BORON: BORANES IN ORGANIC SYNTHESIS

ANNUAL SURVEY COVERING THE YEAR 1983*

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CONTENTS

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A. INTRODUCTION

The role of the organoboranes in organic synthesis continues to expand at an impressive rate. Borane reagents are used in thousands of hydroborations and reductions each year. As in the past, this review is primarily focused on reports concerned with the development of new organoborane methodology and/or reagents and not on the routine use of well characterized borane or borohydride reactions. Not surprisingly, Professor Brown and his research group have been the leading contributors to the field and this year is no exception. However, it is exciting to note that many new names appear among the authors listed in the Reference section. There is little doubt that the list will grow even more rapidly as these versatile reagents become more visible in the literature covering organic synthesis.

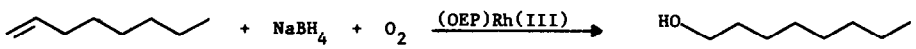
I have presented the chemistry in the format which has traditionally been utilized. As always, such classifications are somewhat arbitrary but, hopefully logical. Thus R_2BBr reagents are found in section B.1.c because they often serve as precursors for R_2BH or are used in reactions (haloborations) which are analogs of R_2BH hydroborations.

B. BORANE REAGENTS

1. Hydroborating Agents

a. BH_3

The hydroboration reaction is fundamental to the organoborane field. It was used hundreds of times in the literature this year but most of the examples were routine. There were, however, a few new modifications which may prove valuable to researchers in the field. Shore and Toft patened a procedure for producing diborane in the absence of solvent [1]. Apparently, B_2H_6 is produced in 95% yield by treating $NaBH_4$ or $LiBH_4$ with BF_3 at -196° and warming the mixture to room temperature for 12-13 h. A report appeared in the Polish literature on the in situ preparation of diborane in dibutyl ether [2]. The investigators utilized a variety of organic acids to generate the diborane from $LiBH_4$. A rather novel approach to the in situ generation of diborane was reported by Aoyama and his co-workers [3]. They found that a rhodium porphyrin complex, octaethylporphyrinatorhodium(III), [(OEP)Rh(III)] catalyzes the reaction of $NaBH_4$ with alkene under aerobic conditions. Thus 1-octene reacts with borohydride in the presence of (OEP)Rh(III) and oxygen to yield 1-octanol.

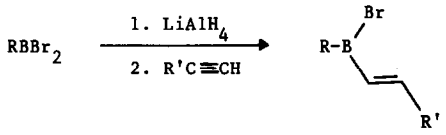


The yield of alcohol is modest (15%) based on borohydride but very high

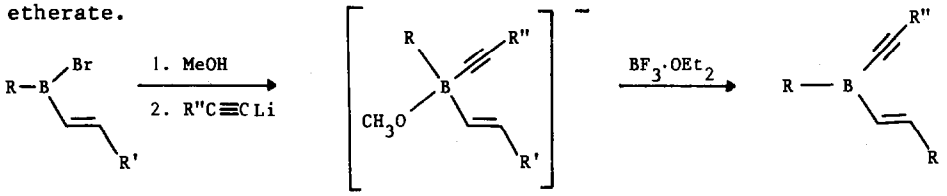
based on the porphyrin complex (2000%). Presumably, the reaction occurs via the reduction of the (EOP)Rh(III) complex by the borohydride to generate borane which then hydroborates the alkene. The reduced porphyrin is presumably reoxidized by the oxygen which also oxidizes the intermediate organoboranes to the product alcohols. It should be noted that the ratio of the anti-Markovnikov alcohol to the Markovnikov product is approximately 84:16 which differs from the normally observed 94:6 ratio but can be readily explained if incomplete oxidation is being observed. (It is known that secondary alkyl groups react preferentially in free radical organoborane reactions such as the oxidation of organoboranes by molecular oxygen.)

b. RBH_2

Brown and his coworkers utilized analogs of the RBH_2 reagents to synthesize totally mixed organoboranes, namely alkylalkenylalkynylboranes [4]. Alkyldibromoboranes, generally obtained via the hydroboration of alkenes with dibromoborane complexes, were utilized to hydroborate alkynes via a controlled hydridation to yield the corresponding alkylalkenylbromoboranes.



These agents were then methanolyzed and reacted with alkynyllithium reagents to yield the corresponding mixed organoborates. The desired products were obtained by treating the "ate" complexes with BF_3–etherate.



c. R_2BH

Brown and Pai reported that borinane could be prepared conveniently, in high yield, by hydroborating 1,4-pentadiene with 9-BBN and then treating the resultant trialkylborane with BH_3-SMe_2 [5]. The regenerated 9-BBN is separated by crystallization. Alternatively, the borinane can be selectively removed from the reaction mixture as its bis-adduct with tetramethylethylenediamine.

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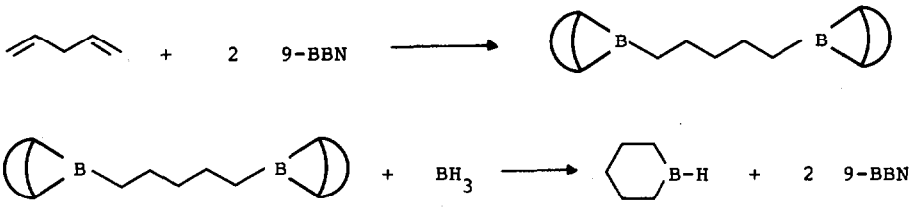
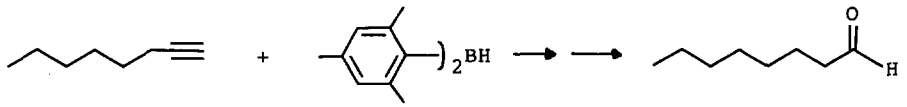
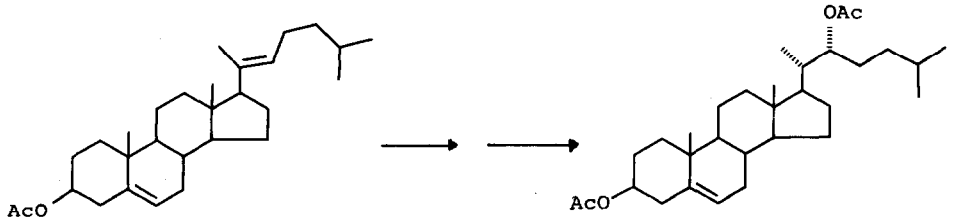


Pelter, Brown, and Singaram reported that the hydroboration of alkenes with dimesitylborane is slow and sensitive to steric effects [6]. Thus the hydroboration of 1-octene required eight hours to produce a 95% yield of 1- and 2-octanol (97:3), after oxidation, whereas 2-pentene was hydroborated only partially (~6%) after 24 hours at room temperature. The reaction could be forced to completion by raising the temperature to 65°C. Interestingly, the hydroboration of alkynes proceeded quite rapidly (5 min at 25°).

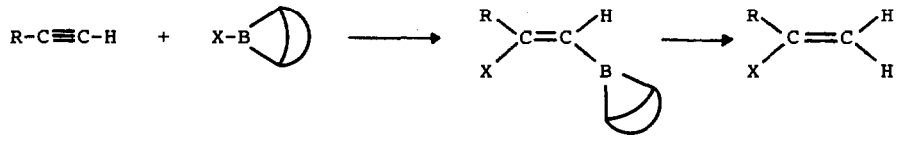


Midland and Kwon investigated the stereochemistry of the hydroboration of α-chiral olefins and the reduction of α-chiral ketones [7]. They found that hydroboration of 20(22)-methylene steroids occurs predominantly from the si face to provide a 20S,22-hydroxysteroid. Thus hydroboration of 5,E-20(22)-cholestadiene with 9-BBN provides essentially pure 20S,22R,22-hydroxycholestenol (isomeric purity 300:1).



The authors discuss conformational models which predict the observed stereochemistry and the application of these model to the experiments reported which also include the reductions of chiral ketones.

Professor Suzuki and his co-workers report that B-bromo- and B-iodo-9-BBN react readily with 1-alkynes to yield the corresponding [Z]-1-boro-2-haloalkenes [8]. The reactions are highly stereoselective



(~98%) and, when coupled with the classical protonolysis reaction, provide an excellent method for producing 2-haloalkenes. The haloboration reaction tolerates a variety of functional groups including halides and esters but, unfortunately, cannot be used successfully with alkenes and internal alkynes. The authors utilized the intermediate [Z]-1-boro-2-halo-alkenes to synthesize a series of [Z]-1-alkynyl-2-halo-1-alkenes (section C.3.).

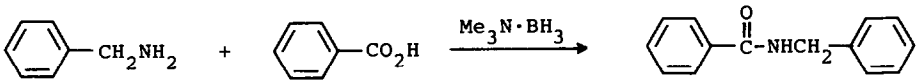
Binnewirtz, Klingenberger, Welte, and Paetzold reported that the haloboration of alkynes is reversible [9]. Furthermore, at elevated temperatures, they report that a 1,1 organoboration occurs which is accompanied by a 1,2 transfer of a substituent from boron to the vinyl carbon.

