol IV in 3 steps from geraniol, III, taking advantage of the selective hydroboration of the 1,3,7-triene.

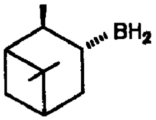


$$CH_3\overset{CH_3}{\overset{|}{C}}=CHCH_2CH_2\overset{CH_3}{\overset{|}{C}}=CH-CH_2OH \xrightarrow[\text{3-hydroboration/ oxidation}]{\text{1-(0)}\ \text{2-Ph}_3\text{P:CH}_2} CH_3\overset{CH_3}{\overset{|}{C}}=CHCH_2CH_2\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH_2OH$$

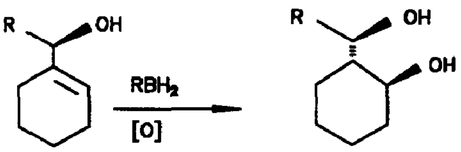
III IV

b. RBH_2

The preparation of optically active compounds by asymmetric hydroboration of di- or tri substituted olefins with monoisopinocamphenylborane was reviewed[4].



Birturstle and coworkers[5] hydroborated allylic endocyclic alcohols sterioselectively with thexylborane.

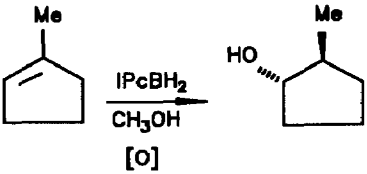


(a) R=CH_3 (87%)

(b) R=i-Pr (100%)

(c) R=Ph (100%)

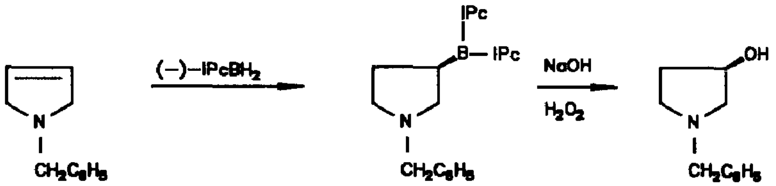
Thexylborane proved useful in synthesizing the left-hand portion of the ionophore antiboitic X14547A[6]. Brown and coworkers[7] used monoisopinocampheylborane to hydroborate alkene V to produce VI in 100% enantiomeric excess.



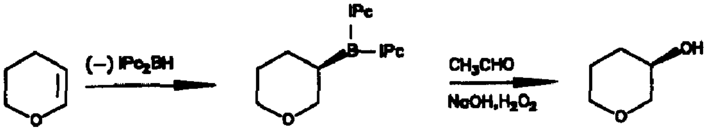
V VI

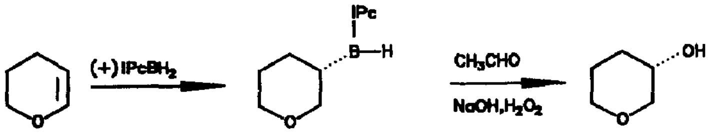
c. R_2BH

Brown and his group[8] investigated the hydroboration of N-substituted-3-pyrrolines using diisopinocampheylborane, oxidation of the intermediate yields enatiomerically pure N-benzyl-3-pyrrolidinol. The

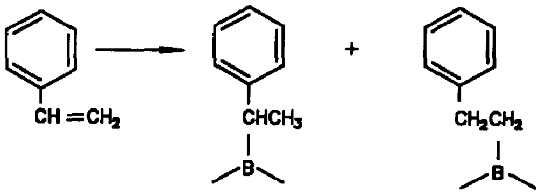


group investigated the reaction of the 3-pyrroline with borane methylsulfide, 9BBN, dicyclohexylborane and Sia_2BH. Brown, and Prasad[9] used diisopinocamphylborane and monoisopinocampheylborane for the hydroboration of heterocycles bearing an endocyclic double bond. The trialkylboranes readily eliminate α-pinene on treatment with CH_3CHO to give the corresponding boronates. Oxidation of these trialkylboranes affords high yields of the epimeric heterocyclic alcohols. They also investigated 2,5-dihydrofurans, 1,4-epoxy-1,4-dihydronaphthalene, and 2,3-dihydrothiophene.



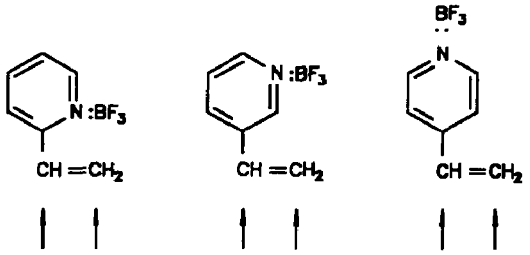


Brown and coworkers[10] reported the preparation of two new hydroborating agents, $MeBH_2$ and Me_2BH. The new boranes react with alkenes to give the dialkylmethylborane (R_2BMe) and alkyldimethylborane ($RBMe_2$). The new boranes are more regioselective than BH_3 but not as selective as 9-BBN and Sia_2BH. Dimethylborane is unstable in solution and undergoes disproportionation at room temperature.



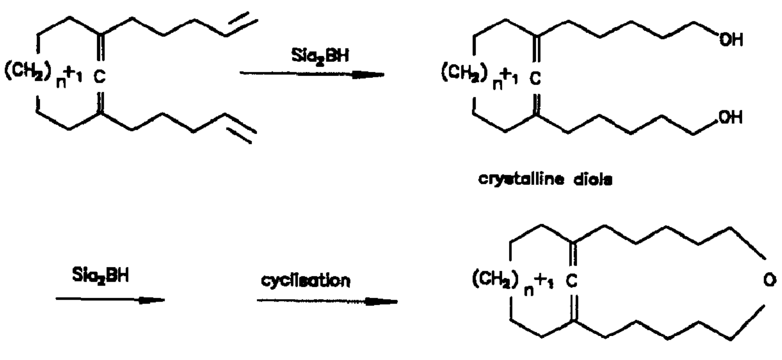
BH$_3$	19%	81%
Me$_2$BH	14%	86%
Sia$_2$BH	2%	98%
9−BBN	1·5%	98·5%

Brown and his coworkers[11] investigated the directive effects of 9-BBN, disiamylborane, dicyclohexylborane and borane-Me$_2$S in the hydroborations of vinyl and propenyl heterocycles. As expected the directive effects observed for 2-vinylfuran and 2-vinylthiophene are similar to styrene giving the β-organoborane predominantly with 9-BBN and BMS, and exclusively with Chx$_2$BH and Sia$_2$BH. The nitrogen atom in vinyl pyridine required protection with BF$_3$ or excess hydroborating agent. When the vinyl group is ortho or para to the pyridine nitrogen, α-organoboranes are the major products in the hydroboration. However when the vinyl group is meta to the pyridine nitrogen, β-organoboranes are formed predominantly. The distribution of boron in the hydroboration of 2-propenyl heterocyclic compounds is almost exclusively in the α-position.



BH$_3$·SMe$_2$	83	17	40	60	85	15
9−BBN	44	56	14	86	74	26
CHx$_2$BH	84	16	29	71	59	41
Sia$_2$BH	88	12	13	87	53	47

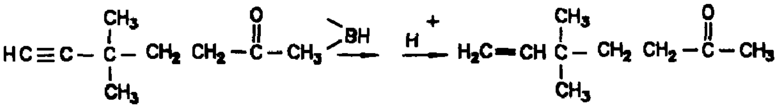
Marshall and Rothenberger[12] used disiamylborane in the selective hydroboration-oxidation of terminal alkenes. The intermediate diols were then cyclized to give the oxabetweenallenes.



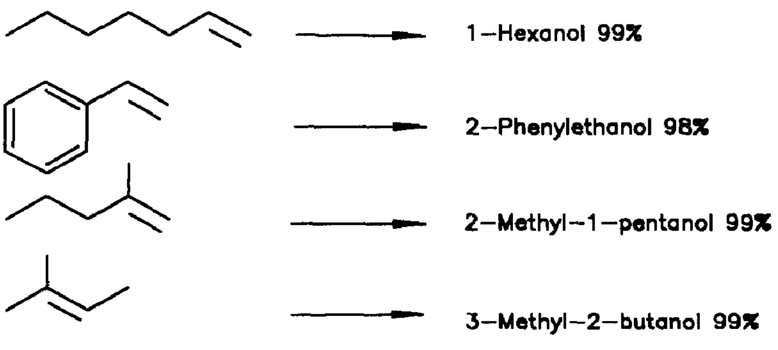
crystalline diols

Oxabetweenallenes

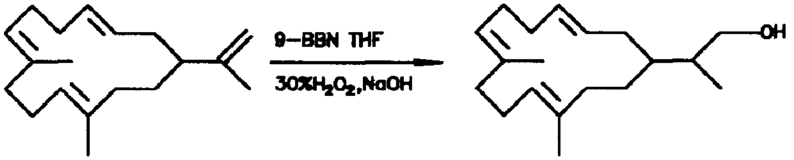
Yoon and his coworkers[13] reported a potentially exciting hydroborating agent, thexyl-2-butoxyborane. Although, few details are available in the abstract, the reagent apparently can be used to hydroborate alkynes and alkenes in the presence of ketones.



In an effort to establish the regioselectivities and reaction times of dihaloborane-dimethyl sulfide ($HBX_2.SMe_2$, X = Cl, Br or I) complexes, Brown [14] re-examined the hydroboration of alkenes with these agents. The reactions using $HBBr_2.SMe_2$ required 1-5 hours but ultrasound reduced the time considerably.

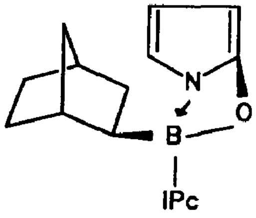


9-BBN was used in a selective hydroboration of an isopropenyl double bond by Singh and coworkers[15] The authors synthesized [16-3H]-cembrene-A from unlabeled cembrene-A in 4-steps.



This selective hydroboration is of general utility for labeling polyisoproenoid hydrocarbons for metabolic studies.

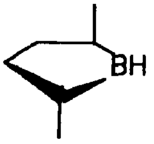
In an effort to upgrade the optical purities of intermediates used in asymmetric hydroboration, Brown and Prasad[16] reacted β-methoxy-9-borabicyclo[3.3.1]nonane, as well as methyldicyclohexyl- and diisopinocampheylborinate with various amino alcohols to form the corresponding chelates. For example, crystallization of 2-pyrrolidinylmethylisopinocampheyl-exo-norbornylborinate, VII, of 83% enantiomeric excess gives a product approaching 100% ee.



VII

Treating dimethylcyclopentyl, di-exo-norbornyl- and disiamylboronate with various amino diols gave the corresponding boronates.

Masamune[17] reviewed asymmetric synthesis involving hydroboration of alkenes, reduction of dialkyl ketones, and aldol reactions using (R,R)-and (S,S)-2,5-dimethylborolane.



(R,R)

(S,S)

Okamoto[18] prepared 2-aminopyridine-borane and studied its application to stereo- and chemoselective reductions.

2. Reducing Agents

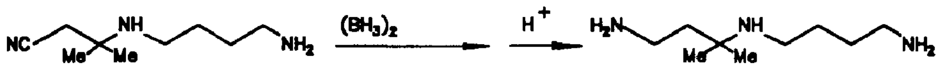
a. BH_3

Borane is an excellent reducing agent. Numerous reports appear in the literature. Among the more interesting is a report by Kende and coworkers[19] who reported the preparation of 4-hydroxycrotonate via a BH_3 reduction.

$$HOOC{-}CH{=}CH{-}CO_2Et \xrightarrow[2\cdot H_2O]{1\cdot BH_3\cdot THF} HO{-}CH_2\,CH{=}CH{-}CO_2Et$$

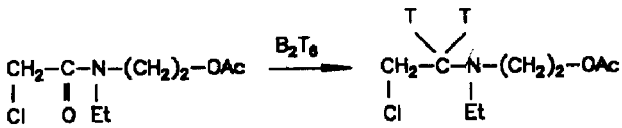
67%

Diborane was also used to reduce a nitrile group by Nagarajan and Ganem[20] in the synthesis of five gem-dimethylspermidines; the triamine was produced from VIII by reduction with diborane.

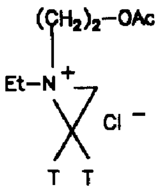


VIII

Fischer[21] prepared tritium labelled N-mustard type compounds, IX, using B_2T_6 for the reduction of the carbonyl group.

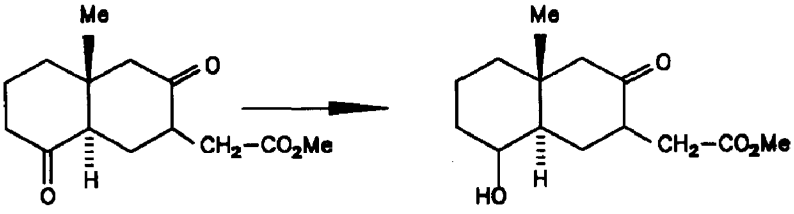


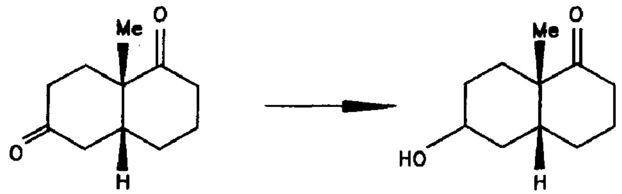
$$\underset{\displaystyle Cl}{CH_2}{-}\underset{\displaystyle O}{\overset{}{C}}{-}\underset{\displaystyle Et}{N}{-}(CH_2)_2{-}OAc \xrightarrow{B_2T_6} \underset{\displaystyle Cl}{CH_2}{-}\overset{\displaystyle T\ \ T}{C}{-}\underset{\displaystyle Et}{N}{-}(CH_2)_2{-}OAc$$



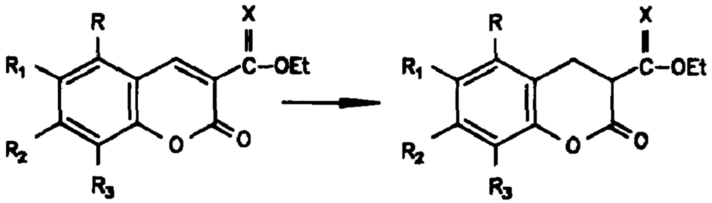
IX

In a novel approach, Gohzu and coworkers[22] used borane-amine complexes to reduce polyketones regioselectivly, Bicyclic diones were adsorbed on silica gel and reduced with $BH_3.NMe_3$.

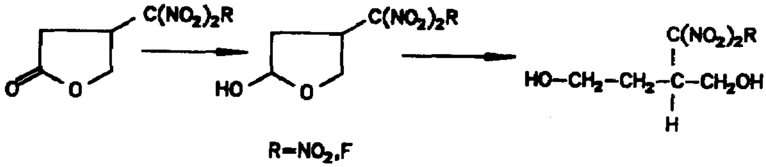




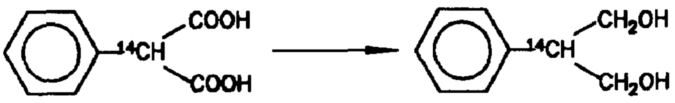
In a selective reduction of 3-substituted esters via boranes Kirkiachrian and Danan[23] used BH_3, $BH_3.SMe_2$, 9-BBN and bis(tert-butylthio)ethane-diborane. Coumarins (R, R_2, R_3 = H, OMe, R_1 = H, X=O, S; RR_1 = benzo, R_2 = R_3 = H, X = O) gave dihydrocoumarins.



Sitzmann and others[24] used BH_3.THF to reduce lactones to 2-furanols The authors were able to isolate the 2-furanols prior to further reductions to the corresponding diols.



Choi and coworkers[25] used BH_3.THF to reduce 2-phenylmalonic acid to 2-phenyl-1,3-propanediol as part of a synthetic procedure for the preparation of 2-phenyl-1,3-propandiol-2-^{14}C dicarbamate



Itsuno, Shinichi and others[26] used BH_3.THF in the asymmetric reduction of chiral acetophenone oxime ether to optically active primary amines $MeCHPhNH_2$.

Yoon and Lee[27] used BH_3 with LiCl (1:1) in THF to reduce glutaric anhydride to 1,5-pentanediol. Nose and Kudo[28] used BH_3-$NiCl_2$ in a study of functional group reductions.

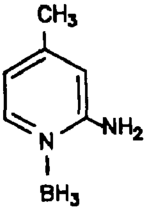
$$RC_6H_4NO_2 \xrightarrow{BH_3-NiCl_2} RC_6H_4NH_2$$

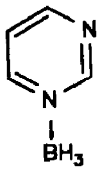
$$R'CN \xrightarrow{BH_3-NiCl_2} R'CH_2NH_2$$

Quinoline, quinolidine and acridine were reduced selectively in the N-containing ring. The NO_2 group was reduced selectively in the presence of cyano, carbonyl, carbamoyl or carboxylate functions.