2. Reducing Agents

a. BH_3

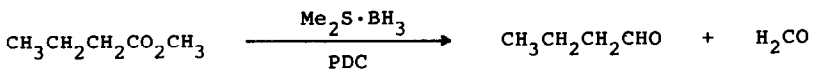
The use of BH_3 for the reduction of functional groups is well documented. A number of investigators have begun to investigate the use of BH_3 complexes for chemoselective reductions. Kikugawa reviewed the use of pyridine-borane in acidic media for selective reductions [10]. Babler and Sarussi reported that the chemoselectivity of pyridine-borane could be enhanced by adsorbing it onto solid supports such as activated alumina and silica gel [11]. They found that aldehydes are readily reduced to the corresponding alcohols when alumina was used as the solid support but simple ketones were inert under identical conditions. Ketones were, however, reduced when silica gel was used as the support.

Trapani, Reho, and Latrofa found that trimethylamine-borane can be used for the N-acylation of amines by carboxylic acids [12]. By changing the ratio of the reagents, N-alkylation can also be achieved.



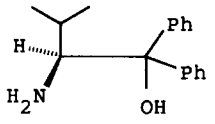
Ek, Garegg, Hultberg, and Oscerson utilized trimethylamine in the presence of aluminum chloride to reduce 4,6-O-benzylidene acetals of hexopyranosides to the corresponding O-benzyl ethers [13]. The reductions are solvent dependent. In toluene, the 4-O-benzyl ethers are formed whereas 6-O-benzyl ethers are formed when THF is used as solvent.

Duranti, Micheli, Salvatori, and Staccioli utilized borane-dimethylsulfide in the presence of pyridinium chlorochromate to reduce carboxylic esters to the corresponding aldehydes [14].



b. RBH_2

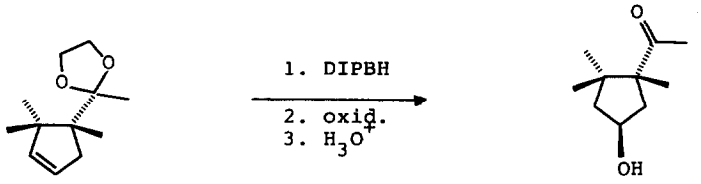
Itsuno, Ito, and Nakahama reported that prochiral aromatic ketones could be reduced in high optical and chemical yield utilizing what, presumably, is an optically active alkoxyborane complex [15]. They prepare (S)-(-)-$HOCPh_2CH(NH_2)CHMe_2$ via the addition of a phenyl Grignard to the methyl ester of valine which is then added to BH_3 to form the chiral reducing agent. The (R)-alcohols are formed in excellent optical yield (91-100%).



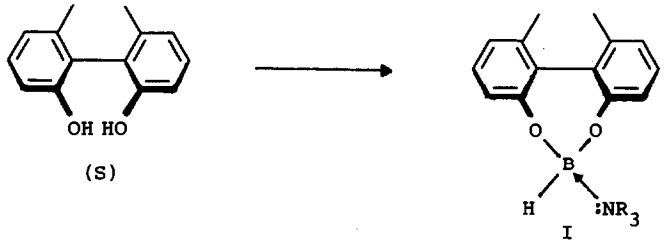
(S)

c. R_2BH

A new approach to optically active, five-membered-ring carotenoid building units using borane reducing agents was reported by Ruttimann, Englert, Mayer, Moss, and Weedon [16]. They utilized (+)-diisopinocampheylborane to reduce an unsaturated acetal to yield the desired hydroxyketone.



Suda, Kanoh, Umeda, Nakajo, and Motoi related an interesting approach to inducing optical activity via borane reagents [17]. They reduced a series of aromatic ketones with a chiral reagent prepared *in situ* from 2,2'-dihydroxy-6,6'-dimethylbiphenyl. Using the (S)-biphenyl reagent, they prepared the (S)-alcohols in 60% optical yield.



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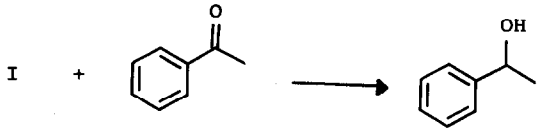
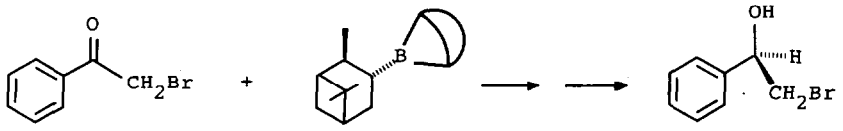


(S)

d. R_3B

Alpine borane (B-3-pinanyl-9-borabicyclo[3.3.1]nonane) has emerged as an exceptionally versatile reducing agent. Brown and Pai have found that the reagent will reduce haloketones to the corresponding chiral halohydrins in nearly quantitative chemical yield and with high optical induction [18]. The reactions are carried out in the absence of solvents over a period of days.



e. R_4B^-

The use of borohydrides in organic syntheses continues to grow at an incredible rate. A number of researchers are studying the reactivity of borohydride reagents which have been modified by replacement of one or more of the hydrides with alkoxy, etc. groups or by interchanging the associated cation. As an example, Nakata, Tanaka, and Oishi report that the reduction of α-hydroxy ketones with zinc borohydride affords the erythro diols with high regioselectivity [19]. This contrasts with the formation of threo diols when aluminum hydride reagents are employed. Along similar lines, Ito and Yamaguchi note that 3-oxo amides yield syn 2-alkyl-3-hydroxy amides when reduced with zinc borohydride [20]. Finally, Kim, Hong, and Yang report that tertiary and benzylic halides are readily reduced by zinc borohydride whereas primary, secondary, and aryl halides are unaffected [21].

For selective reductions, the alkoxy and acyloxyborohydrides remain popular. Brown, Nazer, and Sikorski report that the normal preparation of potassium triisopropoxyborohydride results in a product which contains a significant impurity, probably the tetraisopropoxyborohydride. They have found that the impurity is readily removed by simply refluxing the THF solution of the triisopropoxyborohydride over potassium hydride or, alternatively, by preparing the reagent in the presence of excess potassium hydride (and storing it over the excess KH) [22].

Nutaitis and Gribble have found that the tetra-n-butylammonium salt of triacetoxyborohydride will readily reduce aldehydes but not ketones [23]. Yamada, Takeda, and Iwakuma utilized chiral acyloxyborohydrides to asymmetrically reduce cyclic imines [24]. They report, for example, that (S)-norlaudanosine is formed in 60% optical yield.

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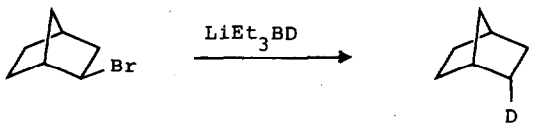
The alkylborohydrides have also been investigated extensively this year. Pyun, Son, and Yoon have examined the reducing characteristics of lithium n-butylborohydride and report that it is more powerful a reducing agent than lithium borohydride but less powerful than lithium triethylborohydride [25]. Biffer, Noeth and Sedlak report that the formation of lithium monoorganotrihydroborates should be approached with caution [26]. In a careful study, they found that the reaction of lithium alkyls with a variety of borane complexes resulted in the formation of all members of the $LiBH_nR_{4-n}$ series. Furthermore, the proportions of each of the series members varied with solvent, complexing agent and steric bulk of the alkyl group.

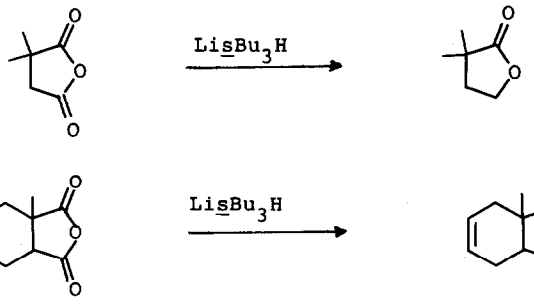
Lithium triethylborohydride was examined as a selective reducing agent by a number of groups. Krishnamurthy and Brown report that lithium triethylborohydride exhibits enormous nucleophilic power in S_N2 displacement reactions with alkyl halides [27]. The reactions follow 2nd order kinetics and exhibit typical characteristics of S_N2 nuclophilic substitutions. It is interesting to note that even hindered alkyl halides, neopentyl etc., undergo facile reduction to the corresponding alkanes. The corresponding deuteride can be readily prepared from lithium deuteride and triethylborane and can be used to stereospecifically incorporate deuterium.



Brandaenge, Dahlman, and Oelund found that lithium triethylborohydride can be used to cleave carbon-fluorine bonds [28]. The reaction is very sensitive to steric interactions. Kobayashi, Jadhav, Zydowsky, and Floss utilized tritiated triethylborohydride to synthesize chiral acetic acid [29]. Interestingly, they utilized alpine borane (section B.2.d) to synthesize the necessary chiral precursor.

Brown, Narasimhan, and Somayaji investigated structural effects on the reduction of epoxides by lithium triethylborohydride [30]. They found that the reactions all exhibit 2nd order kinetics and that substitution decreases the reactivity of the epoxide. Cis epoxides react twelve times faster than the corresponding trans isomers.

Kayser, Salvador, and Morand investigated the reduction of unsymmetrically substituted cyclic anhydrides [31]. The regiochemistry of the reductions depends on the conformation of the substrates.