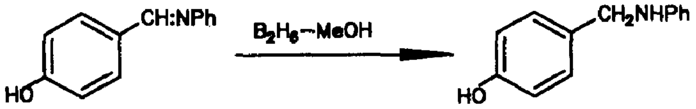
Itsuno and others[29] achieved the asymmetric reduction of acyl ketones by adding the ketone and borane to a polystyrene column upon which they had adsorbed an optically active amino alcohol.

Okamoto, and coworkers[30] used 2-amino-4-methylpyridine borane and 2-aminopyrimidine borane in a variety of selective reductions.

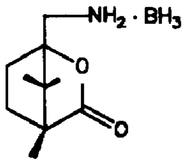




A diborane-methanol system was used by Nose and Kudo[31] for the selective reduction of imines.



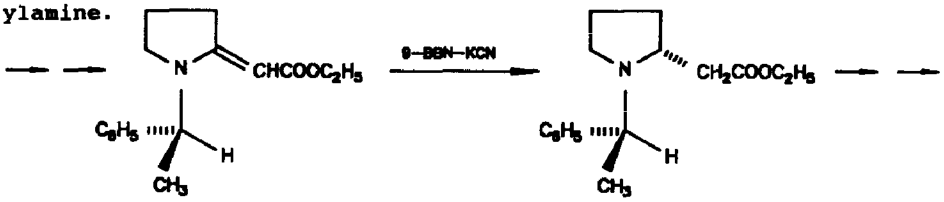
In a study of the absolute conformation and configuration of exogeneous anabolic zeronol the authors[32] used X; prepared by treatment of the amine in toluene with excess BH_3 at -60°C in a diastereoselective hydrogenation.



X

Yukio et.al.[33] used B_2H_6 in THF at RT to reduce malic acid into the triol as part of the convenient and practical method in synthesizing 3-mercaptopyrrolidine derivatives.

Stanchev, Milenkov and Dimitrov[34] used the 9-BBN-KCN complex as a key step in a 7 step preparation of pyrrolidine from (S)-1-phenylethylamine.



The authors[34] noted that ester groups did not interfere with the reactions at -25°C.

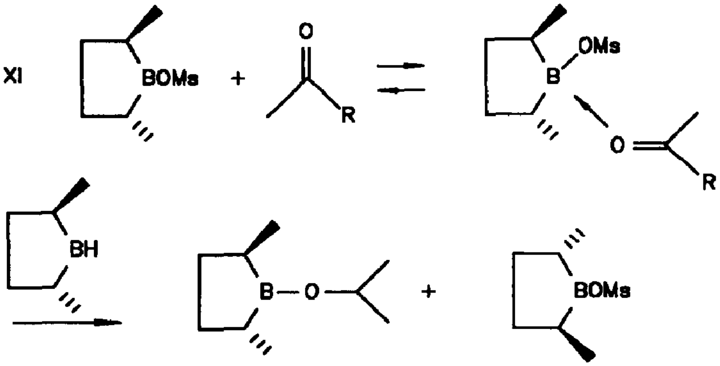
b. RBH2

Suzukamo and others[35,36] prepared a series of aminoalcohol-borane complexes which they used to reduce ketones to chiral alcohols in good enantiomeric excess (~80%). Similarly Komeyoshi and his coworkers[23] used chiral hydroxyphenethylamine complexes of borane to reduce triazolyl(dichlorophenyl)pentenone.

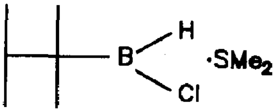
c. R_2BH

Masamune and his co-workers[37] examined the mechanism of the reduction of prochiral dialkyl ketones with (R,R)-2,5-dimethylborolane prepared via the reaction of the borolane borohydride with methanesulfonic acid. They attribute the asymmetric induction to the formation of a complex between the mesylate byproduct XI, and the ketone prior to reduction by the borolane.

XI

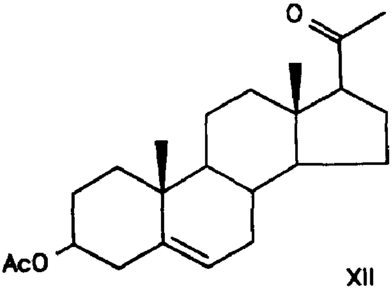


A paper by Brown and coworkers[38] provided an extensive study of ThxBHCl-SMe_2 with 56 selected organic compounds.



The selectivity of the reagent was compared to that of thexylborane and diborane. Unlike thexylborane and diborane the reagent, shows good stereoselectivity toward cyclic ketones. The authors examined the following types of organic compounds: Active H compounds, aldehydes and ketones, quinones, carboxylic acids and acyl derivatives, esters and lactones, epoxides,amides, nitriles, as well as nitrogen and sulphur compounds.

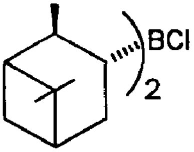
Toshiro, Todashi, Akira and Truneo[39] used (R,R)- or (S,S)-2,5-dimethylborolane to reduce dialkyl ketones $RCOR_1$ such as pregnenolone, XII, in 99-100% enantiomeric excess.



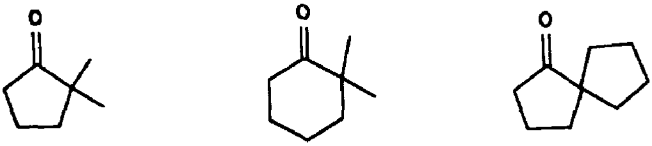
XII

d. R_3B

A paper by Brown and his group[40] demonstrates that diisopinocampheylchloroborane is a highly efficient reducing agent for alpha-tertiary alkyl ketones.



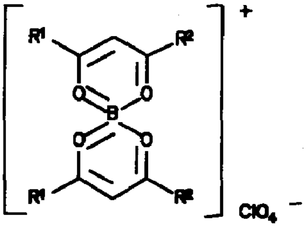
The cyclic ketones, 2,2-dimethylcylopentanone; 2,2-dimethylcyclohexanone; and spiro[4,4]nonan-1-one were reduced rapidly.

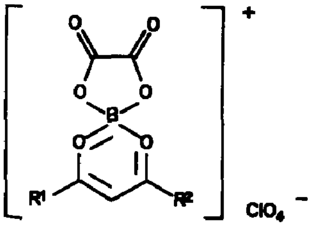


3. Mechanism and Theory

a. Theory

Nelson[41] studied carbonyl complexes of several cations and uncharged Lewis acids using MNDO molecular orbital calculations. The geometries of the bent and linear conformations of carbonyl complexes of boron were calculated and partial searches of potential energy surfaces were carried out. In complexes with the uncharged species the bent conformations are more stable. Mohn, Lipscomb and William[42] carried out a theoretical study (HF/6-31G) to determine the optimized rotational barrier of borane. In a study of the excited states of antiaromatic systems, Padma and Jug[43] investigated singlet to triplet excited states of the 5-membered ring, C_4H_5B. Ortiz and Lipscomb[44] performed ab initio calculations on small boranes. Ilge and Hartmann[45] studied the spectroscopy, photochemistry and photophysics of boron chelates.





Magnusson[46] monitored atomic orbital deformation in bond formation by the parallel use of flexible and constrained basic sets in MO calculations. They concluded that the stabilization associated with orbital deformation in BH_3 is due to an increase in the attractive, one-electron term in the molecular energy expression relative to the electron-repulsion term. Yuzhakova and coworkers[47] measured the dipole moments of tiarylborane complexes and found that electron-donating R groups lowered mu and delta; while electron withdrawing R groups increased them. Glaso and Fronzoni[48] used ab initio calculations to study the boron-boron and boron-proton coupling constents in polyboranes.

Kanev and Monev[49] used ab initio calculations to study the structure of boradiazirine and concluded that the nonplaner structure is more stable than the planer form. Studies on peculiar electronic characteristics of hetero-π-systems were reviewed by Maier[50]. Ott[51] studied the relative stabilities of positional isomers and isomerization processes of the closo-carboranes. Sebestyen[52] calculated the potential barriers to internal rotation for $X_3P.BY_3$, CX_3SO_2Y and $XF_2P.BY_3$ (X=H, D, F, Cl; Y=H, D, F, Cl, Br, I).

b. Kinetics

In a study on the hydroboration of alkenes, Nelson and Cooper[53] found additional evidence supporting an early transition state which retains alkene character. Mann, Cutts and McKenna[54] studied the secondary kinetic isotope effect of deuterium on enantioselective hydroboration with (+)-diisopinocampheylborane. The studies indicated that the steric effect of the vinyl H atom was negligible, but that the allyl H atom exhibited a strong steric effect. Pelter and Keating[55] proposed a possible explanation to the resistant isomerization of dimesityl-3-hexylborane as compared to diphenyl-3-hexylborane. Brown and coworkers[56] found that dialkylhaloboranes reduced benzaldehyde at a much faster rate than trialkylboranes.

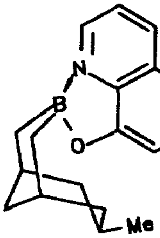
c. Spectroscopy

Schevchenko, Nazarenko and coworkers[57] conducted a mass spectrometric study of the transformation of $LiBH_4$ while heating in a vacuum. Srebnik and Cole[58] carried out mass spectral studies of selected isopropyl borinic esters. Nelson[59] conducted mass spectrometric investigation of tri(exo-2-norbornyl)borane. Davidson and Ewer[60] obtained the IR and Raman spectra of 1,3-dithia-2-boracyclohexanes for a vibrational spectroscopic study. Noeth and Prigge[61] studied the NMR and He(I)PE spectra of diisopropyl and di-tert-butylaminoboranes. The diisopropylboranes correspond favorably with dimethyl and diethylboranes while di-tert-butylboranes deviate from the planar C_2BNC_2 conformation. The more bulky the R_2N group the stronger the deviation while approaching an orthogonal conformation.

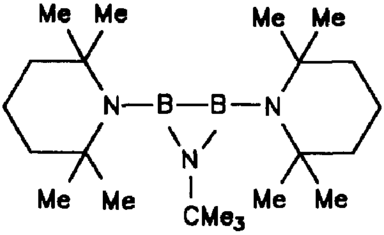
Zhao, He, Lu and Zhang[62] studied the reaction of BH_3SMe_2 with CCl_4 by ^1H NMR spectroscopy. Van Duin and others[63] conducted a structural analysis of borate esters of polyhydroxy carboxylates in water using ^{13}C and proton NMR spectroscopy; they established that borate esters of the threo-3,4-diol functions of gluconate, glucarate and idarate are preferred.

Wrackmeyer[64] investigated the influence of unresolved multinuclear, long-range nuclear spin-spin coupling for aminoboranes and organoboranes.

Kliegel and coworkers[65] studied the X-ray crystallography of 5-methyl-5-nitro-2-phenyl-1,3-dioxa-2-boracyclohexane, and found it to be a monocyclic borate structure, in agreement with earlier predictions. Mikhailov and coworkers[66] synthesized and determined the structure of (7-endo-methyl-3-borabicyclo[3.3.1]non-3-yl)-8-quinolinolate by X-ray analysis.



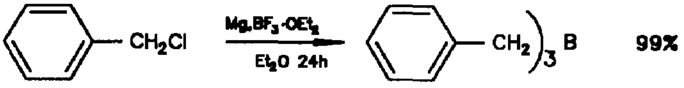
Dirschl and others[67] determined the structure of azadiboriridines by X-ray analysis.



X-ray crystallography was used by Feng et.al.[68] to determine the crystal structure of (diphenylphosphene)dimesitylborane. The configuration was found to be in agreement with theoretical calculations. Koelle and Noeth[69] also used X-ray studies to determine the structure of (benzyl-tert-butylamine)boranes and bis(benzyl-tert-butylamino)boron(1+) salts.

4. Synthesis of Organoboranes

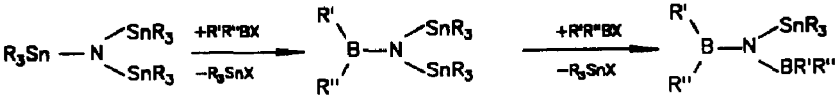
Triorganylboranes are valuable intermediates in organic synthesis. Boron chemists often require organoboranes containing groups which will not tolerate hydroboration. Brown and Racherla[70] reported a convenient, highly efficient synthesis of triorganylboranes via a modified organometallic route involving the direct reaction of magnesium, organic halide, and boron trifluoride etherate. Allyl and benzyl chlorides are accomodated with little or no coupling observed.



Ultrasound dramatically accelerates the reaction, and the authors suggest the application of the procedure in the synthesis of large quantities of organoboranes including difficult to handle materials such as trimethylborane.

Albert and coworkers[71] report that racemization occurs when certain steroidal Grignard reagents are used to prepare steroidal boranes.

Noeth, Otto and Storch[72] synthesized diborylamines of type R_3SnN-$(BR'R'')_2$ XIV from $N(SnMe_3)_3$ or $N(SnEt_3)_3$ and boron halides, R'R"BHal, via [bis(triorganylstannyl)amino]boranes XIII.



XIII

XIV

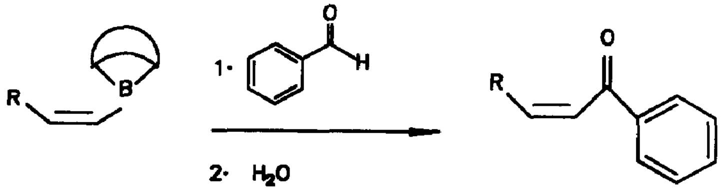
R=Me,Et

R'=Et,iPr,Bu,Ph,Me,Et,iPr,Cl,Cl,Br,Br

R"=Et,iPr,Bu,Ph,Me,Et,iPr,NMe_2,Cl,NMe_2,Br

Compound XIV is labile if R'=R"=Cl or Br. The B-bromo compounds are much less stable than the corresponding B-chloro derivatives.

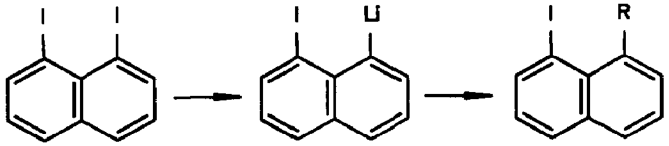
Brown, Bhat and Rajagopalan[73] prepared B-(Z)-1-alkenyl-1-borabicyclo[3.3.1]nonanes in good yields from the corresponding lithium complex. These reagents undergo smooth reactions with benzaldehyde and methyl vinyl ketones providing the corresponding allylic alcohols and 4-alkenyl-2-butanones, respectively.



Brown and coworkers[74] demonstrated that alkylboranes can be prepared from the corresponding borohydrides. The preparation of monoalkyl and dialkylboranes using a variety of acids was discussed.

$$n\text{-}C_8H_{13}BH_3Li + HOAc \xrightarrow{\text{EE or n-pentone}} n\text{-}C_8H_{13}BH_2 + \downarrow LiOAc + H_2$$

Katz[75] prepared a variety of novel disubstituted aromatic compounds by a boron-lithium exchange.



$R{=}B(OH)_2, B(OEt)_2, BMe_2$, etc·

Brown, Srebnik and Cole[76] prepared boronic and borinic esters using two different routes. One route involves the thermal dissociation of the corresponding lithium "ate" complexes.

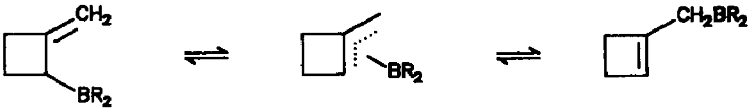
$$LiRBR'_3 \xrightarrow{\Delta} RBR'_2 + LiR'$$

$$LiRR''BR'_2 \xrightarrow{\Delta} RR''BR' + LiR'$$

In the second route, the lithium "ate" complex is treated with an acid chloride.

Altman, Bohnke, Steigel and Wulff[77] prepared N-substituted-2-carboxamidophenylboronic acid anhydrides by lithiation of 2-phenyl-2-oxazolines and subsequent reaction with trimethyl borate or borane.

Bubnov, Gurskii and Lavrinovich[78] prepared borane XV by treating lithiated methylenecyclobutane with R_2BBr.



XV

R=Bu, R_2B=9-borobicyclo(3,3,1)non-9-yl

XV reacts with aldehydes and ketones.

Wolfgang and others[79] used exchange reactions between $ArSiMe_3$ and BX_3 [or RBX_2, RR'BX, R_2BX] to prepare aryl and diarylhaloboranes.

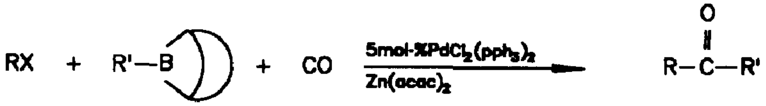
X=Cl or Br

Lin[80] reported the preparation of triethylborane via the reaction of triethylaluminum with borate esters. Brown, Jadhav, and Singram[81] reviewed the preparation of chiral organoboranes and their reactions to give enantiomerically pure organic compounds.

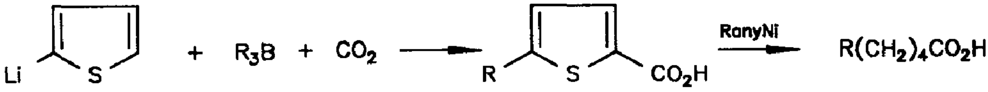
C. Carbon-Carbon Bond Formation

1. Homologation

Wakita, Yasunaga, Akita and Kojima[82] used several borane reagents in a carbonylative cross-coupling reactions to prepare unsymmetric ketones.