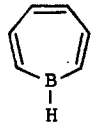


Yoon and his coworkers studied the reactions of lithium trialkylborohydrides formed in situ. In one series, they examined the stereochemistry of ketone reductions using lithium borohydride in the presence of various trialkylboranes [32]. The product distribution was similar to that obtained using preformed trialkylborohydrides. In another series, they investigated the reduction of esters using lithium borohydride in the presence of triethylborane [33]. They found that the triethylborane acts as a Lewis acid catalyst in addition to forming the triethylborohydride reducing agent.

3. Mechanism and Theory

a. Theory

Disch, Sabio, and Schulman carried out a series of ab initio MO calculations which showed that borepin is planar and more stable than its valence isomers, boranorbornadiene and boranorcaradiene [34]. Apparently, borepin has 40-43% of the delocalization energy of tropylium.

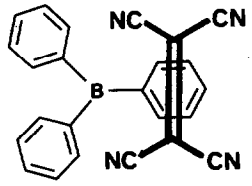


Binkley, and Thorne studied the borane ammonia complex using several ab-initio, electronic-structure methods and Gaussian basis sets [35]. Geometries were calculated at the Hartree-Fock level and with the electron-correlated Moeller-Plesset perturbation method at 3rd order (MP3) with double-zeta polarized quality basis sets. The calculated MP3 geometry agreed with recent microwave data. Hartree-Fock dipole moments and harmonic vibrational frequencies are presented and discussed. Moeller-Plesset perturbation theory at 4th order with triple-zeta-plus-polarization basis sets was used to calculated a B-N dissociation energy of 34.7 kcal/mol and a rotational barrier of 2.065 kcal/mol which agreed with the experimental value.

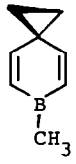
Linert, Gutmann and Perkins calculated the charge distribution in alkylboranes and their ammonia adducts using four different methods:

the CNDO-MO-SCF method, the Jolly and Perry procedure, the MNDO method and the modified Sanderson method [36]. All gave reasonable results for the isolated alkyl boranes. Only the modified Sanderson method gave fair agreement between calculated results and experimental data for the adducts.

Frey and Kitchen studied the pi complexes of a series of arylboranes with tetracyanoethylene [37]. They found that triphenylborane, tri-o-tolylborane, and trimesitylborane form 1:1 colored complexes with tetracyanoethylene in which the triarylborane donates pi-electrons from its phenyl rings to the vacant antibonding orbital of tetracyanoethylene.



Ashe, Abu-Orabi, Eisenstein, and Sandford synthesized 6-methyl-6-boraspiro[2,5]octa-4,7-diene, a boron analog of the phenonium ion [38]. The ^{1}H-, ^{11}B-, and ^{13}C-NMR spectra were obtained and used to assess the magnitude of cyclopropyl conjugation.



b. Kinetics

Brown and Chandrasekharan measured the relative reactivities of a number of alkenes and alkynes toward hydroboration by catecholborane [39]. Catecholborane is less selective than other monofunctional hydroborating agents such as 9-BBN, disiamylborane, thexylborane, and dibromoborane although the trend is the same as that for the dialkylboranes. The lower selectivity may be due to the inherent low steric and electrophilic properties of the reagent and party due to its lessened reactivity which necessitates reaction temperatures of 65°. Brown, Nelson, and Scouten also investigated the regiospecificity and kinetics of the hydroboration of isomeric cis and trans alkenes with 9-BBN [40]. In contrast to other hydroborating agents, 9-BBN does not predictably hydroborate the cis or trans isomer selectively. Furthermore the selectivity is rather low. The reactions are 1.5 order, being first order in alkene and 0.5 order in the 9-BBN dimer.

Brown, Wang, and Chandrasekharen also investigated the mechanism and

kinetics of the reduction of aldehydes and ketones with 9-BBN dimer [41]. Aldehydes and reactive ketones followed first-order kinetics whereas the less reactive ketones exhibited three-halves-order kinetics (or intermediate between first and three-halves). The mechanism appears to be very similar to that of the hydroboration of alkenes. 9-BBN is less susceptible than sodium borohydride to steric effects though the same trend is observed with both reagents. Increasing the steric hindrance on one side of the carbonyl function in ketones leads to a modest rate decrease while hindering both sides leads to a considerable rate decrease. Electron-withdrawing substituents decrease and electron-releasing ones increase the rate of reduction.

Brown, Chandrasekharan and Wang extended their 9-BBN study to include the kinetics and mechanism of the protonolysis reaction [42]. In carbon tetrachloride, the protonolysis of 9-BBN with t-butanol was first order in 9-BBN dimer supporting the conclusion that the reaction proceeds via a dissociation mechanism. However, in less hindered alcohols such as methanol, there is a competition between the dissociation pathway and one involving direct attack of the alcohol on the dimer. In THF, both hindered and unhindered alcohols exhibited first-order kinetics indicating that the dominant pathway involves prior dissociation of the 9-BBN dimer. Electron-withdrawing substituents enhance, and electron-releasing ones decrease the protonolysis rate. The same workers also examined the kinetics and mechanism of the complex formation of 9-BBN dimer with representative amines [43]. In all cases, symmetrical cleavage of the B-H bridge bonds of the dimer was observed. However the cleavage proceed through a dissociation mechanism or a bimolecular direct attach mechanism depending on the steric requirement and the nucleophilicity of the amine. The reaction of unhindered amines with 9-BBN dimer exhibits 2nd-order kinetics indicating that the rate limiting step involves the direct reaction of dimer and amine. More hindered amines exhibit first order kinetics being first order in 9-BBN dimer. These reactions presumably proceed through dissociation of the dimer followed by a rapid reaction of the monomer with the amine.

Brown and Racherla investigated the thermal isomerization of B-(3-hexyl)bis(bicyclo[2.2.2]octyl)borane [44]. The material isomerizes approximately three times faster than the bis(dimethylcyclohexyl)borane derivative and 60 times faster than the dinorborylborane derivative.

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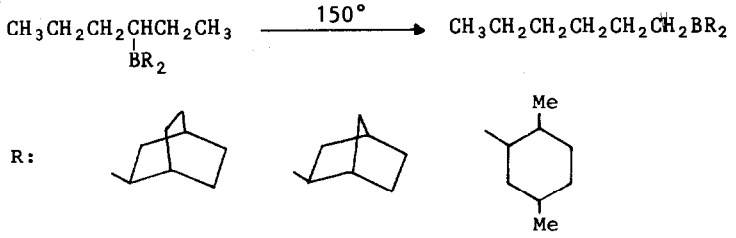


Brown and Racherla also report a remarkable reversal in the direction of boron migration in the thermal isomerization of organoboranes derived from 2-methyl-2-butene [45]. Normally, isomerization at 150° occurs to place 90% of the boron on the least hindered carbon of the 2-methylbutyl system (carbon 4). The alkyldiiodoborane derived from 2-methyl-2-butene and diodoborane-dimethylsulfide undergoes isomerization to place 100% of the boron on the relatively hindered carbon at C-1.

c. Spectroscopy

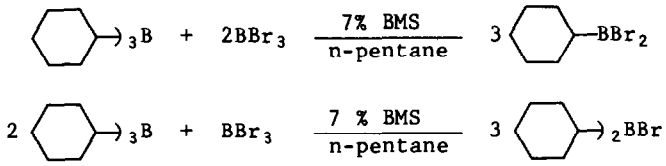
Blue and Nelson carried out a carbon-13 NMR study of the products of hydroboration of 1-alkynes and 1-halo-1-alkynes with 9-BBN [46]. Cragg and Miller report C-13 NMR correlations of the ortho, para, and meta carbon resonances in a series of phenylboranes [47]. Cragg and his coworkers also studied the effect of substituents on the free enthalpy of rotation about the B-N bond in series of dialkylaminophenylboranes ($PhBXNR_2$) [48]. The results indicate that when NR_2 is small, the barrier to rotation is governed principally by the mesomeric and inductive effects of X. When NR_2 is bulky, the steric effect of X affects the rotational barrier to a larger extent. As the steric hindrance of NR_2 is increased, the rotational barrier decreases. The rotational barrier results principally from p.pi-p.pi back donation from N to B; when the amino groups are excessively bulky, there is also an inherent steric resistance to rotation.

Baxter, Sands, and Wilson prepared and studied the dynamic NMR of two dimesitylboryl selenium compounds of the type Ar_2BSeR [49]. Free energies of activation for rotation about the B-C and B-Se bonds were calculated and were found to be lower than those for the O, N, and S analogs.

4. Syntheses of organoboranes

As the use of organoboranes in organic syntheses increases, a number of investigators have begun to report new routes to organoborane reagents which do not involve direct hydroboration. In general these routes utilize classical transmetallation reactions. Brown, Basavaiah,

and Bhat report that alkyldibromoboranes and dialkylbromoranes can be synthesized via a simple redistribution reaction involving tribromoborane and trialkylboranes [50]. The product obtained, R_2BBr or $RBBr_2$,



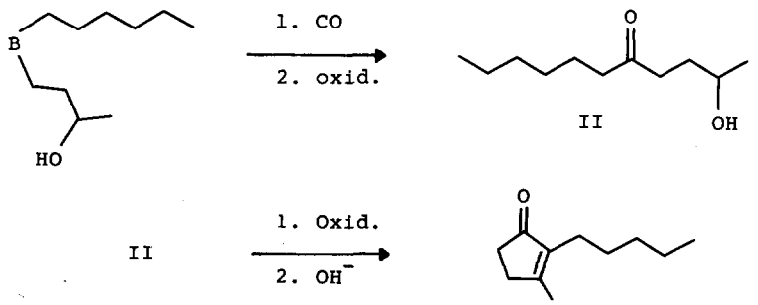
is dependent on the stoichiometry employed. The reaction is general, with a few exceptions, for trialkylboranes generated from terminal, internal and cylic alkenes. Gerwarth and Weber report that dichlorophenylborane can be prepared via the reaction of tetraphenyltin with boron trichloride [51].

Brown and Cole report that boronic esters can be prepared in excellent yield via the reaction of organolithium reagents with triisopropoxyborane [52]. The initial reaction product is the alkyltriisopropoxyborate which disproportionates in the presence of anhydrous HCl to yield the boronic esters. Kabalka and Sastry reported that arylboronic acids can be prepared via the reaction of borane with arylmagnesium halides. The intermediate arylborohydrides are readily hydrolized to the correspondence arylboronic acids [53].

c. Carbon-Carbon Bond Formation

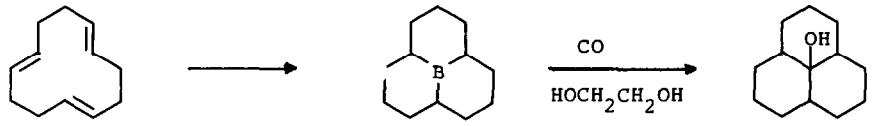
1. Homologation

The synthesis of carbon-carbon bonds is, of course, fundamental to organic synthesis. One of the unique features of the organoboranes is the fact that they undergo a wide variety of reactions in which new carbon-carbon bonds are formed. The "grandaddy" of the homologation reactions is the carbonylation reaction. The reaction has been utilized to synthesize a wide variety of primary, secondary, and tertiary alcohols and the corresponding ketons, aldehydes and acids. This year Brown, Basavaiah and Racherla report that the carbonylation of a readily prepared substituted organoborane yields a dione which can be converted to dihydrojasmone [54].

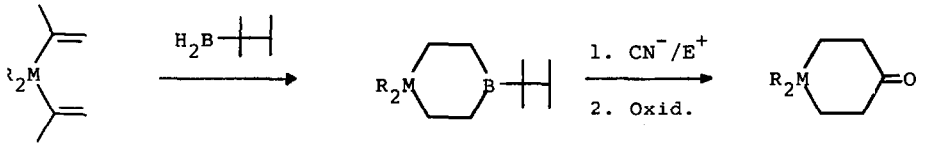


References p. 30

Brown and Negishi utilized the carbonylation reaction to synthesize perhydro-9b-boraphenalene and perhydro-9b-phenalenol [55].

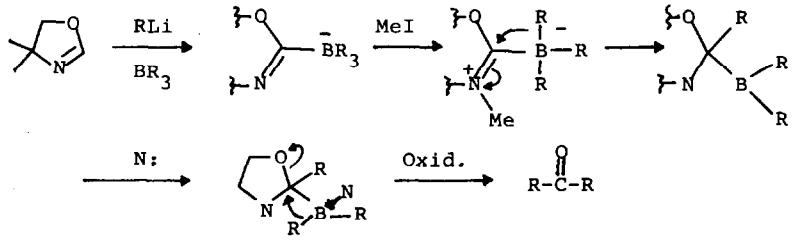


Soderquist and Hassner utilized the related cyanidation reaction in an elegant synthesis of a variety of metallacycloalkanones [56].

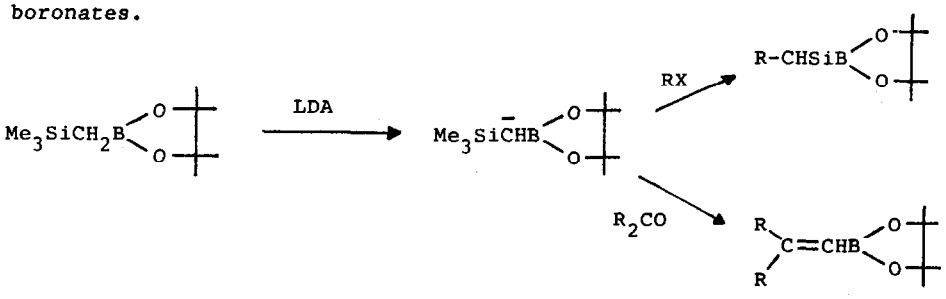


[R_2M = Me_2Si^-; Me_2SN^-, Me_2Ge^-, and phenylderivatives]

Baba and Suzuki developed a new synthesis of ketones which involves the reaction of trialkylboranes with 4,4-dimethyl-2-oxazoline [57].

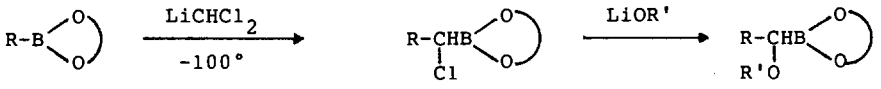


Matteson and his coworkers have continued to develop the use of boronic esters in organic synthesis. Matteson and Majumbar report that trimethylsilylmethaneboronic ester is readily alkylated by reaction with hindered lithium bases followed by the addition of alkyl halides [58]. The reaction of the intermediate lithiated boronate with aldehydes or ketones occurs with elim nation of the silicon to produce 1-alkene-1-boronates.

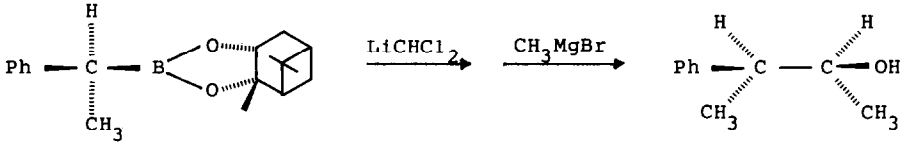


In a related study, Tsai and Matteson homologated (+)-pinanediol phenylboronate with [chloro(trimethylsilyl)methyl]lithium to yield a mixture of (αS)- and (αR)-[α-(trimethylsilyl)benzyl]boronic esters [59]. They report that the alpha silyl esters are readily desilylated using tetrabutylammonium fluoride.

Matteson and Majumdar report that a variety of alkyl and aryl boronic esters are readily homologated to the alpha-chloroboronic esters by reacting them with dichloromethyllithium [60]. The reaction has been

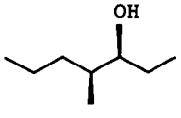


successfully run in the presence of functional substituents. The product alpha-chloroesters readily undergo nucleophilic replacement of the chloride with a variety of reagents including benzyloxide, ester enolates, or lithium alkyls. Matteson, Ray, Rocks, and Tsai utilized this homologation-displacement sequence with optically active pinanediol boronate esters [61]. They were able to prepare the boronate in 100% enantio eric excess via recrystallization of sodium bis(pinanediol)-borate. The synthetic utility of the process was demonstrated in the highly stereoselective synthesis of (2S,3S)-PhCHMeCHMeOH:



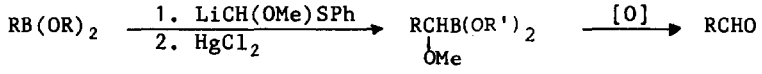
Matteson and Erdik reported that these very useful optically active alpha-chloro alkylboronate esters epimerize in the presence of LiCl [62]. The rate of epimerization is greatly increased by reagents which promote ionization of LiCl. Zinc chloride also catalysis the epimerization.

Matteson and Sadhu utilized the homologation reaction of the alpha-chloroboronate esters to synthesize the insect pheromone (3S,4S)-4-methyl-3-heptanol (european elm bark beetle) [63].

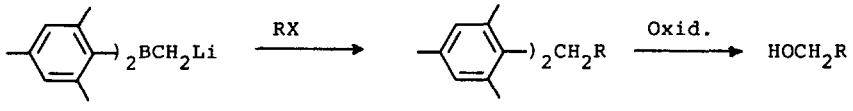


Tsai, Jesthi, and Matteson synthesized optically active alpha chloroboronate esters from the (+)-pinanediol esters of dichloromethaneboronic acid which was then treated with a Grignard reagent [64]. This sequence produces borate complexes which are diastereomeric with the borates previously discussed. Interestingly the diasteroselection in this synthesis is less than that obtained when the alpha chloroesters are synthesized via the reaction of the alkyboronate esters with lithium dichloromethylide.

In a related reaction, Brown and Imai report that 2-alkyl-1,3,2-dioxaborinanes react with methoxy(phenylthio)methyllithium to yield the homologated alpha-methoxy derivatives [65]. These products are readily converted into the corresponding aldehydes.

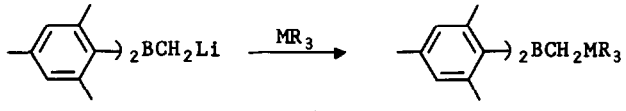


Pelter and his colleagues have investigated the use of the bulky dimesitylboron group in organic syntrheses. Pelter, Singaram, Williams, and Wilson report that hindered bases will abstract a proton from B-alkyldimesitylborane to form the corresponding carbanion [66]. The carbanion intermediate is readily alkylated by a variety of alkyl halides and the method can be used to prepare homologated alcohols [67].