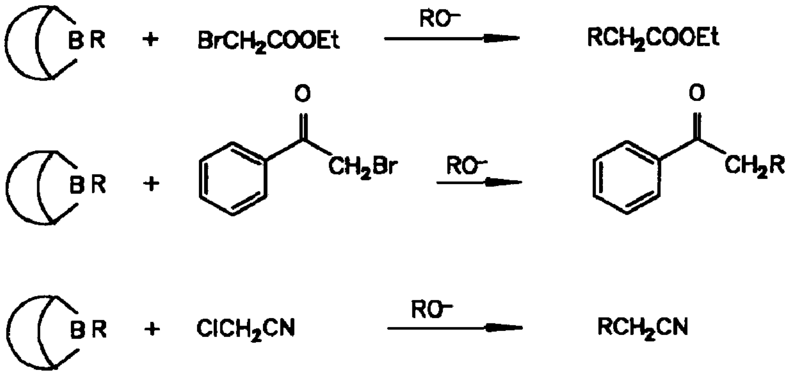


Tang, Deng and Xu[83] report thienyllithium reacts with R_3B and CO_2 to give 5-alkylthiophene-2-carboxylic acids.

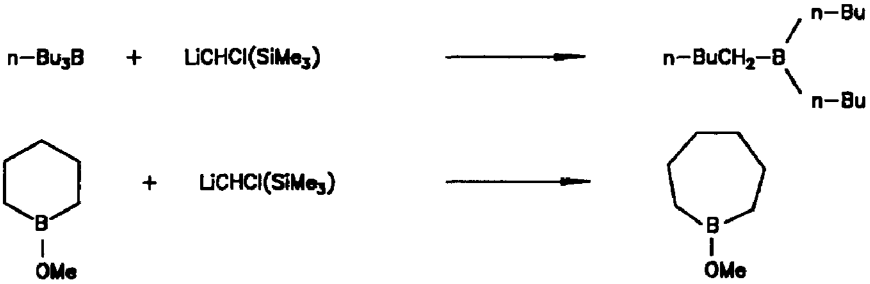


R=Et,n-hexyl,$Me_2CH(CH_2)_{10}$

Matteson[84] reviewed the homologation of boronic esters. Brown, Bhat and Campbell[85] reported the homologation of B-alkenyl-9-BBN derivatives with α-halo carbanions generated from ethyl bromoacetate, phenacyl bromide and chloroacetonitrile.



Brown and Singh[86], in an exploratory study, found that high yields of one-carbon homologation products can be acheived using chloro(trimethylsilyl)methyllithium.



Methoxy(phenylthio)methyllithium was also utilized in the above reactions. It worked efficiently for tri-n-butylborane but required mercury(II) chloride in the case of B-methoxyborinane.

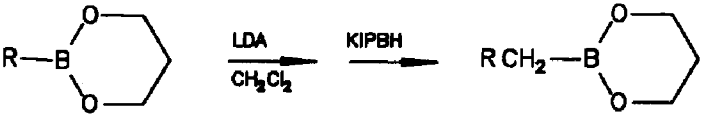
Bestmann and Arenz[87] reacted phosphorus ylides with alkyldichloroboranes.

R=Me

R'=cyclohexyl, thexyl

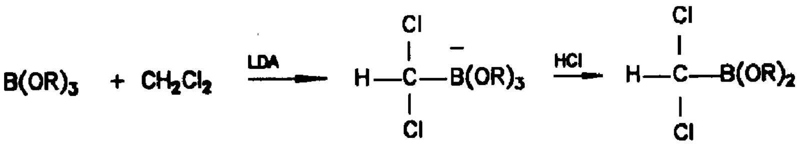
Phillion and others[88] used pinacol iodomethaneboronate in a 3-step procedure to synthese N-acyl aminomethaneboronates starting from primary amines.

New procedures for the homologation of Boronic esters were discussed extensively in two publications. Brown and Singh[89] reported that a mixture of LDA and CH_2Cl_2 reacts with boronic esters to yield the homologated boronic ester after reduction with KIPBH.

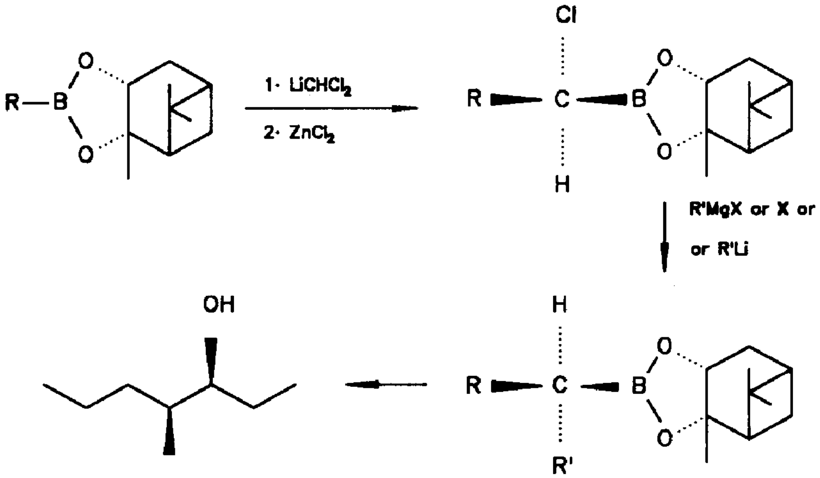


Brown, Singh and Rangaishenvi[90] compared the available homologation procedures using preformed $LiCH_2Cl$ and $LiCHCl_2$.

A need for large amounts of (dichloromethyl)boronic esters prompted Matteson and Hurst[91] to develop an in situ method to generate $LiCHCl_2$ in the presence of triisopropyl borate.



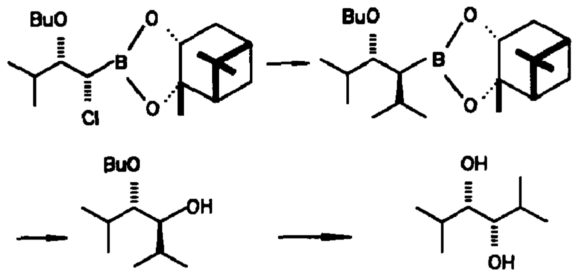
Matteson, Sadhu and Peterson[92] produced chiral boronates using pinanediol boronic esters. XVI Can be homologated further to obtain other insect pheromones.



Insect Phermones

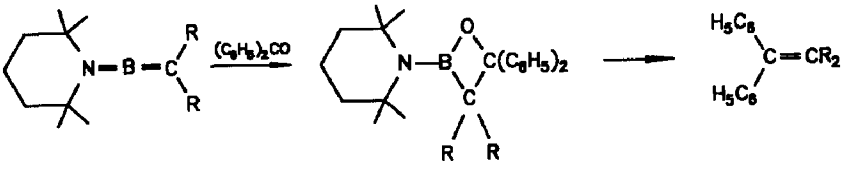
XVI

Matteson and Kandil[93] utilized the homologation of a boronic ester in preparation of (S,S)-Di-isopropylethanediol. ((S)-DIPED)



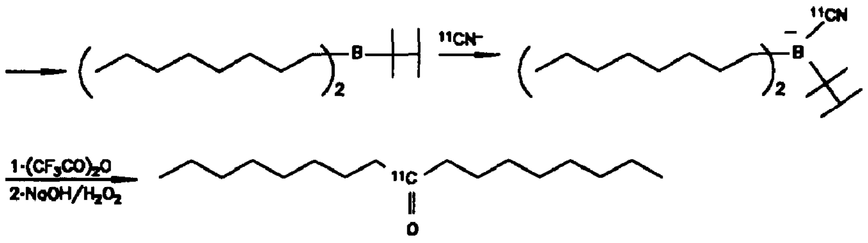
(s)-DIPED

Glaser and Noeth[94] discussed the use of unstable methyleneboranes XVII, as intermediates in olefinic synthesis.



XVII

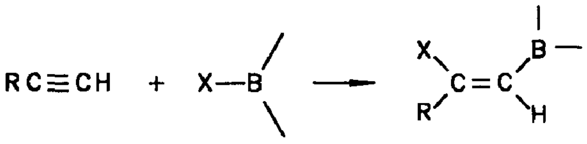
Kothari, Finn, Kabalka, and others[95] utilized the homologation of organoboranes with K^{11}CN to synthesize C^{11} labeled dialkylketones. The rearrangement of the intermediate followed by alkaline oxidation produced the desired compounds.