Pelter, Singaram, and Wilson condensed the anions derived from B-alkydimesitylborane with a variety of ketones to achieve a boron analog of the Wittig reaction [68]. Morton and his coworkers also presented evidence for the intermediacy of a Wittig type reaction in their study of the reaction of carbon dioxide with a boron stabilized carbanion [69].

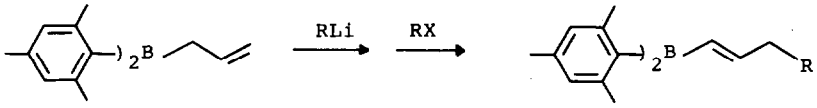
Pelter, Garad, Singaram, and Wilson examined the reaction of lithiated dimesitylborylmethane with a variety of metal halides; the reaction produces the corresponding heteroatom-substituted dimesitylborylmethanes [70].



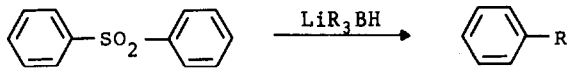
M: Si, Pb, Sn

Pelter, Singaram, and Wilson also investigated the reaction of

allyldimesitylborane with a series of electrophiles including alkyl iodides and aldehydes [71]. The reactions proceeded in good yield.

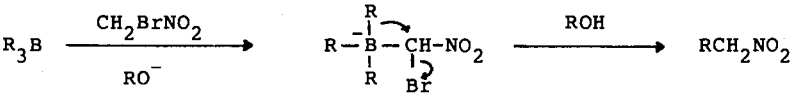


Brown, Kim, and Krishnamurthy reported a novel alkylation of aromatic systems via the reaction of lithium trialkyborohydrides with aryl sulfones [72].

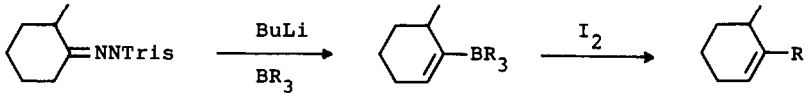


The reaction appears to be general and proceeds satisfactorily for the introduction of a variety of alkyl groups. The incoming alkyl group enters at the original position occupied by the sulfone substituent.

The reaction of halogenated carbanions with organoboranes plays an important role in organic synthesis. Fishwick, Rowles, and Stirling report that the anion of bromonitromethane reacts readily with tributylborane to generate nitropentane [73]. The reaction presumably proceeds via a classical anionotropic migration of the alkyl group from boron to the electron deficient carbon.

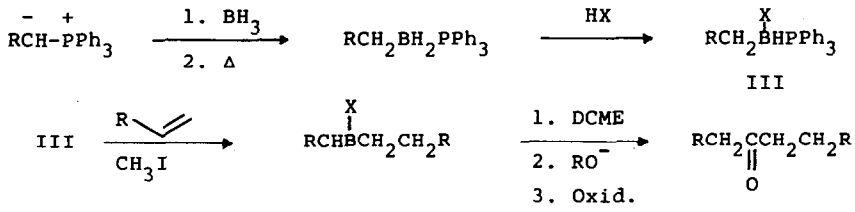


Baba, Avasthi, and Suzuki report that the salts of trisylhydrazones react with trialkylboranes to yield intermediates alkylcyclohexenes which rearrange upon treatment with iodine to yield cycloalkenes via a migration of an alkyl groups and loss of nitrogen [74].

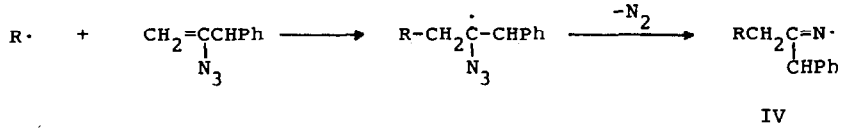


Bestmann and Roeder utilized the dichloromethyl ether reaction to prepare a series of ketones from boranes which they generated via a very

novel reaction which produces mixed boranes from phosphorus ylides [75].

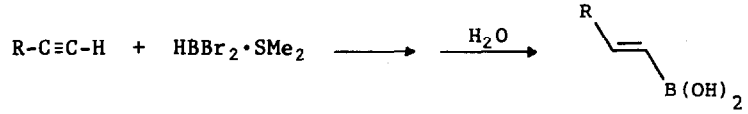


Bamford, Cook, and Roberts report that trialkylboranes react with azidostyrene to yield alkylated products [76]. These reactions proceed through a free radical 1,4-addition sequence rather than an anionotropic rearrangement.

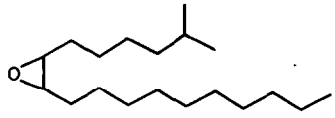


C.2. Alkenylboranes

The vinyl- and allylboranes continue to play an important role in the stereoselective synthesis of a variety of alkenes. Brown, Bhat, and Somayaji report that alkenylboronic (and alkylboronic) acids can be readily prepared via the synthesis, and subsequent hydrolysis, of the corresponding alkenyldibromoboranedimethylsulfide complexes [77]. They also report that the corresponding esters can be prepared in a straightforward manner.

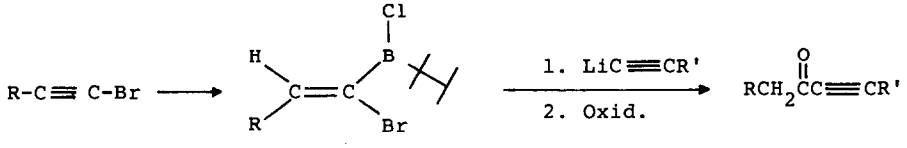


Brown and Basavaiah then utilized the procedure to prepare disparlure, the sex pheromone of the gypsy moth [78]. Brown reviewed

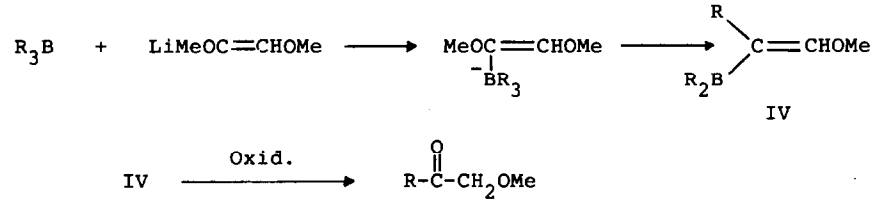


the role of vinylic organoboranes in their applications to the syntheses of a variety of insect pheromones [79].

Brown, Bhat, and Basavaiah hydroborated a series of 1-bromoalkynes with thexylchloroborane to prepare vinylboranes which were then reacted with lithiated acetylenes to yield alkynylalkenylboranes via the classical anionotropic rearrangement [80]. The intermediate boranes were oxidized to yield alkynyl ketones.

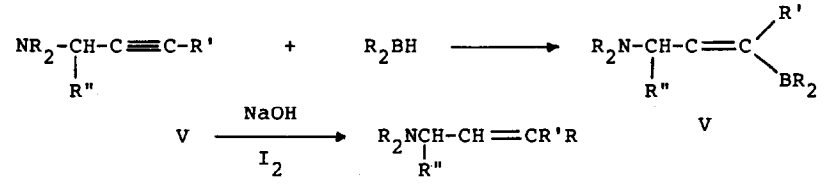


Koshino, Sugaware, Yogo, and Suzuki developed an interesting rearrangement reaction involving vinylborates derived from 1,2-dimethoxyethenyllithium. The reaction produces 1-methoxy-2-alkanones after oxidation [81].

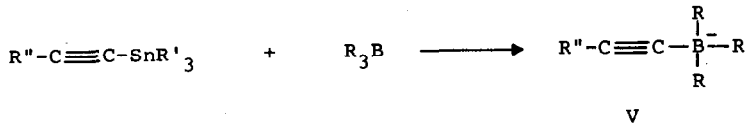


The same group of investigators were able to utilize their unusual intermediate to generate aldehydes utilizing a non-oxidative workup [82].

Torregrosa, Baboulene, Speziale, and Lattes reported that the hydroboration of propargylamine derivatives resulted in formation of allylic amines via the rearrangement of the intermediate vinylborane upon treatment with iodine [83].



Wrackmeyer has continued to investigate the organoborination of stannyl derivatives. He and his coworkers report that the reaction of alkynylstannanes with triethylborane results in the formation of 1-stannyl-2-boroalkenes which react with additional alkynlstannanes to generate a series of allenic derivatives [84].