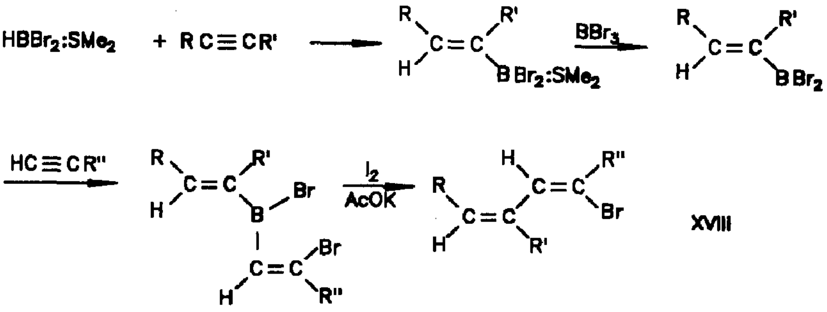
Kabalka[96] reviewed organoborane reactions useful for the rapid introduction of short-lived radionuclides of use in diagnostic nuclear medicine.

2. Alkenyl and Arylborates

The haloboration of 1-alkynes to form adducts which are valuable intermediates in organic synthesis was reported by Suzuki[97].

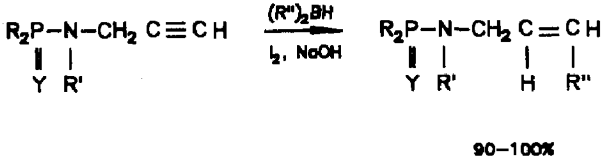


Hyuga, Takinami, Hara and Suzuki[98,99] used a hydroboration-bromination sequence to prepare (Z,Z)-1-bromo-1,3-dienes (XVIII).



XVIII

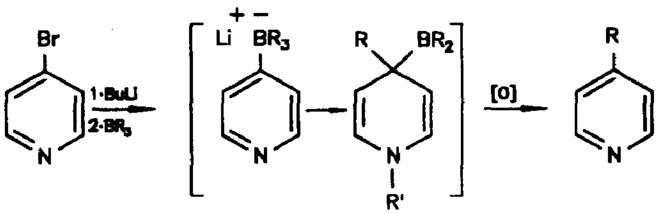
Benmaarouf[100] utilized an analogous reaction to prepare substituted allylic amines.



R=EtO, Me$_2$N; R'=Me·CH$_2$Ph; Y=O, S

R''=cyclohexyl, Me$_2$CHCMe$_2$, Me$_2$CHCHMe

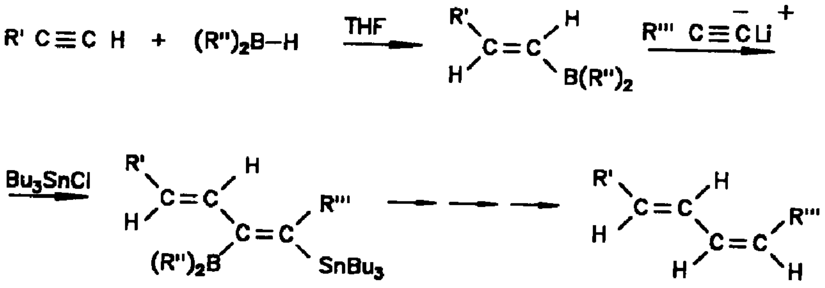
Ishikura Ohta and Terashima[101] synthesized alkylated pyridines via rearrangment of the corresponding borates.



R'=Lewis acid or acyl

BR$_3$=BBu$_3$, Bu–9–BBN, B(sec–Bu)$_3$, B(Hex)$_3$ or B(cyc–Hex)$_3$

Doolittle and Solomon[102] used a tin mediated rearrangment to prepare (Z,E)-3,5-tetradecadienylacetate XIX (a potent moth sex attractant for the carpenterworm).

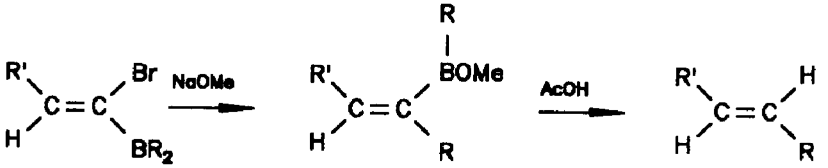


XIX

Kerschl and Wrakmeyer[103] prepared a series of chiral tin substituted alkenyl borates. The chirality was caused by restricted rotation around the B-C bond after complexation with N-azolyl lithium reagents.

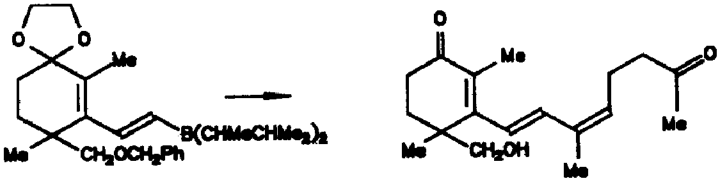
Hoshi,Masuda and Arase[104] utilized phenylsulfinylchloride to initiate the rearrangment of alkenylborates. The method can be used to prepare (E)-alkenes.

Brown and coworkers[105] developed a general stereospecific synthesis of (E)-disubstituted alkenes utilizing a variety of hydroborating agents.

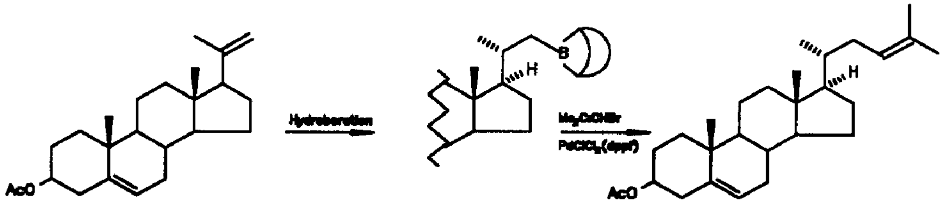


Brown and another group[106] also reported the sterioselective synthesis of (E)-(1-substituted-1-alkenyl)boronic esters via nucleophilic substitution reactions on (Z)-(1-bromo-1-alkenyl)boronic esters using organolithium or Grignard reagents.

Miyaura, Satoh, Hara and Suzuki[107] used a palladium-catalyzed cross-coupling reaction between 1-alkenylborane and a haloalkene to prepare a pheromone.

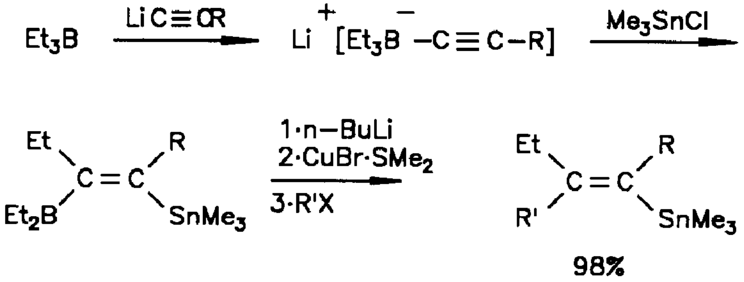


Miyaura and others[108] also used a palladium-catalyzed cross coupling reaction to prepare unsaturated steroids.

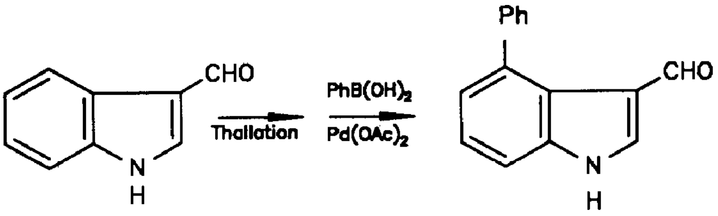


Hoshi and coworkers[109] utilized a copper catalized cross coupling reaction to prepare vinylsilanes from silylvinylboranes.

Chu and Wang[110] prepared trisubstituted vinylstannanes with high regio- and stereoselectivity via the selective transformation of the alkenyl-boranes to alkenylcopper reagents followed by coupling with alkyl halides

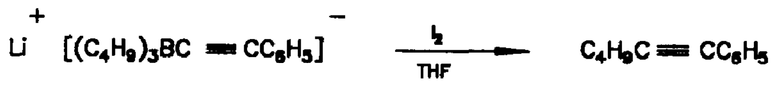


Somei, Amari and Makita[111] reported a new approach to the synthesis of 4-substituted indoles involving a thallation boronation sequence.