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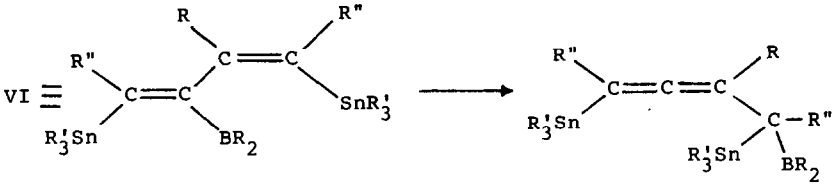
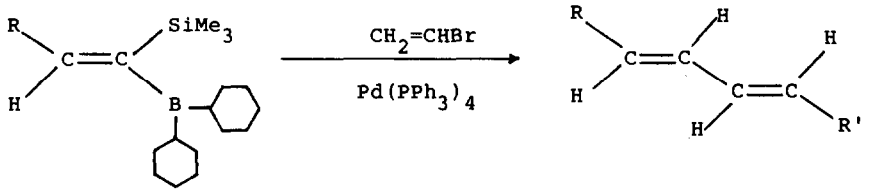
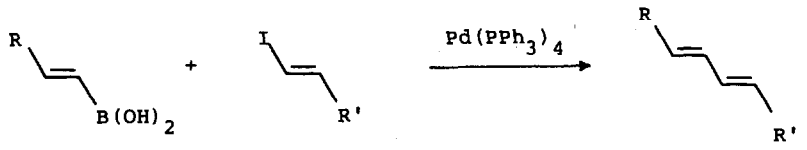


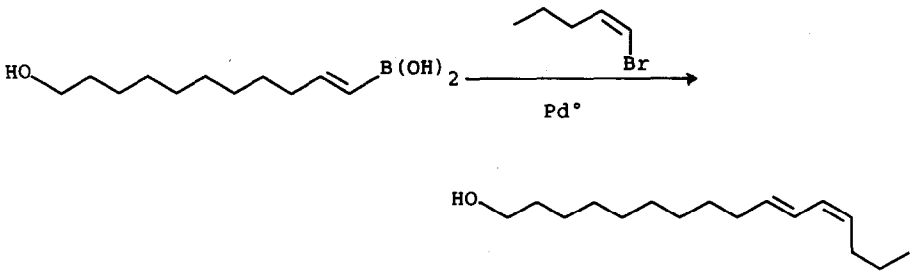
The transition metal catalyzed coupling of vinylborane derivatives to a variety of organic halides continues to play an important role in organic synthesis. Negishi and Luo report alpha-heterosubstituted vinylboranes couple with vinyl iodides in the presence of palladium to produce the heterosubstituted diene [85]. They note that the corresponding alanes and organozinc derivatives undergo the same coupling reaction more efficiently.



Cassani, Massarso, and Piccardi report that vinylboronic acids also couple with vinyl iodides in the presence of tetrakis(triphenylphosphine)palladium [86].

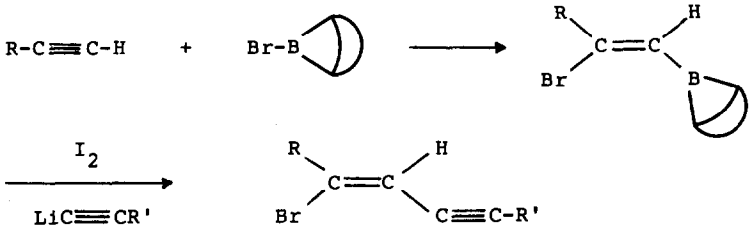


Miiyaura, Suginome, and Suzuki utilized the palladium cross-coupling reaction to synthesize the insect pheromone bombykol [87].

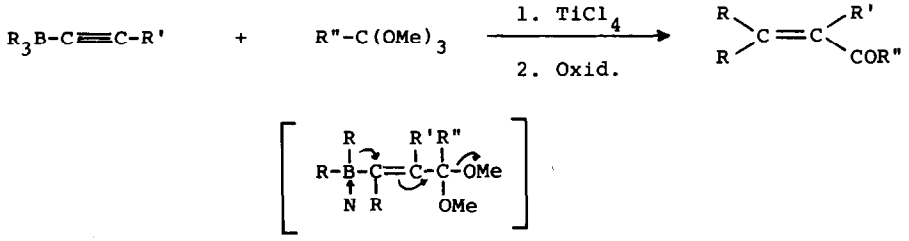


C.3. Alkynylboranes

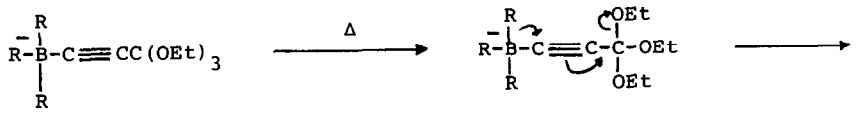
The reactions of alkynylboranes with electrophiles has played a role in synthesis in recent years. Shoji, Yoshitake, Hiroko, and Suzuki utilized the iodine mediated rearrangement of alkynylboranes to synthesize a series of [Z]-alkynyl-2-haloalkenes [88]. The prerequisite haloalkene was prepared via the haloboration of a corresponding alkyne.

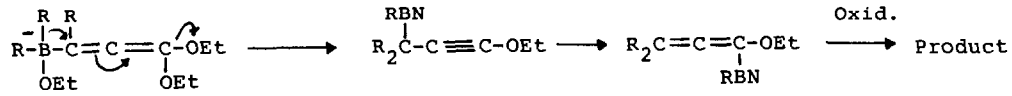


Suzuki and his coworkers also developed a new synthesis of conjugated unsaturated carbonyl compounds. They found that trialkyl(1-alkynyl)borates react with orthoesters in the presence of titanium tetrachloride to produce an intermediate which undergoes an allylic rearrangement of boron to the carbon attached to oxygen and which then generates the carbonyl compound upon oxidation [89].

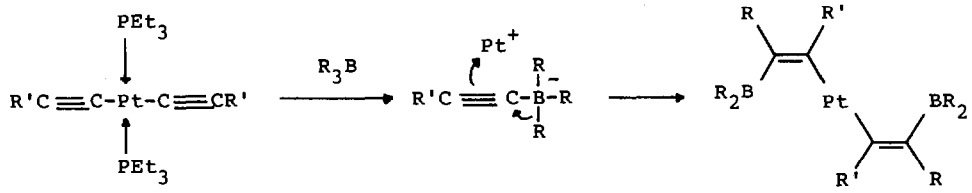


In a mechanistically related reaction, Suzuki, Hara, Doho, and Kato prepared borates from trialkyboranes and acetylides of orthopropiolate to generate beta substituted alpha,beta-unsaturated esters via an intramolecular rearrangement reaction [90].

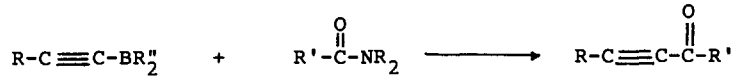




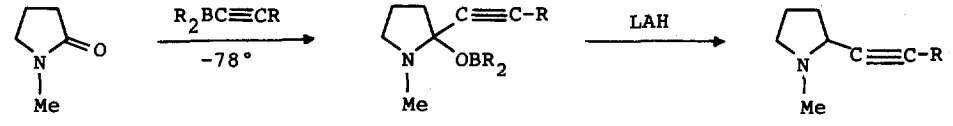
Sebald and Wrackmeyer report that the organoboration of platinum(II) acetylides produces the corresponding platinum(II) alkenyl compounds [91].



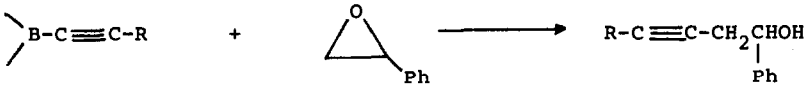
Alkynylborates undergo intermolecular reactions as well as intramolecular rearrangements. Yamaguchi, Waseda, and Hirao report that alkynylborane derivatives prepared via the reaction of lithium acetylides and boron trifluoride react with tertiary amides to produce alkynyl ketones in good yield [92].



The reaction proceeds in a slightly different fashion when lactams are utilized as starting materials [93].

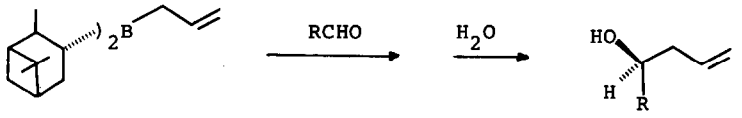


Yamaguchi and Hiro also reacted their acetylenic borane with oxiranes to generate a series of beta hydroxyacetylenes in good yields [94].

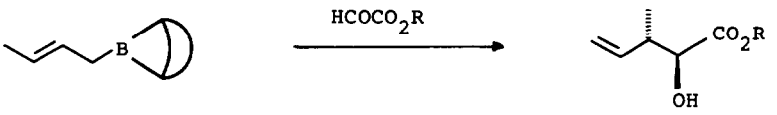


C.4. Allyl and Propargylboranes

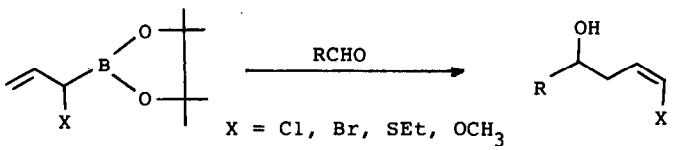
Allylboranes are unique in that they react directly with aldehydes and ketones in a Grignard-like fashion to produce the corresponding homoallylic alcohols. Brown and Jadhav report that the reaction can be used to synthesize optically active products [95]. The authors prepare the optically active allyl reagent by preparing diisopinocampheylchloroborane from optically active alpha pinene and then reacting this reagent with allylmagnesium bromide. This allyl reagent readily reacts with a series of aldehydes to produce the desired homoallylic product.



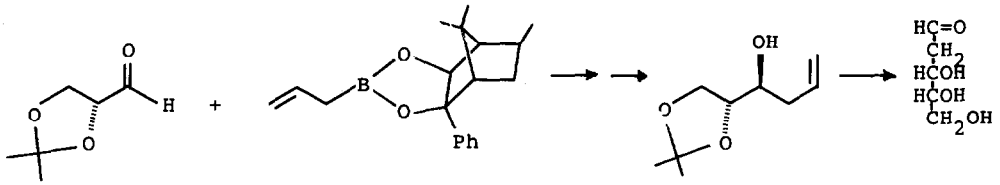
Yamamoto, Maeda, and Maruyama reacted allyl 9-BBN with glyoxylate esters to generate threo-3-alkyl-2-hydroxy-propionate [96].



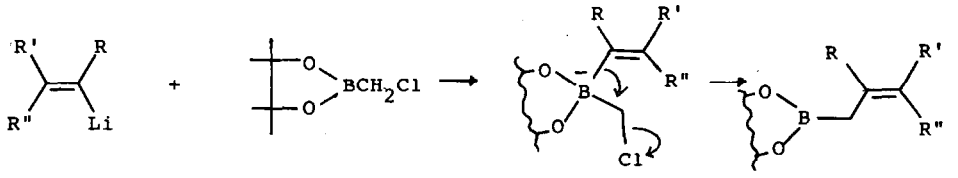
Hoffmann and Landmann report that the reaction of substituted allylboronate with a series of esters generates the Z isomer predominantly [97].



Hoffmann, Endesfelder, and Zeiss also report that allylboronates react cleanly with 3-O-isopropylidene-D-glyceraldehyde to generate dioxolane intermediates which can be converted to 2-deoxy-D erythro-pentose [98].

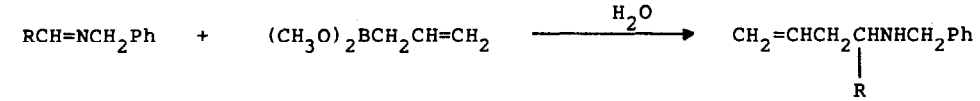


Wuts, Thompson, and Callen reported a stereospecific synthesis of allylboronates using the reaction of vinyllithium reagents with 2-(chloromethyl-4,4,5,5-tetramethyl-2-bora-1,3-dioxacyclopentane [99].

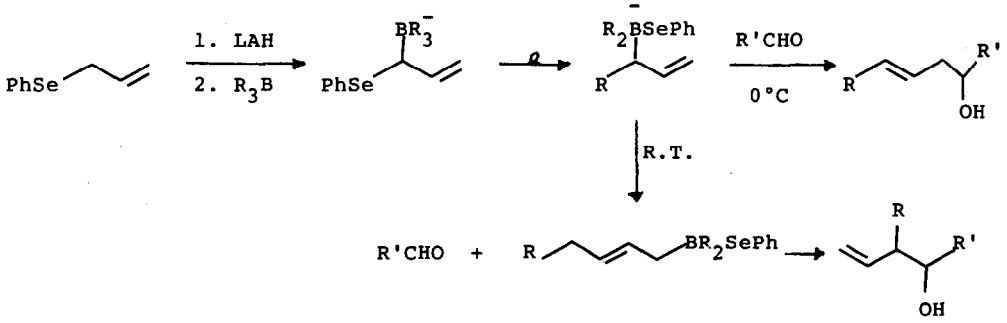


Hutchings, Paget, and Smith generated a 3-bora-1,4-pentadiene via the reaction of diphenylbromoborane with the anion of 1,4-pentadiene and then reacted the reagent with carbonyl compounds to prepare a series of 3-(1-hydroxyalkyl)penta-1,4-dienes [100].

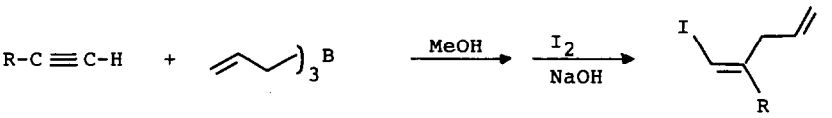
Hoffmann, Eichler, and Endesfelder investigated the reaction of allylboronates with Schiff bases and oximes. They found that the reaction proceeds rapidly in a fashion analogous to the carbonyl addition reactions [101].



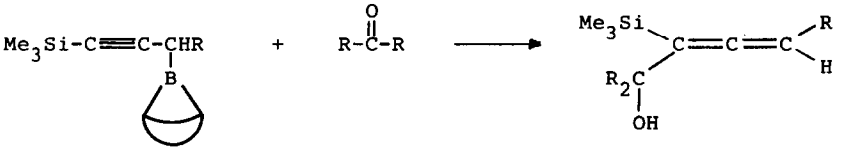
Yamamoto, Saito, and Maruyama prepared a series of allylic borane selenium reagents. These reagents react with aldehydes to yield either branched or linear homoallylic alcohols depending on the experimental conditions [102].



Mikhailov and Lavrinovich continued their investigation of the reactions of allyl boranes. They reported that allylboranes react with acetylenic compounds to yield intermediates which are readily cleaved by iodine and base to yield stereodefined iododienes [103].

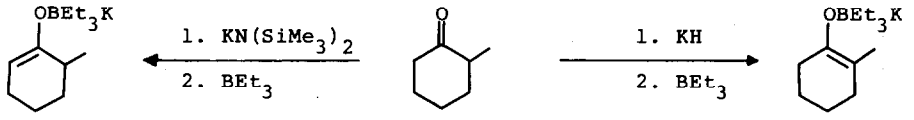


Propargylic boranes undergo reactions which parallel those of the allylic boranes. Wang, Nikam, and Ho report a regioselective synthesis of trimethylsilyl-substituted alpha-allenic alcohols via the reaction of propargylic orrganoboranes containing appropriately substituted trimethylsilyl groups [104].



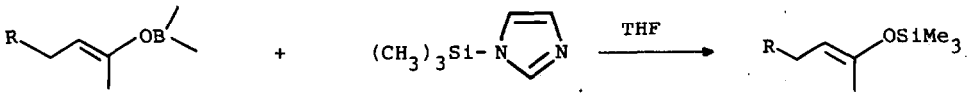
C.5. Boron Enolates

Boron enolates have been prepared via a number of routes. Negishi and Chatterjee report that the thermodynamic boron enolates can be prepared in a highly regioselective fashion via the reaction of trialkylboranes with enolates generated by the reaction of ketones with potassium hydride [105]. The kinetic enolates can be generated by using a hindered base such as $KN(SiMe_3)_2$.

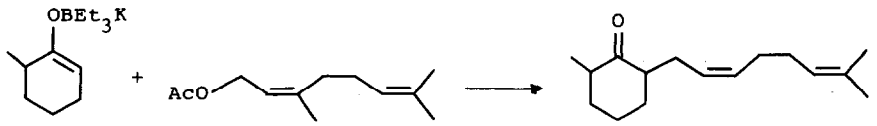


Masamune and Choy were issued a U.S. patent covering the preparation of chiral boron enolates via the reaction of organoboranes with optically active mandelic acids [106].

Hooz and Oudenes found that enol boranes react with N-trimethylsilylimidazole to give the corresponding trimethylsilyl enol ethers [107].



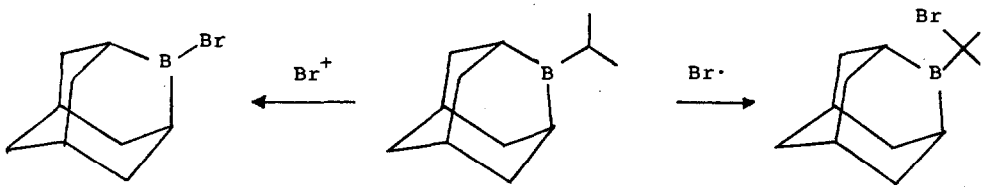
Negishi and John reacted boron enolates with allylboranes in the presence of a variety of palladium complexes to generate new carbon-carbon bonds. They investigated the countercation effects on the allylation of enolates and prepared a series of geranyl and neryl derivatives [108].



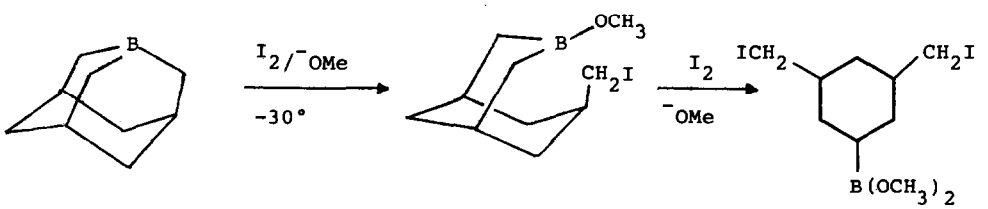
C.6. Adamantylborane

Mikhailov and his coworkers continued their exploration of the chemistry of boraadamantane derivatives, an area which they pioneered. Mikhailov reviewed the chemistry of 1-boroadamantane in detail [109]. He also reported the synthesis of 4-chloroadamantane via the rearrangement of 7-chloromethyl-3-ally-3-borabicyclo[3.3.1.]non-6-ene [110].