3. Alkynylboranes

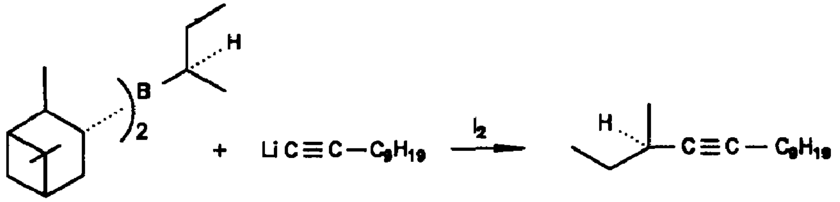
Brown and his coworkers reported that organoborates,such as XX, undergo a facile iodine induced, addition-elimination reaction to form internal acetylenes in high yield. The reaction is applicable to both primary and secondary alkyl groups, as well as aromatic systems. A variety of functional groups are tolerated by the reaction.



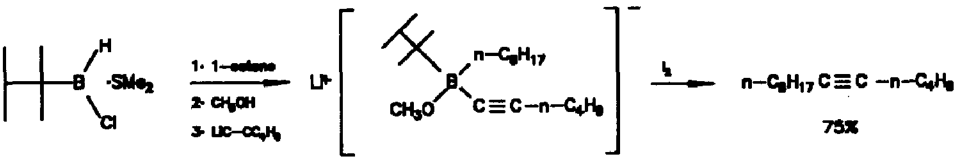
$$\overset{+}{Li}\ [(C_4H_9)_3BC\equiv CC_6H_5]^{-}\xrightarrow[THF]{I_2}C_4H_9C\equiv CC_6H_5$$

XX

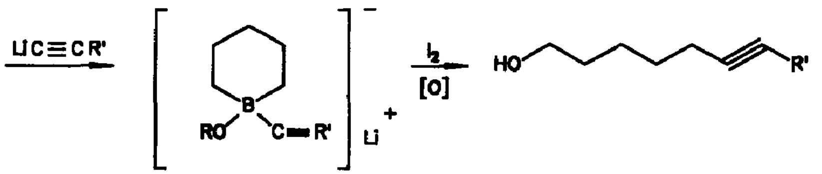
Brown, Desai and Jadhav[112] used the iodine-induced rearrangement of the "ate" complex derived from diisopinocampheylalkylborane and lithium acetylides to synthesize enantioselective disubstituted alkynes.



Sikorski, Bhat, Cole Wang and Brown[113] prepared lithium alkynyl "ate" complexes of thexylalkylborinates as intermediates in the synthesis of unsymmetrical alkynes. The thexyl and methoxy moieties are good blocking groups since they resist migration.

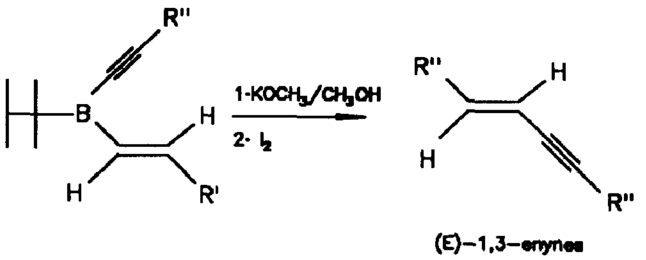


Brown and Bhat[114] used the "ate" complex derived from B-(triphenylmethoxy)borinane and 1-alkynyllithium to prepare 6-alkyn-1-ols in high yields. The reaction sequence was also used successfully starting with borepane derivatives.



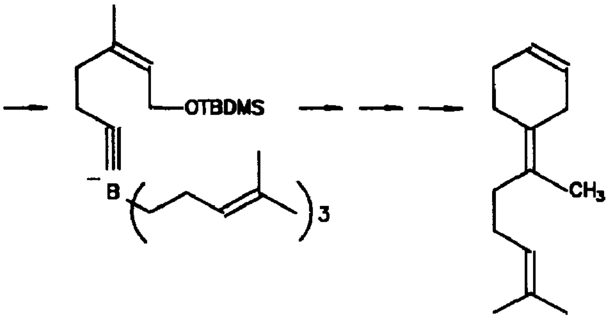
$R=CPh_3$, $CHMe_2$, CMe_3, CEt_3 (highest yield) $R'=n-C_6H_{13}$

Brown, Bhat and Basavaiah[115] used alkenylalkynyl borates as precursors to several pheromones.



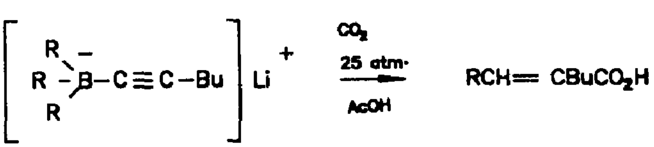
Brown and Wang[116] also used (1-alkynyl)trialkylborates in the preparation of pheromones.

Corey and Siebel[117] prepared E-2-bisabolene XXI via an alkynyltrialkylborate.



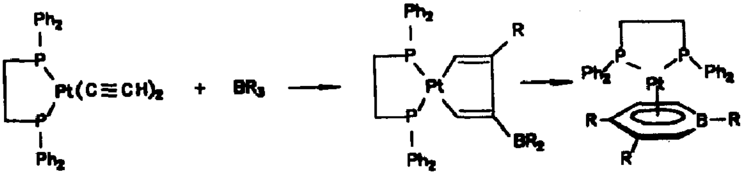
XXI

Deng, Lu and Xu[118] studied the carbon dioxide induced rearangment of trialkylalkynylborates to prepare alkenoic acids. They found the migratory aptitudes were: primary>secondary>> tertiary. They noticed a higher yield of primary group migration at lower temperatures.

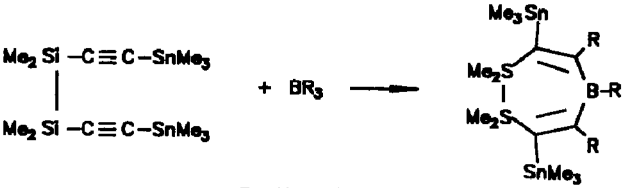


$$\left[R_3\overset{-}{B}-C\equiv C-Bu \right] Li^+ \xrightarrow[AcOH]{CO_2\ 25\ atm\cdot} RCH{=}CBuCO_2H$$

Sebald and Wrackmeyer[119] prepared platinacyclopentadienes via the addition of BR_3 to platinum acetylides. These rearranged to a platinum-borole complex.

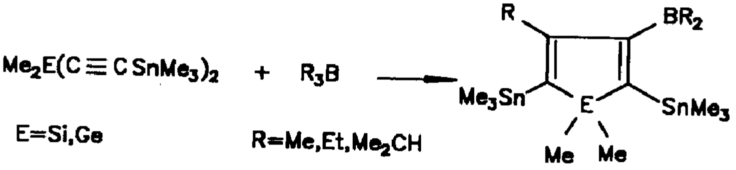


Sebald, Seiberlich, and Wrackmeyer[120] also showed that bis(trimethylstannylethynyl)tetramethyldisilane reacts at with trialkylboranes, to give dihydro-1,2,5-disilaborepines XXII.



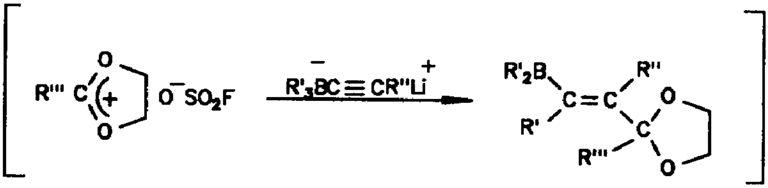
XXII

Wrackmeyer[121] prepared a new silica- and germacyclopentadiene derivatives via the reaction of appropriate alkynyl reagents with trialkylboranes.



Wrackmeyer and Kerschl[122] also synthesized novel fused heterocyclic systems via the reaction of lithiated azoles with intermediates obtained from the reaction of organoboranes with alkynyltin reagents.

Pelter and Colclough[123] found that 2-alkyl-1,3-dioxolan-2-ylium fluorosulfonates, can be used to induce rearrangement of trialkylalkynylborates.

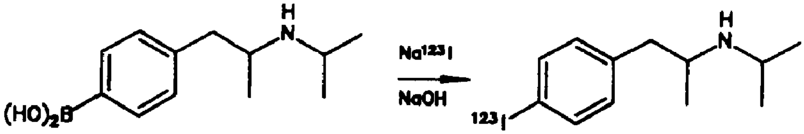


D. Carbon-Heteroatom Bond Formation

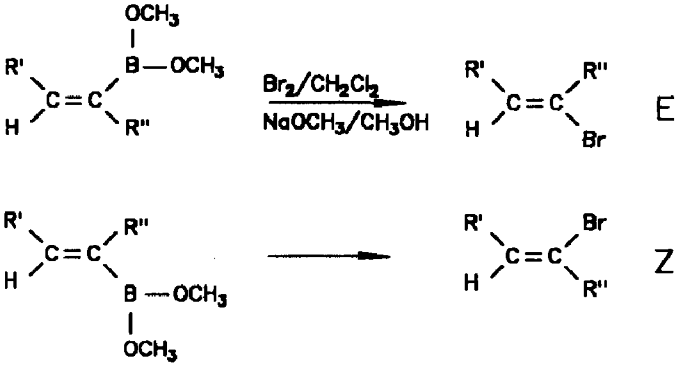
1. Group VII

The synthesis of labeled compounds via organoboranes was extensively reviewed by Kabalka.[124,125]. The incorporation of radiohalogens via versatile organometallic reactions and their applications in radiopharmaceutical chemistry was reviewed by Srivastava, Goodman and Knapp[126].

Kabalka and his coworkers[127] reported a new route to radioiodine labeled amphetamines via the reaction of sodium [I^{123}] iodide with a boronic acid in the presence of an oxidant.

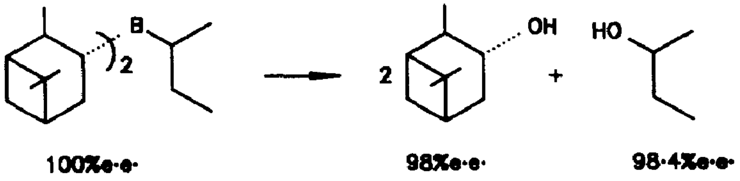


Brown and coworkers[128] prepared (Z)- and (E)-disubstituted vinyl bromides in excellent stereochemical purities (97%) via the bromination of vinylboronic esters.

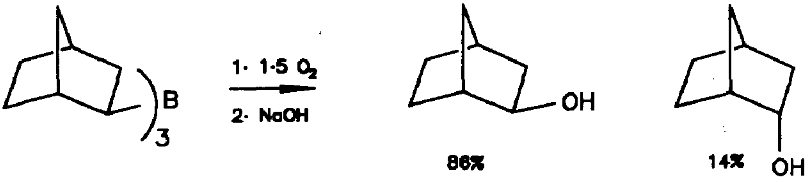


2. Group VI

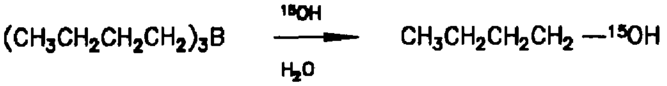
Kabalka[129] reviewed the use of organoboranes for incorporating oxygen isotopes in an organic synthesis. Brown, Snyder, Rao and Zweifel[130] established the conditions necessary for a clean and quantitative transformation of organoboranes into the corresponding alcohols. The reaction tolerates functional groups and no racemization is observed when chiral boranes are oxidized.



Brown Midland and Kabalka[131] reported the direct reaction of molecular oxygen with a variety of organoboranes to yield the corresponding alcohols. The reaction involves the formation of radical intermediates leading to epimerization.

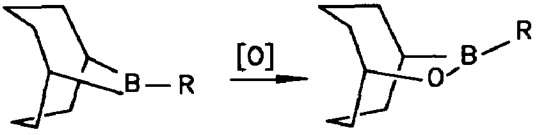


The relative rates of oxidation of alkyl groups are in the order tertiary>secondary>primary consistant with the free radical mechanism. Berridge and coworkers[132] used oxygen-15-labeled butanol for positron tomography using the reaction of oxygen with tributylborane.

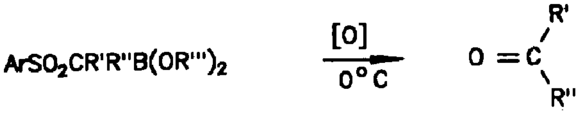


$$(CH_3CH_2CH_2CH_2)_3B \xrightarrow[H_2O]{{}^{15}OH} CH_3CH_2CH_2CH_2-{}^{15}OH$$

Soderquist and Najafi[133] studied the selective oxidation of organoboranes with anhydrous trimethylamine N-oxide. Acyclic trialkylboranes are oxidized sequentially to give first borinate, and finally borate esters. The oxidative reactivity of alkyl groups on boron is $3^0 > 2^0 > 1^0$. Interestingly, the mono-oxidation of alkyl 9-BBN reagents leads to cleavage of the ring carbon-boron bond.

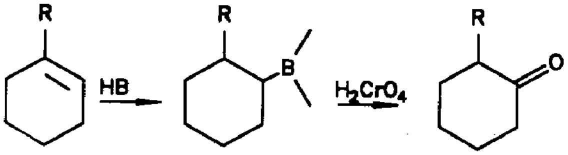


Marc and Christian[134] prepared various carbonyl compounds via the oxidation of organosulfone borates, which were prepared by sequential reaction of phenyl sulfone derivatives with lithium and dimethoxychloroborane.

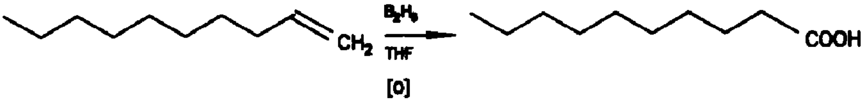


$$ArSO_2CR'R''B(OR''')_2 \xrightarrow[0^\circ C]{[O]} O=C(R')(R'')$$

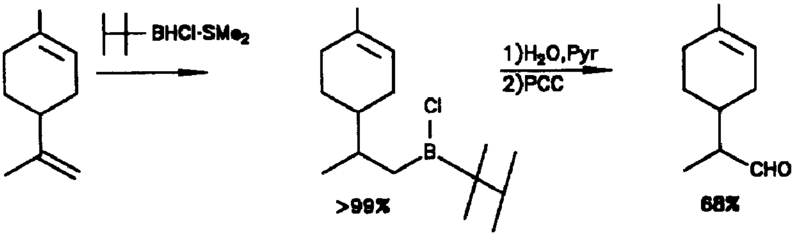
Brown and Garg[135] oxidized organoboranes to the corresponding ketones using chromic acid.



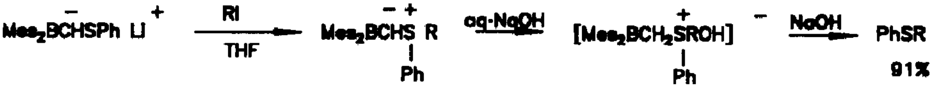
Nguyen, Mavrov and Serebryakov[136] also used used vigorous oxidative agents ($KMnO_4$, H_2CrO_4) to convert terminal olefins to carboxylic acids.



Brown, Kulkarni, Rao and Patil[137] reported that organoboranes can be readily oxidized with PCC pyridinium chlorochromate under mild conditions to afford the corresponding carbonyl compounds. Organoboranes derived from internal alkenes produce good yields of ketones. Terminal alkenes produced moderate yields of aldehydes.

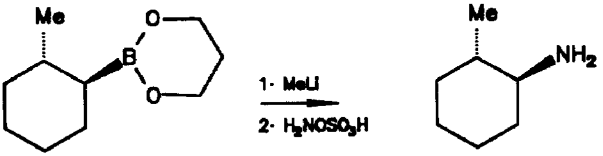


Pelter, Bugden, Pardasani and Wilson[138] noticed an unusual electrophilic attack on sulphur in α-thiocarbanions. The method results in the formation of aryl alkyl sulfides.



3. Group V

Brown and coworkers[139] synthesized primary amines of very high enantiomeric purities via the reaction of boronic esters with hydroxylamine O-sulfonic acid.

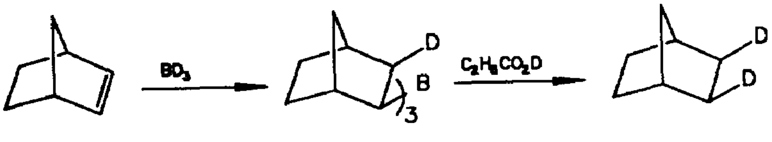


Kabalka, Finn and coworkers[140] reported the synthesis of nitrogen-13 labeled amines via the reaction of ammonia with organoboranes in the presence of an oxidant.

$$3(C_8H_{17}CH{=}CH_2) \xrightarrow{BH_3\cdot THF} (C_{10}H_{21})_3B \xrightarrow[NaOCl]{^{13}NH_3} C_{10}H_{21}{}^{13}NH_2$$

4. Group I

Brown and Murray[141] reported on an extensive investigation of the protonolysis reaction of trialkylboranes. Primary alkyl groups react faster than secondary and other hindered groups. The reaction proceeds with retention of configuration of the carbon attached to boron.



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