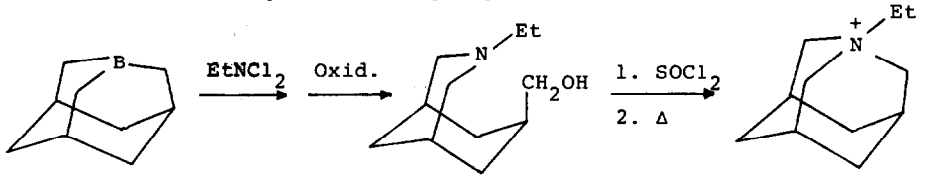
Mikhailov, Schegoleva, Shaskova, and Kiselev report that 2-isopropyl-2-boraadamantane undergoes both free radical and electrophilic bromination [111]. The radical reaction is accompanied by a rearrangement which varies with reaction conditions.



Mikhailov, Gurskii, and Pershin also reported that iodination of boraadamantane derivatives proceeds readily in the presence of base [112].



Mikhailov and Shagova reacted 1-boraadamantane with dichloroethylamine. The reaction generates a 3-ethyl-3-azabicyclo[3.3.1]nonane derivative which is converted to 1-ethyl-1-azoniumadamantane chlorides by reaction with thionyl chloride [113].



Mikhailov and his coworkers synthesized a series of nitrogen containing complexes of 1-boraadamantane and investigated their antiviral activity [114].

D. Carbon-Heteroatom Bond Formation

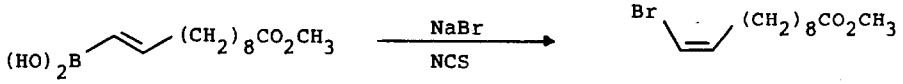
1. Group VII

The reaction of organoboranes with halogens has proven to be a valuable method for synthesizing a variety of functionally substituted organic halides. In recent years, the halogenation reaction has been applied to the syntheses of a variety of radiohalogenated reagents for use in nuclear medicine. Kabalka reviewed the use of boranes for this purpose [115]. Kabalka, Knapp and their coworkers reported the syntheses of an entirely new series of myocardial imaging agents which contain a vinyl iodide moiety which slows the loss of radioiodine in vivo [116]. The radioiodine was introduced via the reaction of the corresponding vinylboronic acid with iodine-125 labeled iodine monochloride.

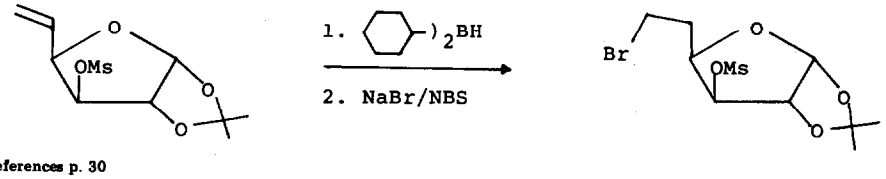
$$^{125}ICH{=}CH(CH_2)_9\text{-}Te\text{-}(CH_2)_5\text{-}CO_2H$$

Srivastava, Guyer, and Knapp reported that the iodovinyl group could also be incorporated into barbituric acid analogs [117 and 118].

Kabalka, Sastry, Knapp, and Srivastava extended the reaction to the synthesis of vinyl bromides [119].

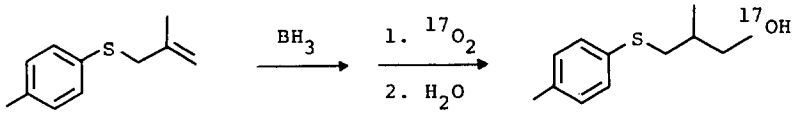


Neeser, Hall, and Balatoni utilized a similar reaction sequence to prepare brominated derivatives of carbohydrates [120].



2. Group VI

The oxidation of organoboranes has been utilized to prepare alcohols ever since the organoboranes were discovered in the 1800s. Kabalka, Reed, and Kunda report that the reaction can be utilized to prepare oxygen-17 labeled alcohols in a regiospecific fashion [121].



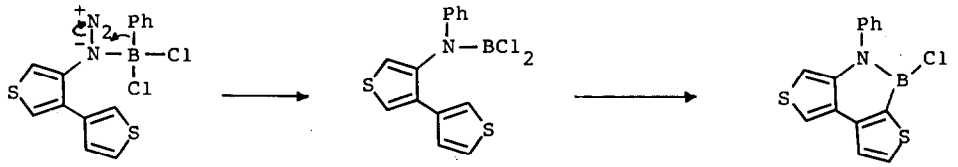
Fenzyl and Koester report that tetraethyldiboroxane can be prepared in greater than 95% yield via the hydrolysis of triethylborane [122]. The product can then be readily hydrolyzed to the corresponding borinic acid [123].

$$Et_3B \xrightarrow{H_2O} (Et_2B)_2O \xrightarrow{H_2O} Et_2BOH$$

The authors also report that the methanolysis of triethylborane results in the production of methyl diethylborinate in excellent yield [124].

3. Group V

Leardini and Zanirato report that aryl dichloroboranes reacts with organic azides to yield N-substituted derivatives of dihydro-1-aza-2-borabenzene [125].



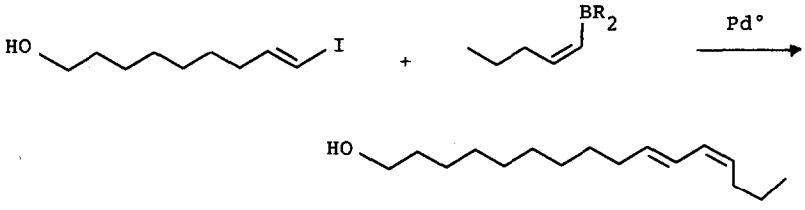
4. Group I

Another classic reaction of organoboranes, protonolysis, has been investigated by Brown and Normand [126]. They report that the hydrolysis of triethylborane (very slow) is unaffected by the addition of hydrochloric acid but that the reaction is inhibited by the addition of sodium hydroxide. The classic reaction with acetic acid involves the rapid removal of the first alkyl group on the organoborane. The second group is removed more slowly and the removal of the third group requires elevated temperatures. The unusual reactivity of carboxylic acid toward protonolysis is attributed to the presence of both acidic and basic sites. To test this hypothesis, various reagents were added to reactions mixtures containing carboxylic acids. Bases such as pyridine inhibit the removal of the first alkyl group whereas hydroxylic solvents

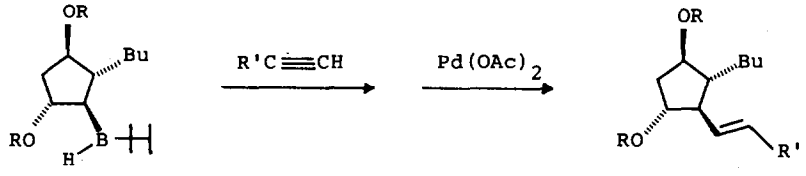
and strong acids and bases hinder removal of the second alkyl group.

E. NATURAL PRODUCTS AND GENERAL SYNTHETIC APPLICATIONS

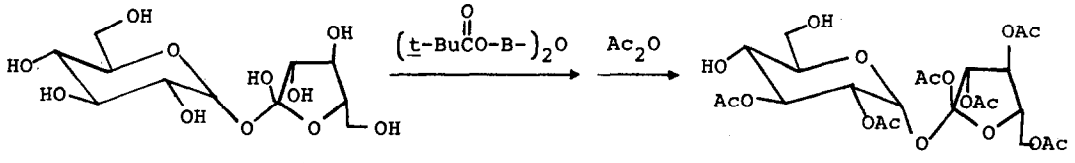
The use of organoborane technology in natural product syntheses is becoming more widespread. Many of the papers quoted in this review were focused on the development of new reactions for use in biologically or physiologically active materials and it would serve no purpose to cite them again at this point. As a further example of the utility of the borane reactions, Miyaura, Suginome, and Suzuki utilized the palladium catalyzed cross-coupling reaction between an alkenylborane and an alkenyl halide to synthesize the pheromone bombykol [127].



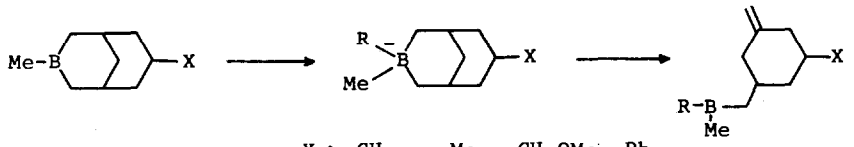
Larson and Prieto gained entry into prostanoid models via the hydroboration of enol silyl ethers [128].



Koester, Taba, and Dahlhoff continued their studies centered on the use of organoboron dissacharides [129]. They reported an improved preparation of 2,3,1',3',4',6'-hexa-O-acylsucrose via O-ethylboranediyl protection.



The final entry this year concerns the interesting synthesis of a series of 5-substituted 3-methylenecyclohex-1-ylmethyl(dialkyl)boranes via an intermolecular beta hydride transfer reaction which was reported by Gurskii, Baranin, Shashkov, Lutsenko, and Mikhailov [130]. The reaction provides a unique entry to these reactive intermediates.



X : CH_2=, -Me, $-CH_2OMe$, -Ph

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